ABSTRACT BOOK

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OCTOBER 9-11, 2024 TÜRKİYE

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PREFACE

We are immensely proud to have successfully hosted IRC in Türkiye. This significant gathering unites leading minds and innovators from around the world every year, sparking impactful discussions and groundbreaking insights. Held from October 9th to 11th in the vibrant city of Istanbul, IRC2024 added another keystone to this bridge for exchanging pioneering research, innovative technologies, and real-world applications that advance the field of rubber science and engineering. It is with great satisfaction that we now present the abstracts of the outstanding presentations, each reflecting the remarkable progress and collaborative spirit that defines the International Rubber Conference.

IRC2024 welcomed 380 leaders from academia, industry, and regulatory organizations representing 29 countries, including 210 attendees from Türkiye. The conference featured 92 oral presentations and 41 poster presentations, providing a robust foundation for in-depth discussions that highlighted the latest innovations and helped shape the future of the rubber industry.

I would like to express my deepest gratitude to all the members of the organizing committee, particularly my co-chairs, Prof. Dr. Murat Şen and Prof. Dr. Bağdagül Karaağaç, as well as Mr. Abdalla Mbaruk Abdalla, Dr. Şehriban Öncel, and Dr. Davut Aksüt, for their exceptional dedication and teamwork, often working through sleepless nights to ensure the conference ran smoothly. The Rubber Association of Türkiye has been preparing for this event for over a decade. I also want to thank our past president, Nurhan Kaya, whose vision made this success possible, as well as the current board members of the Rubber Association. IRCO is the organization that has laid the groundwork for organizing IRC in different countries since 1966, has helped us immensely through the process. Special thanks go to the entire group, particularly Matthew Thornton, the General Secretary of IRCO, and Michael Clayton, the President. I am also grateful to our sponsors, whose support enabled us to host this event effectively during challenging financial times. Finally, I want to acknowledge our Scientific Committee, plenary and invited speakers, presenters, and all attendees; your contributions transformed IRC2024 into a vibrant and insightful event.

It is my hope that the knowledge and experiences shared during the conference, along with the connections made through networking, will foster further advancements in the rubber industry. May these collaborations contribute to innovative solutions that benefit humanity, driving us toward a more sustainable and prosperous future.

Sincerely,
Ö. Doğu Kaya
Chairman, IRC2024

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Plenary Speeches

Ionic Network of Modified Natural Rubber for Sustainability and Heat-Resistant Applications

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Keywords: Epoxidized Natural Rubber; Ionic Crosslinking; Reversible Network; High Temperature Applications.

The ionic network of modified natural rubber offers a sustainable alternative to synthetic rubber for applications requiring high temperature, tear, and fatigue resistance. Traditionally, sulfur-based networks have been employed in rubber production, but their limitations in heat resistance have led to the prevalent use of synthetic rubbers in various applications. This study introduces non-directional ionic bonds into modified natural rubber, enhancing its properties beyond those of synthetic rubbers while maintaining high mechanical performance. Through accelerated aging analysis, temperature scanning stress relaxation studies (TSSR), and temperature-dependent FTIR analysis, the thermal stability and aging resistance of this natural elastomer were confirmed. Remarkably, its initial degradation temperature significantly surpasses that of commonly used di-ene elastomers. Moreover, superior tear and fatigue abrasion resistance compared to sulfur-cured ENR were observed. The presence of an ionic bond network enables inherent micro crack repair, as demonstrated by X-ray microtomography experiments. This self-repairing capability, coupled with the material's natural sourcing, promises to mitigate environmental damage and reduce the carbon footprint associated with petroleum-based synthetic rubber production.

Acknowledgement

Thanks to the Sumitomo Rubber Industries, Japan for partial support of the work.

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Effects of dynamic-mechanical load on chemical aging behavior of elastomers

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Keywords: Thermal oxidative aging, dynamic mechanical load, DLO-effect, tear fatigue analyses.

The service life of elastomers is significantly limited by irreversible chemical changes that are unavoidable depending on time and exposure as a result of complex ageing processes. Depending on the polymer matrix, cross-linking and fillers, thermal-oxidative ageing processes lead to radical polymer degradation in competition with the formation of a secondary network (post-cross-linking) [1, 2]. Corresponding changes in the mechanical properties are the result up to total failure. Heterogeneous post-crosslinking starting from the surface and initiated by radical oxidation is also typical, with an increase in the stiffness and crack sensitivity of the material in layers close to the surface. This is due to the competition between oxygen diffusion (reduction of O_2 input through crosslinking) and O_2 consumption through chemical reactions (DLO effect) [1, 3].

During dynamic deformation, accelerated cracking and softening of a component with the release of new surfaces for accelerated O_2 input is to be expected, in addition to heating due to dissipated energy. Therefore, the aim of the study was to investigate and quantify the influence of mechanical energy input on the multi-variable chemical ageing reactions under aerobic and anaerobic conditions. In particular, ageing reactions on the polymer matrix and in the network, characteristic data on oxygen diffusion and consumption, kinetics, effects of the DLO effect on crack formation and component softening. For the investigations filled and unfilled sulfur crosslinked IR and SBR compounds as well peroxide crosslinked EPDM were used.

The used methods are chemiluminescence, TGA, micro-indentation, infrared spectroscopy for determination of the oxidation kinetics. For discovering the chain mobility ^{1}H-NMR, swelling and tensile tests were performed. For the investigation of the influence of mechanical load on thermo-oxidative aging heat-build-up during mechanical load and the tear-fatigue analysis (TFA) have been conducted. During the TFA-measurements as an important parameter the amplitude was varied and the atmosphere (aerobe, anaerobe) was controlled for detailed separation of degradation, fatigue and oxidation mechanisms [4].

One of interesting results mainly are, that dynamic load influences the thermo-oxidative aging behavior. TFA – measurements show a force decrease within the early steps of aging. After a certain time, the force increases until the specimens finally break. Hereby, amplitude is an important parameter. At 140 °C degradation and fatigue become predominant, so there are only marginally oxidation effects until failure. 10% amplitude reduces the force-decrease-effect, so no failure within the regarded time occurs and further measurements are possible. At an amplitude of 1% the decrease of the force decrease is very small and pronounced hardening effects are able to occur without failure of the samples (dumbbells). In every case, no micro- or macro-cracks are observable [4]. Due to relaxation effects and the continuous degradation and rearrangement of the sulphur network, the dumbbells change their shape. The body of the dumbbells narrow and become longer, dependent on the amplitude. This effect is the main difference compared to load-free aging. Hereby, the resulting surface area increased and thus more material oxidizes. By regarding the shape, indenter measurements show that the hardness is comparable but oxidation effects get deeper into the material in the case of dynamic aging [4]. Density and infrared measurements only show this trend at the surface specimens. The variation of the atmospheres shows the influence of oxygen on the different mechanisms. Via CL-measurements a correlation of oxygen concentration and the temperature is observable.

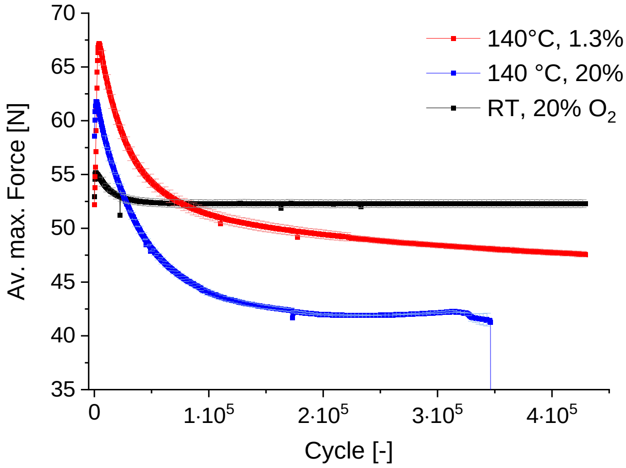

Figure 1: Average maximum force of IR specimens under dynamic load (f = 1 Hz, A = 20 %), RT (gray line), 140 °C aging temperature and nitrogen (red line) or air (blue line) as aging atmosphere *[4]* .

The thermo-oxidative aging behavior of SBR is slightly different compared to IR. The oxidation of the material begins later and the temperature dependency is smaller. Investigations concerning EPDM material show the high aging resistance, compared to the other considered systems. Aging effects can only be observed above an aging temperature of 140 °C. Above 160 °C crosslinking becomes pre-dominant after 14 days. A softening effect cannot be observed at 160 °C, whereas 180 °C leads to softening effects in the observed time. The aging at 120°C and 140°C does not significantly affect the mechanical behavior, whereby at 140°C the polymer hardens in the very late stages of aging [4].

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Effect of proteins as constituents of island-nanomatrix structure on vulcanization of natural rubber

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Keywords: Natural rubber, Island-nanomatrix structure, Protein, vulcanization.

1. Introduction

Proteins present in natural rubber are one of the non-rubber components (ca. 6 w/w%) that form a sea phase in the nanostructure of the rubber (island-nanomatrix structure), in which natural rubber particles with an average diameter of about 1 μm are dispersed as an island phase[1]. The sea phase, itself, is a nanocomposite with a thickness of several 10 nm, in which the non-rubber components such as proteins and lipids are densely dispersed in natural rubber as nanoparticles, and plays an important role in mechanical properties of unvulcanized natural rubber. Based on the previous results, the proteins are expected to affect the mechanical properties of vulcanized natural rubber, although its effect has been less investigated in a rational basis. The effect of proteins on the vulcanization of natural rubber may be, in principle, investigated by comparing the vulcanization of natural rubber with that of protein-removed natural rubber, i.e., deproteinized natural rubber (DPNR). In the present study, we observed the dispersion of Zn and S through focused ion beam - scanning electron microscopy-energy dispersive X-ray spectroscopy (FIB-SEM-EDX) and transmission electron microscopy-energy dispersive X-ray spectroscopy (TEM-EDX) to investigate the effect of proteins on the vulcanization of natural rubber and analyzed the primary structure of vulcanized natural rubber through rubber-state NMR spectroscopy.

2. Experiment

Rubber compounds were prepared by two mixing methods: that is, dry mixing method and wet mixing method. In the dry mixing method, the rubber compounds were prepared with a two-roll mill. First, natural rubber and DPNR were masticated for 15 minutes. Second, the masticated rubbers were mechanically mixed with 2.1 phr ZnO, 0.6 phr accelerator and 1.1 phr sulfur to prepare mechanically mixed rubber compounds. In the wet mixing method, the natural rubber latex and DPNR latex were mixed with 50 w/w% sulfur dispersion, 50 w/w% ZnO dispersion and 35 w/w% CBS dispersion at 200 rpm for 30 minutes, in which amounts of sulfur, ZnO and CBS were adjusted to 2.2 phr, 4.2 phr and 1.7 phr, respectively. The latex mixtures were sprayed onto a hotplate at 150 °C and dried for 45 sec to prepare latex-mixed natural rubber compounds. The resulting rubber compounds were vulcanized with a hydraulic press by pressing and heating at 15 MPa and 150 °C for t_{90}. Natural rubber film and DPNR film were put in a mixture of sulfur, ZnO and CBS with a weight ratio of about 1.67: 3: 1 followed by heating at 150 °C for 5 h to investigate the migration of sulfur and zinc into the rubbers. The resulting rubbers were washed with acetone before morphology observation. Nitrogen content was determined by Kjeldahl's method. Crosslink density of vulcanized natural rubber and vulcanized DPNR were determined by swelling method. The migration of sulfur and zinc into natural rubber was observed with a SII SMI-3050SE equipped with a Oxford Instruments EDX at an accelerating voltage of 3 kV. Rubber-state ^{13}C NMR spectroscopy was performed with a JEOL ECA-400 NMR spectrometer (JEOL, Tokyo, Japan) at 99.55 MHz for vulcanized natural rubber.

3. Results and Discussion

Nitrogen content was 0.256 w/w% for natural rubber and 0.024 w/w% for DPNR. Figure 1 shows FIB-SEM EDX spectra obtained at each 2 μm interval from the surface to 14 μm in depth for the natural rubber film and DPNR film, which were embedded in a mixture of sulfur, zinc oxide and CBS with a weight ratio of 1.67:3:1 followed by heating at 150 °C for 5 h. The signals assigned to carbon, oxygen, and sulfur without zinc appeared for the DPNR film, while all signals appeared for the natural rubber film. For the DPNR film, intensities of the carbon, oxygen and sulfur signals were almost independent of the depth from the surface. By contrast, for the natural rubber film, intensities of zinc and sulfur signals were significantly dependent upon the depth from the surface. These imply that sulfur may diffuse into *cis*-1,4-polyisoprene regardless of the proteins, whereas zinc may not without the proteins.

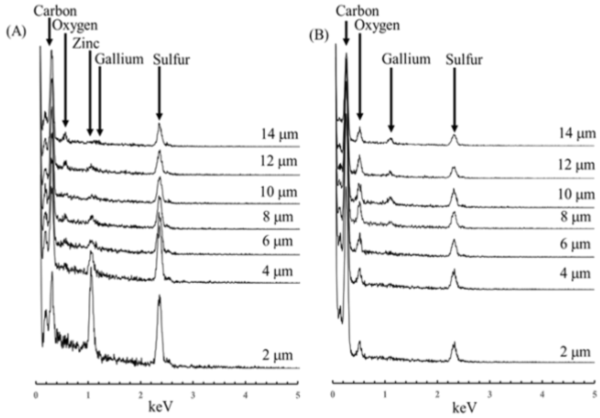

Figure 1 FIB-SEM EDX spectra obtained at each 2 μm interval from the surface to 14 μm in depth for natural rubber film (A) and DPNR film (B).

Figure 2 shows ^{13}C-NMR spectra for the latex-mixed natural rubber vulcanizate and mechanically mixed natural rubber vulcanizate. Five major signals appeared at about 23, 26, 32, 125 and 135 ppm. These signals were assigned to C_5, C_4, C_1, C_3 and C_2 carbons of *cis*-1,4-isoprene units, according to the previous reports. Enlarged ^{13}C-NMR spectra between 35 and 60 ppm are also inserted in Figure 2. Small signals at 37.0, 44.5, 50.0, 50.5, and 57.0 ppm appeared after vulcanization. The signals at 50.0 and 50.5 ppm were assigned to the quaternary and tertiary carbons linking to sulfur formed by addition reaction of sulfur to the carbon-carbon double bonds of *cis*-1,4-isoprene units. In contrast, the signals at 57.3 and 58 ppm were assigned to the quaternary and tertiary carbons linking to sulfur formed by recombination of allyl radicals produced by hydrogen abstraction of *cis*-1,4-polyisoprene with sulfur radicals. The values of chemical shift of the signals appearing after vulcanization for the latex-mixed natural rubber vulcanizate and the mechanically mixed natural rubber vulcanizate were completely identical to each other. This implies that the structure of the crosslinking junctions of the latex-mixed natural rubber vulcanizate is the same as those of the mechanically mixed natural rubber vulcanizate. The difference was found in the intensity of the signals; that is, the intensity of the signals for the latex-mixed natural rubber vulcanizate was lower than those of the mechanically mixed vulcanized rubber vulcanizate. The difference was related to the mechanical properties of vulcanized rubbers.

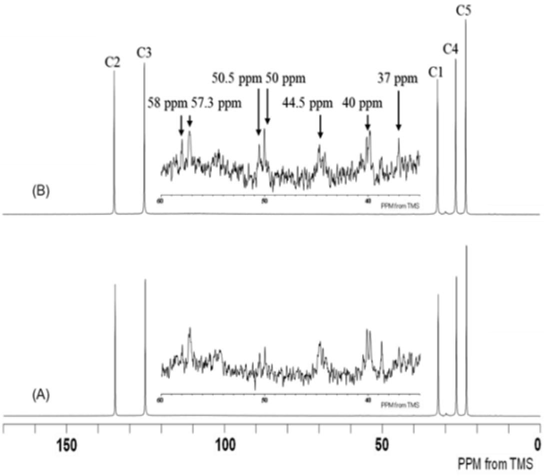

Figure 2 ^{13}C-NMR spectra and Enlarged ^{13}C-NMR spectra between 35 and 60 ppm for the latex-mixed natural rubber vulcanizate (A) and mechanically mixed natural rubber vulcanizate (B).

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Nanocellulose Reinforced Rubber Composites

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Keywords: Nanocellulose; sustainability; reinforcement; rubber composites

Developments of renewable, eco-friendly, and sustainable materials have significantly grown in material science and engineering during the past few decades as they can lead to novel materials with fewer negative environmental effects and carbon footprints [1]. Nanocellulose reinforced rubber composites represent a promising advancement in materials science, offering significant improvements in mechanical, thermal, and barrier properties compared to traditional rubber composites [2]. Derived from renewable and biodegradable sources, nanocellulose, in its various forms such as cellulose nanocrystals (CNCs), cellulose nanofibrils (CNFs), and bacterial nanocellulose (BNC), provides a lightweight yet highly effective reinforcing agent [3].

We explored the integration of nanocellulose into rubber matrices, highlighting the resulting enhancements in tensile strength, modulus, toughness, and overall durability. The three-dimensional network of cellulose nanofibers (cellulose/cellulose network and Zn/cellulose network) in the NR matrix plays a significant role in improving the properties of the crosslinked nanocomposites [4, 5, 6]. We also addressed key challenges, including the need for uniform dispersion, strong interfacial bonding, and effective processing techniques. To improve the compatibility between nanocellulose and rubber, we employed current solutions like surface modification of the alcoholic hydroxyl group and advanced compounding methods. The surface functionality of cellulosic materials triggers their interactions with the rubber matrix [7]. Importantly, the potential applications of these composites are vast, spanning from the automotive and medical industries to packaging and construction, driven by the materials' superior properties and environmental benefits [8].

Our ongoing research aims to optimize these composites further, ensuring they meet the demands of modern engineering applications while promoting sustainability. This study underscores the transformative potential of nanocellulose reinforced rubber composites in developing high-performance, eco-friendly materials for a wide array of industrial uses.

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Design and Preparation of Biobased Elastomers Aiming at Sustainability, Carbon Peaking and Carbon Neutrality Goals

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Keywords: bio-based elastomer; dandelion rubber; thermoplastic vulcanizates; wasted tires

We have designed and fabricated polyester-type bio-based engineering elastomer(BEE) and itaconate BEE, and set up the first 100 tons of pilot-scale production line of polyester-type BEE all over the world, And a 10000-ton per year production line of biodegradable polyester rubber has now landed in Jiangsu, China, and meanwhile the world's first 5000 t/y production line of bio-based itaconate elastomer has been built in Shandong, China. We took the lead to establish the Chinese dandelion rubber industrial technical innovation union and set up the first Chinese extraction model line of dandelion rubber, and prepared the first car-used conceptual tire made of dandelion rubber. Meanwhile, we have invented the complete set of key technologies of reusable and recyclable thermoplastic vulcanizates (TPV) fabricated via dynamic full vulcanization and constructed the first Chinese ten thousands tons of TPV enterprise, which is as well the largest scale up to now in China. We have developed the continuous, effective, green multi-stage screw dynamic desulfurization regeneration rubber technology, and successfully realized the construction and industrial practice of the complete set of technologies of the regeneration rubber produced via a green approach on the level of ten thousands tons of wasted tires, which are exported to the European Union. In addition, we have successfully prepared bio-based silica by utilizing renewable resources such as rice husks and straw as raw materials, and uses carbon dioxide instead of sulfuric acid as a precipitation reagent to produce bio-based silica with a specific surface area of 50 to 500m^2/g, with a carbon reduction of 0.5 tons for every 1 ton of bio-based silica used, which is a globally leading negative carbon technology with significant carbon dioxide reduction effects to achieve carbon neutrality goals. By utilizing citric acid to prepare Carbon Quantum Dots, an excellent anti thermal oxidative aging and bio-based additive has been achieved. [1-13]

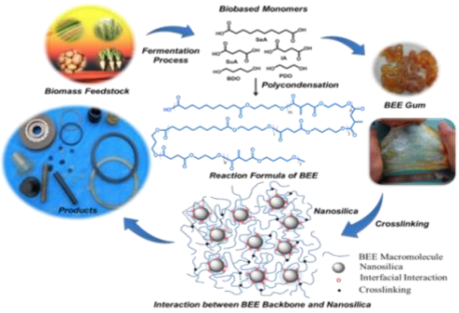

Figure 1. Preparation and application of Chinese original polyester elastomer

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Invited Speeches

Sustainability of Rubber in Mining: Ecosystem & Global trend

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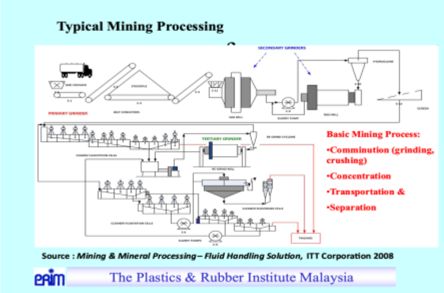
Keywords: Sustainability; mining equipment, carbon emission, rubber liners.

Significant advances of polymer processing technology have been developed and adopted for the manufacturing of a wide array of products not only fulfilling requirement of our daily lives but also meeting multiple industrial needs and application which include mineral processing and application. Rubber consisting of both natural (Hevea Brasiliensis) and synthetics are extensively used in all types of mining application replacing energy intensive counterparts especially metal components.

Rubbers are characterized by its light weight, noise reduction, environmental friendliness, capable of being recycled leading to reduced carbon footprint. The nature of mineral processing entails the constant contact between machinery and abrasive and corrosive media. The increasingly high mineral demand has led to the development of innovative solutions, in terms of rubber lining process in the handling of aggressive operating environments. Such equipment includes rubber liners for different type of grinding mills, chemical storage tanks, hoses, centrifugal slurry pumps, hydro-cyclones, valve liners and much more. The technical attributes of different types of polymers are exploited for use in different stages of mineral processing e.g. crushing, screening, grinding, classification.

Amid the increasing concerns of Climate Change and global warming, mining process can lead to environmental degradation posing many challenges. Hence, this sector is considered the major potential contributors to Greenhouse gasses (GHG) emissions resulting in significant carbon footprint. A number of approaches are underway to address this concern. United Nations members adopted in 2015 an agenda i.e. "Transforming Our World: The **2030 Agenda for Sustainable Development**" (SDGs). Appropriate mapping the linkage between mining process and the SDGs will encourage mining product manufacturers to incorporate relevant SDGs into their business and operation.



Typical Mining Processing

Basic Mining Process:
- Comminution (grinding, crushing)
- Concentration
- Transportation &
- Separation

Source : *Mining & Mineral Processing – Fluid Handling Solution,* ITT Corporation 2008

The Plastics & Rubber Institute Malaysia

It is critical that mining products manufacturers who supply to the Fortune 500 companies must be aware of their Climate Targets; Carbon Neutral, Renewal Energy and Science based Targets, of which emissions are reduced to keep global warming below 2 degrees C. Further, Awareness of Carbon Border Adjustment Mechanism (CBAM) which is a proposed carbon tariff on **carbon intensive products**, such as cement and some electricity, imported by the European Union. Mining rubber products not optimally designed for sustainability will be similarly impacted. This couples with increasing global trend that, under the stakeholder's pressure, global buyers e.g. major mining companies *(Glencore, BHP, China Shenhua Energy etc)*
*are s*hifting purchasing preferences to manufacturers that demonstrate sound Sustainability standards.

Escalating environmental concern warrants mining rubber development to adopt a holistic approach by embracing SDG, IR 4.0, ESG etc. Hence, rubber has a pivotal role in the mining industry's sustainability via extending equipment life cycle while balancing ESG consideration for a resilient future. Towards this end, product manufacturing plants need upgrading to meet future environmental challenges and requirements which include the use of renewal energy, environmental friendly feedstock, waste reduction, circular economy to ensure continuous innovation for green and more efficient mining sector.

Acknowledgement

Grateful thanks to the following for insightful deliberation and invaluable input to my presentation:
1. Mr. Tony Siric, Marketing Manager, Weir Minerals Australia
2. Mr. Jeishen, General Manager, PT. Growth Asia, Indonesia

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Effects of surface modification of dual filler system based on carbon black and carbon nanotube on the positive temperature coefficient behavior of polymer composites

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Keywords: Positive temperature coefficient; Carbon black; Carbon nanotube; Temperature sensor

Positive temperature coefficient (PTC) materials are usually fabricated by mixing a semi-crystalline polymer with various conductive fillers. The resistivity of PTC materials shows a dramatic increase at around the melting temperature (T_m) of crystalline blocks. The PTC effect is widely accepted in devices for the over current protection and over-heating protection [1]. Recently, PTC materials has been studied for a possible application for wearable body temperature sensor by choosing the polymer system with T_m similar to human body temperature and carbon nanotubes (CNT). It was reported that the reproducibility is quite low due to poor dispersion of CNT in polymer matrix, and the negative temperature coefficient (NTC) phenomena above T_m [2-4]. In this work, PTC materials were fabricated using a dual filler system of acrylate copolymer (AC)-grafted CNT (AC-m-CNT) and modified carbon blacks (CB) to achieve the enhanced PTC performance with lower NTC effect and higher reproducibility.

CNT was functionalized (m-CNT) with phosphorus pentasulfide (P_4S_{10}) and the m-CNT was reacted in the presence of acrylate monomer to prepare the AC-m-CNT. Octadecyl acrylate (OA) and butyl acrylate (BA) were used as acrylate monomer by controlling their ratios. CB were modified (Ti-CB) using titanate coupling agent. Ti-CB was mixed with AC-m-CNT to fabricate the AC-m-CNT/Ti-CB composite. CNTs were either directly connected to each other or were connected by Ti-CB in the AC-m-CNT/Ti-CB composite (Figure 1). The PTC effect of the AC-m-CNT/Ti-CB was observed at around T_m of AC. When the crystalline block of AC melts, the volume expansion occurs leading to an increased space among conductive fillers (Figure 2). The AC-m-CNT/Ti-CB showed the enhanced PTC performance (I_{PTC}=3.01), possibly due to low initial resistivity of dual filler system and anti-oxidation action of titanate coupling agent (Figure 3). Furthermore, the NTC effect disappeared because Ti-CB prevent the moving of CNT fillers at above T_m of AC. In addition, the reproducibility was enhanced by higher interactions between AC and CB due to titanate coupling agent. The response temperature of PTC effect can be adjusted by changing the ratio of OA and BA. The prepared AC-m-CNT/Ti-CB sensor showed a good temperature-resistivity response to various temperature stimuli such as hot water and human body temperature.

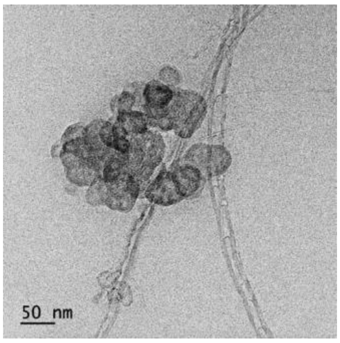

Figure 1. Field-emission transmission electron microscopy (FE-TEM) image of OA-m-CNT3/Ti-CB10

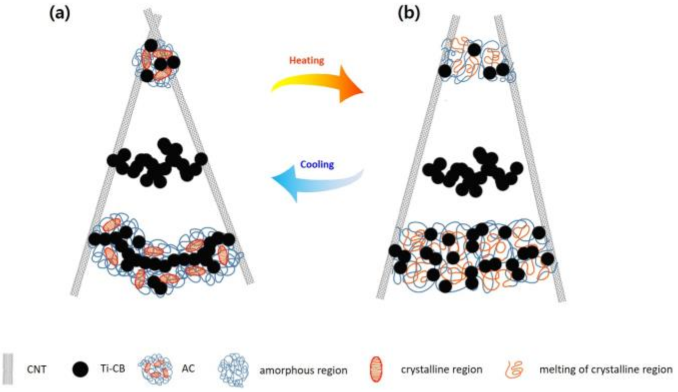

Figure 2. Schematic illustration depicting the reversible PTC behavior of AC-m-CNT/Ti-CB composite; (a) before heating, (b) heating over melting temperature

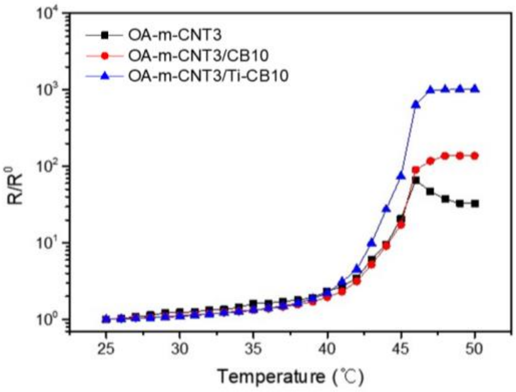

Figure 3. Temperature-dependent resistance of OA-m-CNT3, OA-m-CNT3/CB10 and OA-m-CNT3/Ti-CB10 composite

Acknowledgement

This work was supported by the Technology Innovation Program (20010851, An advanced butadiene rubber and a functional complex development for super abrasion tire) funded By the Ministry of Trade, Industry & Energy (MOTIE, Korea).

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Bio-based processing oil as an alternative in the development of greener tire tread compound

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Keywords: Bio-based processing oil, tire tread compound

Abstract: Mineral oil from petroleum can potentially be replaced with bio-based oil as processing oil in elastomers. Mineral oil is not environmentally friendly and comes from a non-renewable resource. In order to create greener tire treads, this study explores the possibilities of soybean and sunflower oils as bio-based processing oils. The ternary rubber blend mixed with soybean oil and sunflower oil and other ingredients using conventional rubber processing method. As a result, the sunflower oil compound demonstrated higher tensile strength and abrasion resistance compared to the conventional rubber vulcanizate. Soybean oil, meanwhile, significantly improved its tear strength, reaching 98.36 N/mm, and provided good fuel efficiency. When compared to bio-based oil compounds, mineral oil compounds showed equivalent dynamic mechanical performance in the elastic response under dynamic deformation and skid resistance.

1 Introduction

Several prominent tire manufacturers have committed to using only sustainably produced materials in their tire products by 2050 to achieve complete carbon neutrality [1]. The recent focus on creating environmentally friendly tires involves material development, particularly the selection of components from renewable resources such as incorporation of silica and bio-based oils [2]. This study specifically explores the impact of sunflower oil and soybean oil on the properties of a green tire tread compound, emphasizing the potential of bio-based oils to enhance the interaction between filler and rubber in carbon black-filled rubber compounds.

2 Methodology - Sample preparations

The rubber compounds (as shown in Table 1) were mixed using a 1.6 L lab-use intensive mixer (Model: CL-BM16, Calendar Machinery Industry Corp., Taiwan) equipped with Bunbury-type rotor. Mixing was carried out using two-stage mixing process (masterbatch and final mix) and samples for testing were produced using hot press.

Table 1. Formulation of rubber compounds with mineral oil (MO), sunflower oil (SFO), and soybean oil (SBO).

Ingredients	Composition	Ingredients	Composition
Natural rubber (NR)	60	Zinc Oxide	4
Synthetic rubber	40	Stearic Acid	2
Filler 1	28	Antioxidant	2
Filler 2	40	Antiozonant	1
Processing oil (MO/SFO/SBO)	13	Accelerator	1.5
Coupling agent	4.2	Sulphur powder	1.5
Peptizer	1	Retarder	0.35
Wetting agent	1		

3 Results and Discussions

3.1 Physical and mechanical properties

Table 2 outlines the physical and mechanical characteristics of rubber compounds using mineral oil, sunflower oil, and soybean oil. Swelling behavior, often linked to crosslinking density, shows comparable crosslink densities in rubber compounds with sunflower oil and soybean oil, suggesting a similar amount of unsaturated structural contents. Additionally, both sunflower oil and soybean oil contributed to increased swelling in the rubber compound when exposed to toluene, attributed to a reduction in crosslink density [3].

3.2 Dynamic mechanical properties

Rolling resistance and skid resistance are vital parameters for predicting tire performance during dynamic deformation. The ratio of loss modulus to storage modulus, known as loss tangent (Tan δ), is significant. Higher skid resistance is essential for tire safety, while lower rolling resistance contributes to better fuel efficiency. The study uses Tan δ values of rubber compounds with mineral oil (MO), sunflower oil (SFO), and soybean oil (SBO) at temperatures -10°C, 0°C, and 60°C to predict ice traction, skid resistance, and rolling resistance [4]. Notably, the sunflower oil compound shows a slight increase in rolling resistance due to a higher Tan δ value at 60 °C, while the soybean oil compound exhibits a slightly decreased rolling resistance. Both bio-based oil compounds lead to a minor reduction in ice traction and skid resistance.

Table 2. Physical and mechanical properties of rubber composite with mineral oil (MO), sunflower oil (SFO), and soybean oil (SBO)

Properties	MO	SFO	SBO
Swelling index	1.43	1.65	1.64
Crosslink density (x 10^{-5} mol cm^{-3})	8.09	7.96	7.85
Modulus at 300%	9	8	8
Tensile strength (MPa)	19.48	20.42	19.12
Elongation at break (%)	655	661	615
Tear strength (Nmm^{-1})	89.55	92.89	98.36
Abrasion resistance (ARI)	214	227	213

4 Conclusions

The study explored the feasibility of using two bio-based oils as substitution of petroleum-based mineral oil in rubber processing. Both bio-based oils demonstrated the capability to serve as processing oils without causing notable adverse effects on the properties of environmentally friendly rubber vulcanizates.

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Modified natural rubber latex: A smart material for sustainable development

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Keywords: Epoxidized natural rubber; Green process; Silica-reinforced rubber; Waterborne coating

Nowadays, global warming and environmental concerns are very much paid attention worldwide. Natural rubber (NR), a renewable material is considered a green alternative to petroleum-based products. The NR in the form of latex is derived from rubber trees that capture and store well carbon, hence the utilization of NR serves to mitigate climate change. The NR latex can be modified via one or two steps at the carbon-carbon double bond to extend its utilization in various targeted applications [1]. Modification of NR using epoxidation and hydrogenation reactions has been successfully reported [2-3]. The epoxide groups could provide the increased polarity of NR, hence being used as a toughening agent for compostable poly(lactic acid) [3].

In this presentation, a low degree of epoxide functionalized NR (ENR5) latex was prepared using a small amount of hydrogen peroxide and formic acid. The ENR latex was explored to mix with 40 phr silica particles previously treated with the ultrasonication process (USi). It is a simple and environmentally friendly method to prepare USi-ENR5 composite in the latex stage (Figure 1). It was found that the silica particles could infiltrate the rubber matrix without silica flocculation on the tray after water evaporation. It can be postulated that the silica particles were well dispersed in the ENR5 via the hydrogen bonding between the silanol groups of silica particles and the epoxide groups of ENR5 (Figure 2). The mechanical properties of the cured USi-ENR5 were compared with those of silica-filled NR using a conventional mixing process (SiC-NR) and NR filled with silica treated by a silane coupling agent (SSiC-NR). As a result, the mechanical properties of USi-ENR5 were higher than those of SiC-NR and SSiC-NR. This might be because the strong interaction between the silanol groups of silica particles and epoxide functional groups of ENR5 leads to good silica dispersion in the rubber matrix, hence improved mechanical properties, without a petroleum-based silane coupling agent.

Furthermore, a higher degree of epoxidation of NR latex was explored, followed by oxidative degradation using hydrogen peroxide, resulting in low molecular weight epoxidized natural rubber (LENR) latex. Due to the high degree of epoxide content in LENR, it could mix with epoxy resin to prepare waterborne coating material. As a result, the properties of cured epoxy/LENR coating applied on a tin substrate show better adhesion than that of pure epoxy coating. The LENR could be used as an impact modifier of the epoxy coating.

The modified NRs prepared in latex form, ENR5, and LENR could be easily handled in an environmentally friendly medium (latex). They can substitute petroleum-based silane coupling agents and/or synthetic toughening agents. It can be noted that the modified NR latex is a sustainable material for valuable development.

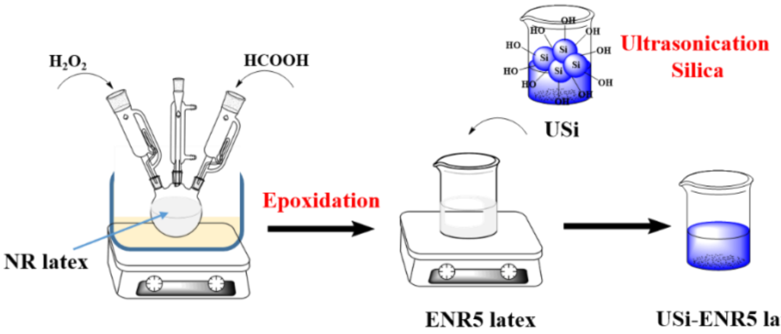

Figure 1. Diagram for preparation of ENR5 latex mixed with ultrasonicated silica particles

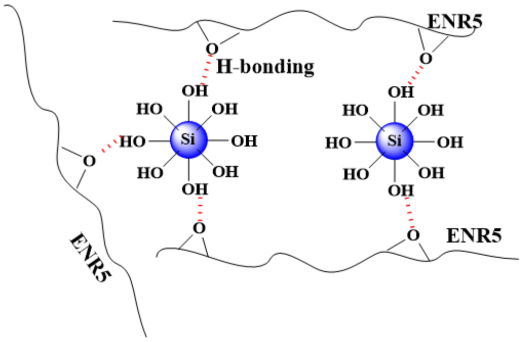

Figure 2. Proposed interaction of silica particles and ENR5 mixed in latex stage

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Oral Presentations

Exploring the Various Characteristics of Epichlorohydrin Based Elastomers: A Comparative Analysis of Damping Properties CO, ECO and GECO Elastomers

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Keywords: Epichlorohydrin, homo-, co- and terpolymers, mechanical properties, energy dissipation.

Epichlorohydrin (ECH) is a versatile monomer foundational to various industrial polymers, each exhibiting unique properties tailored for specific applications [1-3]. This study presents a comprehensive comparative analysis of three types of epichlorohydrin-based elastomers: poly(epichlorohydrin) homopolymers (CO), poly(epichlorohydrin-co-ethylene oxide) copolymers (ECO), and poly(epichlorohydrin-co-ethylene oxide-co-allyl glycidyl ether) terpolymers (GECO), as illustrated in Figure 1. We systematically explored the curing, mechanical, and energy dissipation properties of each polymer. Homopolymers demonstrated superior chemical and oil resistance with low moisture absorption but required innovative curing methods due to the absence of unsaturated double bonds. Copolymers, incorporating ethylene oxide, displayed enhanced flexibility and toughness, while terpolymers, incorporating allyl glycidyl ether, offered effective cross-linking sites for improved curing.

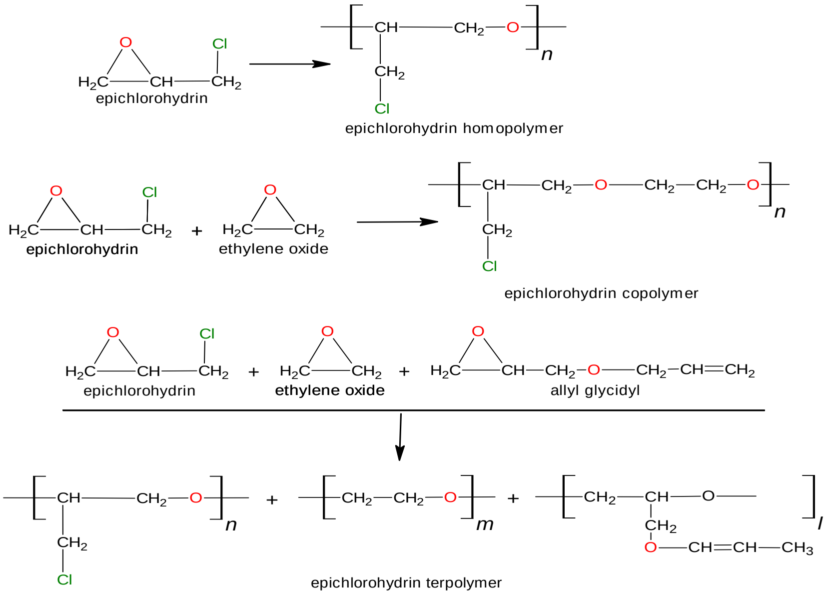

Figure 1. Molecular Structures of Epichlorohydrin Homopolymer (CO), Copolymer with Ethylene Oxide (ECO), and Terpolymer (GECO) Elastomers.

The comparative analysis of curing characteristics reveals that ECO initiates and completes vulcanization faster than both GECO and CO, as evidenced by its shorter scorch and cure times. ECO's higher CRI value indicates a quicker crosslinking rate. GECO exhibited the highest ΔTork value at 7.26 dNm, followed by ECO at 7.00 dNm, and CO at 6.05 dNm. This discrepancy suggests that GECO may achieve a higher crosslink density compared to the other elastomers, potentially indicating the presence of unsaturated bonds on its polymer chains.

The mechanical properties of elastomers were investigated following curing at 190°C until reaching the t90 time for each of the CO, ECO, and GECO based compounds. The comparative analysis of the mechanical properties of CO, ECO, and GECO reveals distinct differences in their performance characteristics. ECO demonstrates the highest stiffness with an Emod of 1.55 MPa and the greatest hardness at Shore A 40, making it the most rigid among the three. CO, on the other hand, exhibits the highest tensile strength at break (1.71 MPa) and elongation at break (346%), indicating superior flexibility and ability to withstand higher strains before failure. GECO presents intermediate properties, with moderate stiffness (Emod of 1.12 MPa), tensile strength (1.33 MPa), and elongation at break (248%). The Shore A hardness of GECO is 38, making it softer than ECO but harder than CO.

For the energy dissipation calculations, compression tests were conducted on all elastomers. The experiments were carried out at a constant rate of 50 mm/minute, corresponding to a frequency of 6.72 Hz, and were repeated for 10 cycles. Relative hysteresis loss, which compares to total input energy loss, provides a normalized measure of the material's energy dissipation efficiency [4]. The comparison of relative hysteresis loss among GECO, ECO, and CO elastomers reveals that GECO has the lowest relative hysteresis loss, indicating the highest efficiency in energy dissipation, and CO has the highest relative hysteresis loss is the least efficient in terms of energy dissipation.

This comparative analysis highlights the versatile properties of epichlorohydrin-based polymers, supporting their use in various industrial applications. The study underscores the importance of selecting the appropriate polymer type to achieve desired performance characteristics.

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Effect of Biochar as Hybrid Particulate Filler on Mechanical Properties of Pineapple Leaf Fiber Reinforced Natural Rubber

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Keywords: Pineapple leaf fiber; Reclaimed rubber; Hybrid rubber composite; Biochar.

This study aims to examine the effect of particulate hybrid fillers, namely biochar derived from the non-fibrous component of pineapple leaf, on the mechanical properties of vulcanized pineapple leaf fiber (PALF) reinforced natural rubber composite. The investigation focuses on the utilization of PALF, reclaimed rubber, and biochar to produce rubber composites with low carbon footprint. The rubber matrix was natural rubber (NR) mixed with reclaim rubber at the ratio of 80:20. PALF content was fixed at 10 phr while that of biochar was varied at 10, 20 and 30 phr. Stress-strain curves were analyzed to assess the alterations induced by PALF and particulate biochar on the rubber's behavior. It was found that biochar influenced the stress transfer pattern and elongation at break. Interestingly, it was found that the addition of biochar reduce the ability of the matrix to transfer the stress to the reinforcing fiber and reduce elongation at break. As the content of the biochar increased, the stress transfer ability of the matrix seems to recover to that without biochar. However at this high biochar content, the elongation at break decreased drastically. The findings shed light on the limit to which biochar can be added into the rubber composite or improvement in the mixing should be further studied.

The growing interest in sustainable materials has led to research on incorporating plant-derived fillers into polymer composites. This study explores the development of a rubber composite with biochar from non-fibrous pineapple leaf [1] and a fixed amount (10 phr) of pineapple leaf fiber (PALF). By varying the biochar content, we aim to manipulate the rubber matrix stiffness, altering the stress transfer to the reinforcing fiber and potentially enhancing mechanical properties. Biochar's carbon stability offers better sequestration than other organic fillers. The rubber matrix consists of natural rubber (NR) and reclaimed rubber (80:20 ratio), with biochar content varied at 10, 20, and 30 phr. Composites with unidirectionally aligned fibers will be prepared and tested for mechanical properties, targeting materials with adequate strength and high resistance to deformation. This investigation focuses on stress-strain characteristics and elongation at break.

Table 1 displays the composition of the rubber compounds used in the study. The compounds were mixed on a laboratory two-roll mill and then sheeted out to create unidirectionally aligned PALF [2]. These aligned sheets were subsequently compression molded for testing.

Figure 1 displays representative stress-strain curves of different rubber composites. The control rubber, made of a blend of natural rubber and reclaimed rubber, provided satisfactory strength. When 10 phr of unidirectionally oriented PALF was introduced, the curve changed drastically, with stress shooting up suddenly at very low strain. With the introduction of 10 phr biochar, the stress dropped to almost half but continued to rise with increasing strain, with the material failing at a slightly lower strain. Further addition of biochar brought the stress in the low strain region up towards that of the composite with only PALF. However, the stress and strain at break dropped sharply to about 8.5 MPa and 250%, respectively. This could be due to the large size of biochar which could greatly weaken rubber composites by causing localized stresses and fracture points within the rubber matrix [4,5]. It suggests that the content of biochar may be limited to about 10 phr. Work is now underway to improve the mixing process to achieve higher performance.

Table 1. Formulations of rubber compounds

Ingredients	phr
Rubber (NR (STR5L):Reclaim Rubber = 80:20)	100
Carbon black (N330)	30
Zinc oxide	5
Stearic acid	2
6PPD	1.5
CBS	1
Sulphur	2
PALF	10
Biochar (80 mesh)	10, 20, 30

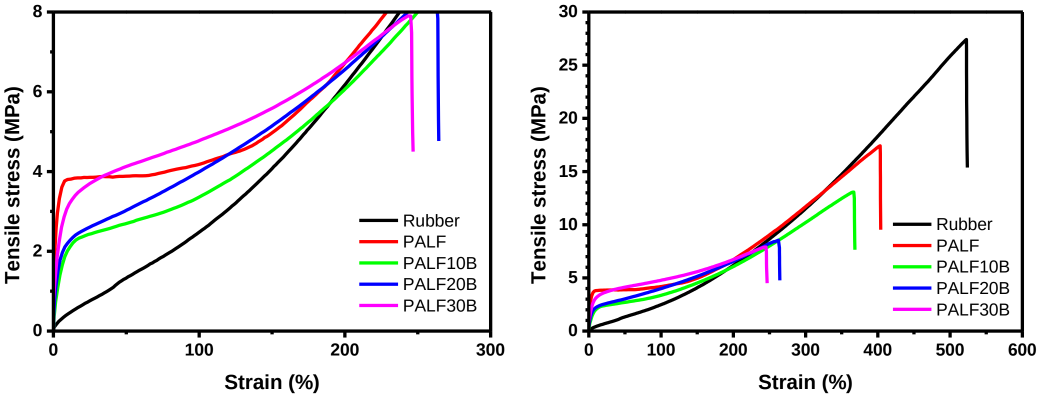

Figure 1. Stress-strain curves of rubber composites containing PALF and different amounts of biochar in the low strain region (left) and overall strain (right).

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Investigating the antioxidant properties of lignin on rubbers

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Keywords: Lignin, fractionation, antioxidant properties.

Lignin is a naturally abundant, low-cost, low-density, bio-renewable, and environmentally friendly biopolymer, while only around 2 wt% of technical lignin has been used to create products with added value, and the majority ended in landfills or pyrolysis [1, 2]. Lignin can be a good alternative to antioxidants because of its naturally abundant phenolic groups. However, the heterogeneity of lignin makes it a major challenge to produce uniform properties and manufacture additional value. At this point, fractionation provides an essential contribution. Through fractionation, it becomes feasible to segregate lignin into distinct high- and low-molecular-weight fractions. Lignin with low molecular weights typically exhibits strong antioxidant activities [3].

In this study, lignin from three different sources (Sigma Aldrich Kraft lignin from softwood, UPM BioMotion^{TM}X40 sourced from hardwood and enzymatic hydrolysis lignin (EHL) from corn cob) was fractionated, and three different fractions were prepared from each procedure. The process of fractionating Kraft lignin (KL) was carried out in two steps. In the first stage, the insoluble component was isolated from the raw materials (F0) using 100% ethanol. In the second step, the insoluble part was fractionated by using 70% ethanol. The initial portion yielded the lowest molecular weight, and this trend is consistent across other sources.

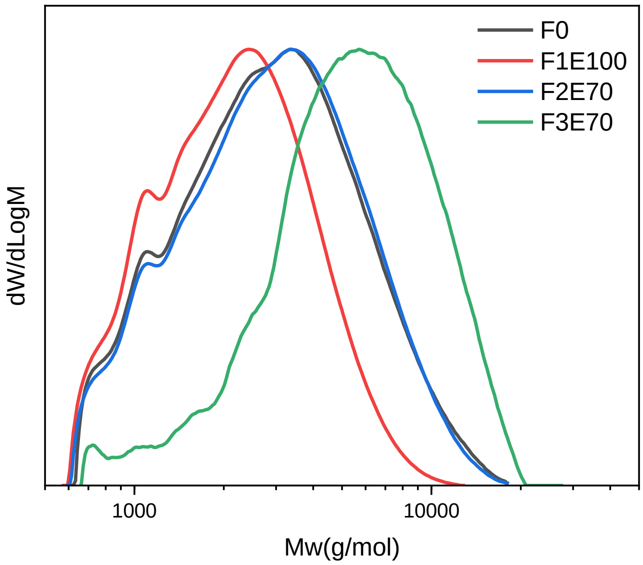

Figure 1. GPC results of KL and its fractions

While the F1 of UPM yielded the lowest molecular weight (Mw), it also exhibited the lowest overall yield, as illustrated in Figure 2. Chemical structure differences have a direct impact on yield and Mw. Because of its large molecular weight, the F0 and F3 from UPM and EHL exhibited low solubility, posing challenges in the preparation of GPC samples. The antioxidant properties of F1 derived from different sourced lignin and its effect in rubber composites were studied.

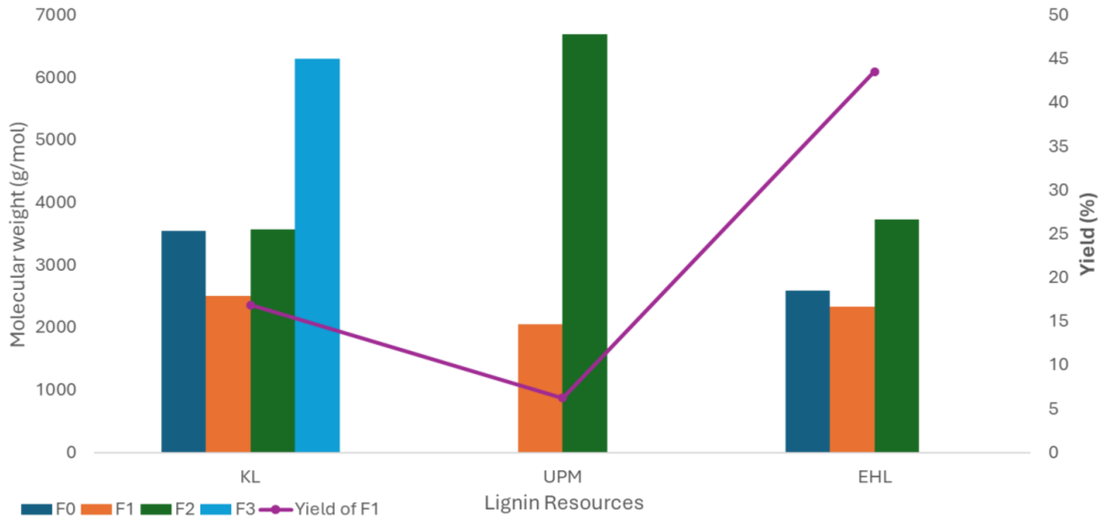

Figure 2. Mw of fractions from different resources and the yield of F1

Acknowledgement

O.N. Arslan would like to acknowledge the financial support provided by the Republic of Türkiye Ministry of National Education.

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Large amplitude oscillatory shear rheology of liquid silicone rubber: insights into filler structure and viscoelasticity

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Keywords: liquid silicone rubber; rheology; simulation; viscoelasticity.

One of the most employed methods to determine polymers' resistance to shear flow is applying rotational rheology under oscillatory shear, which is able to quantify complex viscosity η^* values. In the case of liquid silicone rubber (LSR), the linear viscoelastic conditions necessary to achieve meaningful η^* values are limited to small strain amplitudes (SAOS, or small amplitude oscillatory shear) [1] that are not compatible with the shear range experienced during injection moulding. However, departing to large amplitudes (LAOS) leads to a non-linear viscoelastic scenario that is complex to analyse [2], mainly concerning the calculation of η^*. Within this context, the present work introduces considerations concerning non-linear viscoelasticity of liquid silicone rubber and how these considerations impact the determination of η^*. By employing a strain-controlled rheometer (cone-and-plate geometry), LSR samples (32wt% filler, M_w = 88673 g.mol^{-1}) were analysed under linear (SAOS) and non-linear (LAOS) viscoelastic conditions and the deviation to linearity was assessed.

As shown in **Figure 1**, G' presented fairly constant values up to $\gamma = 0.2\%$, while G" remained constant until $\gamma = 0.6\%$. The range up to 0.2% can be then defined as the linear viscoelastic range for this sample, in accordance with Weißer et al. [1]. Within this range, G' > G", meaning that the sample behaves as an elastic solid gel. The solid gel-like behaviour can be justified by the high content of filler particles and the molecular weight above the critical molecular weight for entanglements formation (32 kg.mol^{-1} according to [3]). As the strain amplitude increases, the sample departs from mechanical equilibrium and G' and G" decrease, i.e., shear thinning occurs. Shear thinning is the consequence of two phenomena: chain orientation and microstructure alignment along the flow direction and breakage of the filler structure (Payne effect). The passage from G' > G" to G' < G" represents the transition between the solid gel-like and the liquid-like states of LSR, where it goes from low to high fluidity.

As a quantitative parameter to measure non-linearity, the 3rd harmonic's intensity $I_{3/1}$ in relation to the strain amplitude is also shown in **Figure 1** (right). Below $\gamma = 0.1\%$, $I_{3/1}$ varies with the instrument noise and is lower than 0.01. While the strain amplitude further increases, $I_{3/1}$ increases with γ^2 for sufficiently small amplitudes. $I_{3/1} \propto \gamma^2$ already occurs even when G' and G" seem to be constant, which means that phenomena ultimately leading to non-linearity already take place. The apparent two-step increase of $I_{3/1}$ may be related to the changes in the interactions among poly(siloxane) oligomers (entanglements, for example) and to the filler microstructure damage. From the $I_{3/1}$ values, it is reasonable to state that at $\gamma = 0.1\%$ the fundamental harmonic fully describes the stress response. At $\gamma = 10\%$, however, $I_{3/1}$ reaches 0.1, which signifies that the 3rd harmonic is 10% of the fundamental harmonic, indicating non-linearity. At 10% strain, though, LSR's microstructure in terms of polymer-polymer, filler-filler, and polymer-filler interactions is closer to the one that is found during the injection moulding cycles.

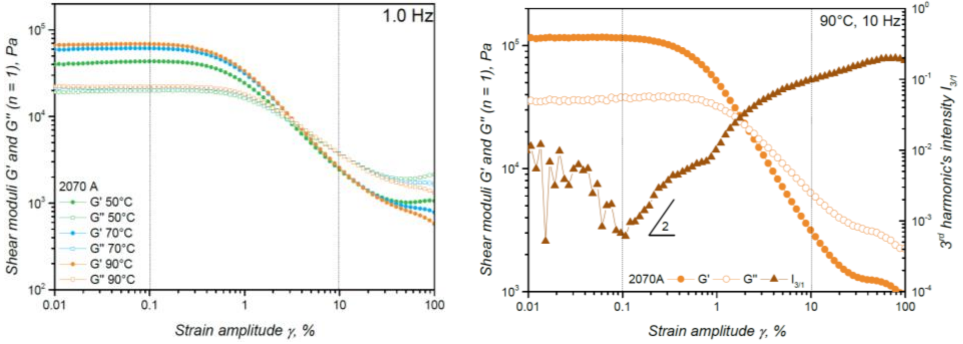

Figure 1. Variation of G' and G'' (left) and of the 3rd harmonic's intensity (right) with imposed strain amplitude

Thus, the variations of G', G", and η^* with the imposed frequency was studied at 10% amplitude and are shown in **Figure 2**. G' and G" increase with frequency due to the response of the polymer chains to the rapid applied strain associated to high frequencies. At the lowest frequency, the close-to-terminal slopes for G' and G" are obviously different and lower than respectively 2 and 1 for net PDMS as theorized by the Rouse model, since solid fillers are incorporated to the polymer matrix. The main difference between frequency sweeps at 0.1% and 10% is the sample's state during the decreasing frequency sweep. At 0.1%, the filler structure is intact, justifying G' > G", while at 10% the filler structure is damaged and G" overcomes G'. This is an important consideration when calculating complex viscosity, also shown in **Figure 2** (right). Complex viscosity values are lower for 10% amplitude due to the destruction of the filler structure; however, these values represent more faithfully LSR's condition during injection moulding. Therefore, the *modus operandi* for complex viscosity determination should be adjusted to account for these morphological changes, mainly when determining the resistance to shear flow for processing simulation purposes.

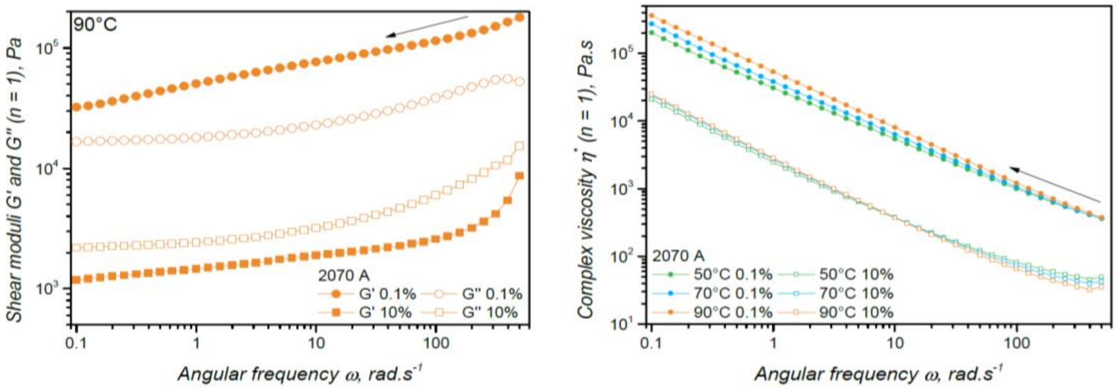

Figure 2. Variation of G' and G'' with strain frequency (left) and the calculated complex viscosity (right)

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New crack growth testing method for rubber compounds by advanced image processing software for DMA instruments

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Keywords: Crack Growth, Dynamic Mechanical Analysis, Rubber,

In last century, the use of rubber increased significantly due to their pioneer performances. One of the main challenges limiting the lifespan of rubber is the apparition and the propagation of cracks when material are submitted to intense energies level or/and exposed to rough surfaces. In order to study crack propagation, only few techniques of crack monitoring have been developed. The original point of the present work is the use of a new method developed by Metravib Material Testing, which combines a Dynamic Mechanical Analyzer (DMA) and an accurate optical system detecting automatically the crack tip position changes with a great accuracy. The aim of the paper is to use of this new method to determine the effect of the temperature and the frequency of the mechanical excitation on the crack growth behavior of SBR and silicone rubbers.

Crack growth monitoring of SBR compounds were performed at 1 Hz, 10 Hz and 95 Hz at 23°C. Figure 1 below presents the crack growth rate as a function of the tearing energy (J/m²) for SBR material. For each frequency, a power law shows a clear dependence between the crack growth rate (nm/cycle) and the energy G. This result is a common one and shows that the crack growth rate versus the tearing energy follow a power law equation. Results show that for a given value of energy supplied, the propagation speed is higher as the frequency is lower. This phenomenon can be explained by the fact that at low frequency, the rubber is stretched during a longer time at maximum strain. Consequently, the crack get a longer time to progress during this temporal contribution.

The crack growth tests have been performed at three temperature stages: -10°C, 23°C and 100°C at 10 Hz. The effect of temperature on crack growth rate is depicted in Fig. 2. For a given value of energy supplied, the speed of propagation is higher as the temperature is high; this clearly shows that temperature increases the propagation rate of the crack tip. This behavior is explained by the weakening effect of the temperature on the polymer chains constituting the rubber material.

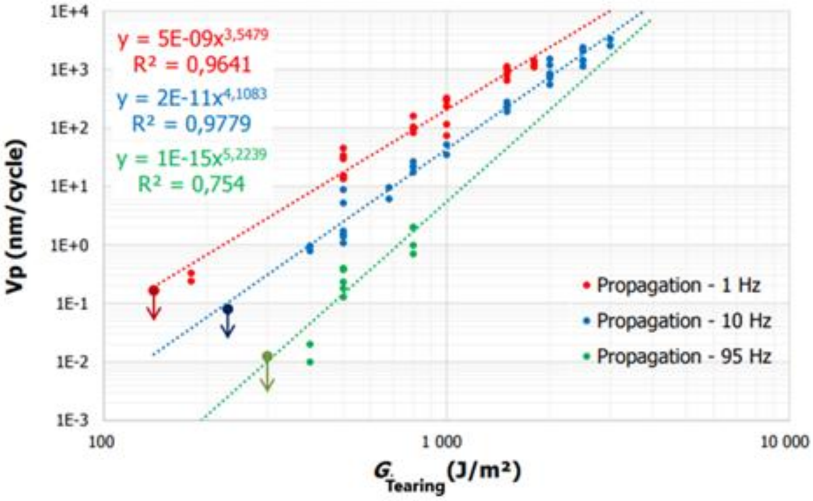

Figure 1. Crack Growth rate as a function of the provided energy, tests were performed at 1, 10 and 95 Hz

For the SBR material, the comparison of the results at 23 and -10°C is close: the curves are almost parallel and the exponents of the power law are similar. On the other hand, the behavior at 100°C is quite different: the exponent of the power law representing the behavior is very different from those obtained at -10 and 23°C and depicts a faster crack growth propagation for the same level of energy. This result can be explained by a phenomenon of degradation of the material due to holding time at 100°C for a long time.

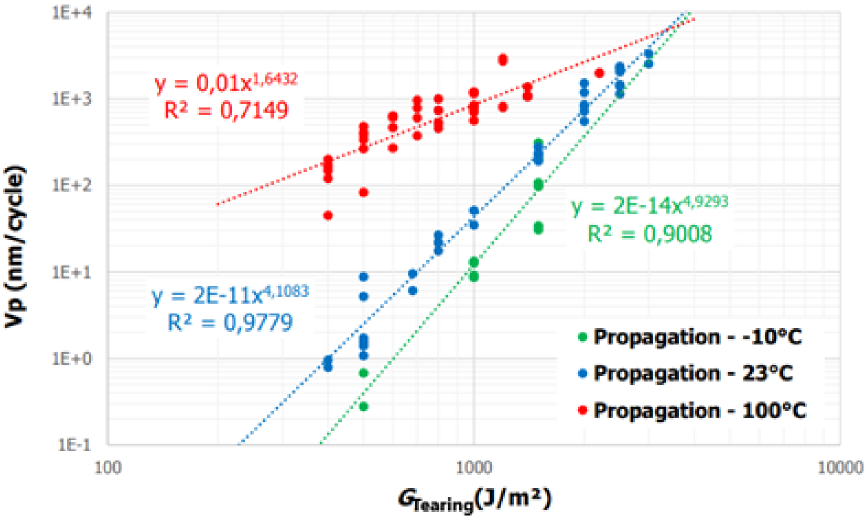

Figure 2. Crack Growth rate as a function of the provided energy, tests were performed at -10, 23 and 100°C

Acknowledgement

We warmly thank Nathan Selles and his coworker from Elanova for their important contribution to this paper.

De Mattia Fatigue test with automatic storage and AI analysis of sample images

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Keywords: Rubber fatigue, ISO 132, ISO 6943, crack growth, Crack detection.

Gibitre Instruments presents a new Fatigue tester with Environmental chamber and multiple video-Cameras that permits to:

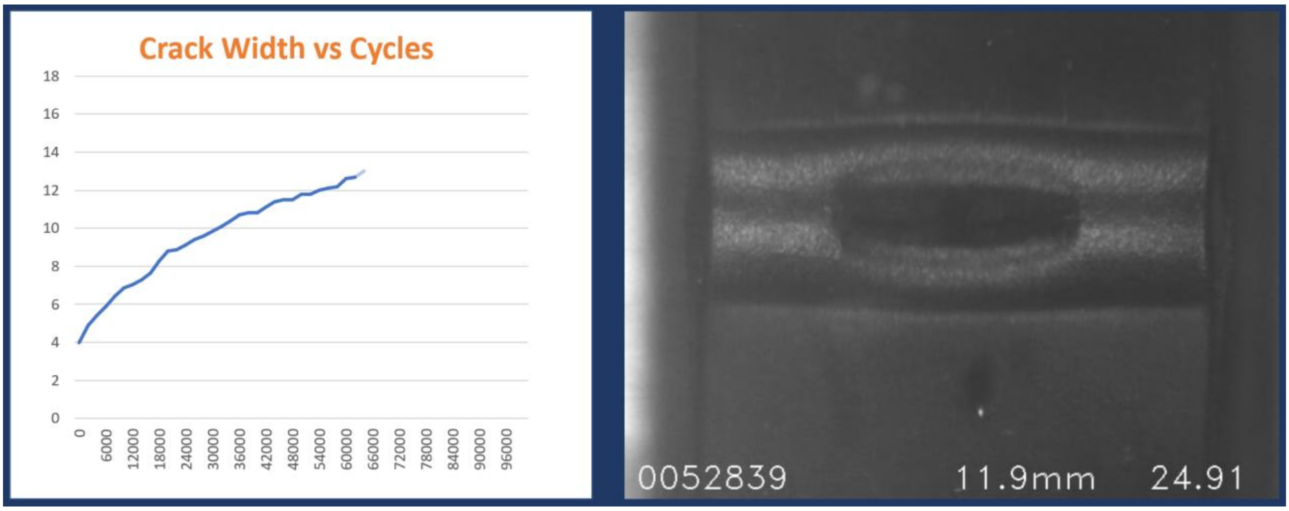
- Set test temperature (-40 to 200°C)
- Set the oscillation speed (0 to 300 rpm)
- Store images and produce a movie for each sample without stopping the test
- Use AI to automatically detect the presence of cracks in the sample (Fatigue Test)
- Use AI to automatically detect the size of the crack (Crack-Growth Test)
- Prepare excel file reporting Crack Growth evolution

The capability of the instrument to produce and analyze images without manual intervention and without stopping the test sequence permits to improve the quality of the results by eliminating errors related with manual data detection, lighting changes in the image preparation, change of testing conditions depending on the interruption of the test for the measures.

The automatic detection of the results permits to enhance the use of the instrument in order to:

- Understand the shape of the crack evolution by analyzing the movie automatically produced by the instrument.

- Produce curves for Number of Cycles vs. Crack size without manual intervention.



Experimental tests have been performed using a NBR formulation at different test conditions.

Results are provided for:

- Correlation between test temperature (-40 to 200°C) and Crack growth speed
- Correlation between test cycle speed (50 to 300 rpm) and Number of cycles to obtain a defined crack width.

The results of the study provide evidence of the importance of the use of De Mattia test method, in addition to other fatigue test methods, for a deeper understanding of rubber behavior.

Peroxide cured silicone rubber optimization of property combinations with Aktisil Q

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Keywords: Aktisil Q; Neuburg Silicious Earth; HTV; Silicone.

High-temperature curing (HTV) solid silicone rubbers are used in molded articles, e.g. in the automotive industry, in technical molding articles etc., as well as in extruded articles, e.g. cable applications and hoses.

The versatile application possibilities of these polymers are based on:

- easy processing
- excellent general mechanical properties
- outstanding compression set
- very good thermal and chemical resistance

Hoffmann Mineral offers Aktisil Q, a functionalized Neuburg Siliceous Earth that has been specially developed for use in silicone rubber. Aktisil Q facilitates the processing of silicone rubber, since on the one hand it reduces or eliminates tack - depending on the dosage - and on the other hand it increases the collapse resistance of profiles during extrusion. In this study we will show how Aktisil Q can enhance the physical properties of silicone rubber.

Also, normally, an improvement in compression set means a simultaneous deterioration of, for example, tear resistance, since these are two opposing properties. Aktisil Q, on the opposite side, at low dosages leads to a constantly high, in some cases even to an additionally improved tear resistance, as the following results show.

The results of this investigation show that Aktisil Q can be used to improve the performance of different silicone polymers, often even to optimize contradictory properties such as compression set and tear resistance at the same time.
In addition, processing is greatly facilitated, as Aktisil Q reduces tack. Furthermore, costs can be reduced, in part significantly.

Natural-based antioxidants for natural rubber compounds

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Keywords: Natural rubber; natural antioxidant; degradation.

Rubbers are very important materials in the industry, used to produce tires, hoses, sealing elements, etc. They stand out in the ability to withstand significant deformation without damage, with this deformation being mostly reversible. One of the most important representatives is natural rubber. It has excellent tack for fabrication, and its vulcanizates have high tensile strength.

Recently, the European Union has been releasing regulations and initiatives aimed at reducing harmful environmental impacts, improving sustainability, and increasing the share of renewable resources across different industries, including the rubber industry. For example, proposing "European Stage VII emission standards" (Euro 7) to regulate tire-related pollution. In addition, U.S. authorities are considering adding tires containing N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD) to the list of hazardous products, which would motivate tire manufacturers to explore safer alternatives. Consequently, there is a growing trend towards increasing number of natural compounds in rubber products.

Vulcanized rubber, during long-term storage, slowly changes its properties; this process is called ageing. Usually, this is caused by chemical reactions with oxygen or ozone from the atmosphere. The weakest places in rubber to undergo these reactions are double bonds. To prevent degradation, rubber should be stabilized with antidegradants. Antioxidants protect rubber from the impact of oxygen, whereas antiozonants protect it from reacting with ozone. Antioxidants can be divided into two major groups based on their mechanism of action: those that interrupt the kinetic chain and hydroperoxide deactivators. In this work different natural antioxidants were used, like: 2-isopropyl-5-methylphenol (Thymol), 5-isopropyl-2-methylphenol (Carvacrol), DL- α-tocopherol, Cashew nut shell liquid (CNSL), Green tea extract and trans-β-farnesene. The chosen antioxidants will then be compared with two antidegradant systems: pure 1,2-dihydro-2,2,4-trimethylquinoline (TMQ) and a typical commercial system containing TMQ + 6PPD.

This work focused on comparing mixtures of natural rubber with various natural antioxidants with mixtures with synthetic antioxidants. Artificial ageing tests were performed and the degradation of the vulcanizates was evaluated and mechanical properties were compared.

Eco-Friendly Rubber Compound Design for Industrial Hose Products

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Keywords: Ethylene propylene diene rubber (EPDM), Recovered carbon black (rCB), Rice Husk Ash, Mechanical properties.

Abstract

Sustainability has become a very important and unavoidable topic when designing new (chemical) materials or products. Sustainable products can broadly be defined as products that can be produced and re-used indefinitely without affecting the natural eco-system equilibrium. The carbon footprint, the carbon dioxide greenhouse gas emission, and the recycle potential of the material after the product life have become key issues that should be taken into consideration in the development of new, sustainable materials. Within this viewpoint, the rubber industries focus on the use of sustainable materials to protect natural resources, control environmental pollution caused by industry and support the country's economy.

The purpose of this study is to produce new generation environmentally friendly products with reduced carbon footprint by using recovered carbon black, bio-based silica and Epoxide soybean oil in the rubber compounds used in the production of industrial EPDM hose products as inner and cover compound. Furthermore, the study contains investigate the effect of these materials on the generic NBR based rubber and generic EPDM/SBR recipes as compared to commercial grades. In summary, this study has shown us that although sustainable recycled materials cause performance losses, especially in the mechanical properties of rubber compound, these difficulties can be overcome with optimization.

1.Introduction

Recovered carbon black material is processed by pyrolysis of waste tire. So it is a complex mixture of compounds that is included inorganic fillers, vulcanization activators, etc during tire production. For this reason rCB has chemically 90% carbon of content. Its structure is near commercial N330 but has not completely agglomerate forms.

Silica has been used as a reinforcing filler in rubber industry for improving mechanical and thermal properties of rubber composites such as tensile strength, tear strength, hardness, abrasion resistance, thermal stability. However, the production of silica particles for commercial applications is still high cost, high energy consumption and hazardous to the worker. Rice husk is an interesting agricultural wastes to produce silica due to its high content of silicon, low cost, abundant availability in Thailand. [3] The use of this ash in a synthetic process produced silica. RHA and commercial silica has nearly same chemical structure. It reached 90-95 % $SiO2$. That means it is a good alternative for silica type fillers for the rubber compounding.

Vegetable oils are environment friendly, biodegradable, less costly and readily available. The use of these oils in many applications has attracted the attention of many researchers due to their potential as substitutes to petrochemical derivatives. ESBO is the one of the most avaiable plasticizer. On the other hand, the challange of ESBO usage has not good compatibility with most of the common natural and synthetic elastomers. [4]

All these new generation sustainable raw materials were analyzed in various ratios in the standard NBR, EPDM/SBR rubber formulation and the final new generation EPDM based hose formulations were developed.

2. Experimentals

EPDM (KELTAN 8570C), NBR (LG 2850) rubbers were used in the study. standard carbon blacks N330, N550 were supplied from BIRLA. Commercial Silica grades were EGESIL BM30 and Ultrasil 880. Rice husk ash grade was RHAsil TM175 as bio-silica. ESBO (Epoxide soybean oil was supplied from AKKIM, Recovered Carbon Black EGOM-1 supplied from ECOSAVE.

The rubber compound was made on a laboratory scale open shaft. Rubber compounds have been mixed in laboratory type mixer and rubber test plates have been prepared in press mold. After that, compound curing characteristics, green strength, physical properties like hardness, tensile strength, elongation at break, elastic modulus, tear strength and heat ageing properties were analyzed.

Mechanical properties of the compounds are carried out with ZWICKROEL Z020 tensometer and the compound rheological properties tested with ALPHA MDR2000. The Mooney viscosity tested with ALPHA MV2000.

3. Results

With this project, a new generation eco-friendly hose has been designed for our Danfoss Polymer Kauçuk product portfolio. The total sustainability rates are 60% sustainable material replacement for inner tube formulation and 56% sustainable material replacement for the green colored cover compound formulation. In addition, as reinforcement rPET textile yarn used.

Acknowledgement

This project is being carried out the scope of the new product development project within Polimer Kaçuk Paz. A.Ş

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3. Preparation and characterization of rice husk ash for using as a filler in natural rubber Anupong Boonmee, Palida Sabsiriroht, Kasama Jarukumjorn* School of Polymer Engineering, Institute of Engineering Suranaree University of Technology Nakhon Ratchasima 30000, Thailand.
4. Epoxidized vegetable oils as processing aids and activators in carbon-black filled natural rubber compounds J.Natn.Sci.Foundation Sri Lanka 2011 39 (3):243-250 Ganga Chandrasekara1 , M.K. Mahanama2 , D.G. Edirisinghe2 and L. Karunanayake1* 1 Department of Chemistry, Faculty of Applied Science, University of Sri Jay

Wear study of tire tread materials under low-severity wear conditions

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Keywords: Wear; Tribometer; Rubber.

Tire wear debris give a major contribution to microplastic pollution of the environment, which is a major public health concern [1]. Therefore, enhancing the comprehension of abrasion wear for tire tread materials to improve their wear resistance is a key challenge. However, tire manufacturers are facing huge costs to perform in-field wear tests of tire treads, which are also time consuming. Besides, in-field wear processes are very complex to manage and analyze as many factors can have a large impact on results, like the type of road, climate conditions and driving. Therefore, developing a reliable accelerated laboratory test in controlled model conditions is a key alternative to facilitate experiments and the choice of materials.

The general concept of wear test is to apply a normal load together with slip between the material of interest and an abrading surface. Wear is induced by interfacial friction. The wear rate of the material can be described by the weight or volume loss per unit sliding length or per unit frictional dissipated energy.

In this work, an original dynamic tribometer is used to simulate low-severity wear conditions on rubber tire materials (Figure 1). It allows performing quantitative and accelerated wear tests which mimic real usage conditions in terms of kinematics and dynamics of the contact [2].

Silica-filled Styrene Butadiene Rubber (SBR) and cis-Butadiene Rubber (BR) blend materials, usually used for passenger vehicles were tested (Table 1). Throughout the test, the wear rate was quantified, and wear patterns were analyzed using X-ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscopy (SEM).

The XPS results have revealed chemical changes in the worn surface of the material, in particular sulfur oxidation. These changes have been observed on several materials which show different wear mechanisms. Wear debris were also analyzed and have the same chemical composition as the worn surface.

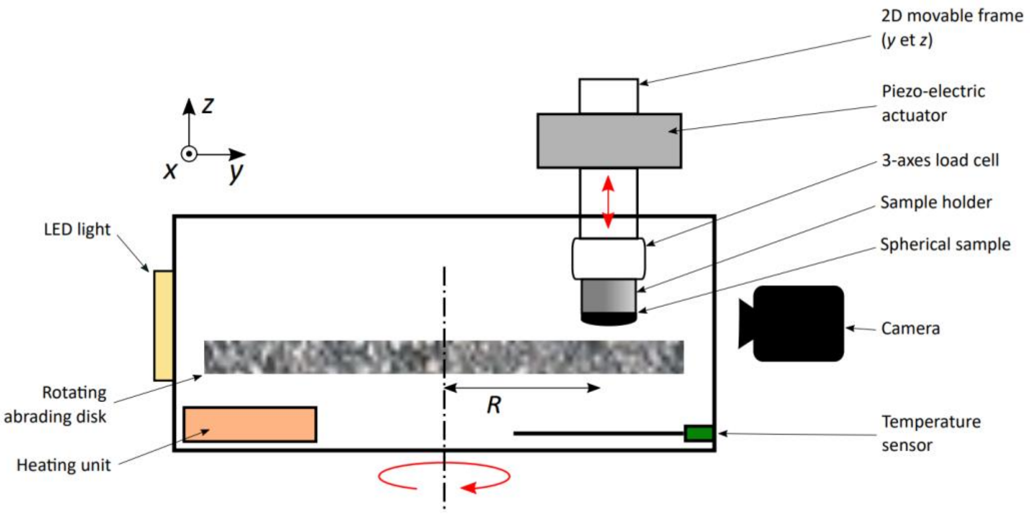

Figure 1. Rotary tribometer diagram

Table 1. Sample compositions

Components [phr]	**Sample notations**	
	S1	**S2**
SBR[a]_1	82.6	
SBR_2		70
BR	30	30
Silica Z1165	80	
Silica ZP200		60
Carbon black	6	6
ZnO	2.5	2.5
TESPT	6.4	6
Stearic acid	2	2
Antioxidant	2	2
Plasticizer	1.5	1.5
Sulfur	1	1
DPG	1.5	1.5

[a] Styrene butadiene rubber
[b] Butadiene rubber
[c] triethoxysilylpropyltetrasulfur
[d] N,N'-Diphenylguanidine

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Optimizing Rubber Vulcanizate Performance: Investigating the Impact of Mixing Time on Rheological Properties and Cured Characteristics through Advanced Characterization Techniques

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Keywords: mixing; rheology; rubber-filler interaction; fatigue.

This study explores the impact of varying mixing durations on the rheological and mechanical properties of rubber, which are crucial for determining the performance and lifespan of rubber products. Rubber compounds were subjected to different mixing times, and their effects on rheological characteristics and post-vulcanization mechanical properties were meticulously analyzed using advanced characterization techniques like Rubber Process Analyzer, Dynamic Mechanical Analyzer (DMA) etc. Rheological evaluations indicated substantial changes in the viscoelastic properties of the rubber compounds with extended mixing times, affecting processability and revealing variations in flow behavior and processing ease. Moreover, the research investigates how mixing duration influences essential performance metrics such as hardness, tensile strength, resilience, aging retention, crosslink density [1], thermal properties, air permeability, fatigue resistance, cut initiation, growth, wear properties etc. Through an in-depth examination of filler-filler interactions by DMA [2], optimal mixing conditions were established to enhance the performance and durability of rubber products. The microstructural characteristics of the rubber compounds, influenced by different mixing times, were studied using advanced techniques such as Transmission Electron Microscopy (TEM). The findings highlight the critical importance of mixing time in balancing the processability and mechanical performance of rubber vulcanizates. This study emphasizes the significance of precise control over the mixing process in the rubber industry, providing valuable insights for improving product quality and consistency. The research primarily focused on general-purpose rubbers such as Natural Rubber (NR) and Styrene-Butadiene Rubber (SBR).

Introduction

Rubber, known for its versatility and indispensability, is utilized across various industries due to its unique combination of elasticity, resilience, and durability. The performance of rubber products, ranging from automotive tyres to industrial seals and consumer goods, depends on a delicate balance of rheological and mechanical properties. Mixing is a crucial step in rubber compounding, ensuring the uniform distribution of fillers, plasticizers, and other additives within the rubber matrix. The duration of mixing is especially important as it significantly influences the final properties of rubber compounds. The incorporation and dispersion of carbon black (CB) particles significantly influence the fatigue life of elastomers. Fillers like carbon black enhance the fatigue life of rubber primarily by reinforcing the matrix, which increases its strength, and by inducing higher hysteretic effects [3]. Despite its critical role, the effect of mixing time on the rheological and cured properties of rubber has not been extensively studied in existing available literature. This gap highlights the necessity for a detailed investigation into how mixing time affects the performance of rubber products through advanced characterization techniques.

Table 1. Compound Recipe

Ingredients (phr)	NR (N)	SBR (S)
NR[a]	100	-
SBR[b]	-	100
DBD[c]	0.15	-
Carbon black[d]	50	50
Plasticizer	10	10
Antioxidant	4	4
ZnO	5	3
Stearic acid	2	2
Sulphur	2	2
TBBS[e]	0.4	0.4
DPG[f]	0.1	0.1

[a] Natural rubber
[b] Styrene Butadiene Rubber
[c] 2,2′-Dithiobisbenzanilide
[d] Carbon Black N330
[e] N- tert-butyl-benzothiazole sulfonamide
[f] Diphenyl Guanidine

Table 2. Mixing Sequence (Master >>>> Final)

Master Batch (Rotor Speed: 60rpm; Temperature Control Unit: 90 °C) – sec.					
Compound	**N2/S2**	**N4/S4**	**N5/S5**	**N8/S8**	**N10/S10**
Rubber	0	0	0	0	0
Dry carbon black + Chemical	30	30	30	30	30
Wet carbon black	60	90	120	240	300
Ram Scrap	90	180	210	360	480
Dump	**120**	**240**	**300**	**480**	**600**
Final Batch (Rotor Speed: 30rpm; Temperature Control Unit: 70 °C) – sec.					
Master + Curatives			0		
Ram up			90		
Dump			180		

In conclusion, this study highlights the significant influence of mixing time on the rheological and mechanical properties of rubber compounds, critical for determining product performance and longevity. Through meticulous examination of varied mixing durations, we have explained the profound impact of rubber filler interaction on compound properties, particularly concerning mechanical strength and fatigue properties. Additionally, our findings emphasize the importance of considering polymer breakdown with extensive mixing, which can affect the ultimate performance of rubber products.

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Preparation of new thermoplastic rubber via controlled polymerization

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Keywords: preparation; thermoplastic rubber; coordination polymerization; radical polymerization.

Thermoplastic rubbers are considered to be recyclable rubbers since they can be re-processed after discard, namely “green rubber”. To date, three generations of thermoplastic rubbers have been developed, which are the first generation of the styrene-butadiene(isoprene)-styrene triblock copolymers and their hydrogenation derivatives, the second generation of polypropylene kinetics vulcanizate with propylene-ethylene rubber and the third generation is polyolefin elastomer. Herein we report a new type of thermoplastic rubber synthesized via controlled polymerization of the commonly used monomers that are use to fabricate the commonly used plastics or rubbers. The copolymerization of ethylene with butadiene or isoprene or 2,3-methyle butadiene etc, to give multiblock copolymers that may behave as plastic, rubber and thermoplastic elastomers at specific sequences, which bearing double-bonds in the main-chain also can be degraded into functional ethylene oligomers. Addition of a third monomer to the above polymerization systems, a thermoplastic rubbers with higher strength and tear-resistance properties are achieved as shown in the following Scheme. Meanwhile, ethylene and alfa-olefins copolymerization with polar monomers to prepare rubbery materials with various functionalities are also realized means of Lewis-acid. More over, Lewis acid accelerated step-growth reduction polymerization of CO_2 with silanes is achieved to afford a series of poly(silylphenylenoxane)

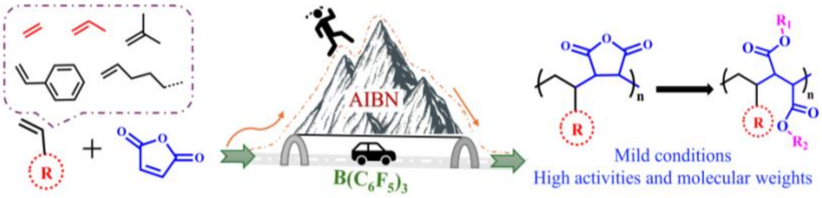

Figure 1. Control radical polymerization of olefins with maleic anhydride mediated by Lewis acid

Acknowledgement

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Striving for Excellence beyond just a Rubber Process Analyzer

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Keywords: Sub-Zero, Rubber Process Analyzer, Dynamic Mechanical Analyzer, viscoelasticity.

Rubber elastomers are versatile materials that are utilized in various aspects of everyday life. Numerous well-known applications of rubber include vehicle tires, seals, gaskets, and engine mounts. Recent advancements in the field of testing have made it feasible to characterize the properties of raw polymers, green compounds, and final vulcanizates using a Rubber Process Analyzer (RPA). However, one drawback of this equipment is its limited ability to assess viscoelastic properties at temperatures lower than ambient conditions. Consequently, rubber manufacturers often opt for a Dynamic Mechanical Analyzer (DMA) to conduct tests below zero degree Celsius. Nonetheless, the utilization of DMA is hindered by its time-consuming sample preparation requirements and the need for the specialized operators, thus restricting its application in research and development activities[1].

To address these challenges, Alpha Technologies has introduced a new solution called Sub-Zero. This cutting-edge technology integrates the functionalities of the Premier™ RPA and enabling users to conduct tests at temperatures as low as -25 °C. A recent research endeavor carried out by Alpha engineers and scientists on four tread compounds illustrates how the viscoelastic properties can be efficiently and accurately determined using this innovative technology.

The results obtained from temperature sweep test offer precise data on crucial parameters such as dynamic moduli, glass transition temperature, rolling resistance and ice traction. Furthermore, the study demonstrates the correlations between these properties and outputs generated by DMA.

Results indicate that the Sub-Zero technology is an essential tool for analyzing low temperature viscoelastic properties. By utilizing this technology, the reliance on a DMA can be eliminated, leading to a faster product development process across different research fields within the rubber industry.

Acknowledgement

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Using injection molding simulation software to accurately quote rubber anti-vibration elements

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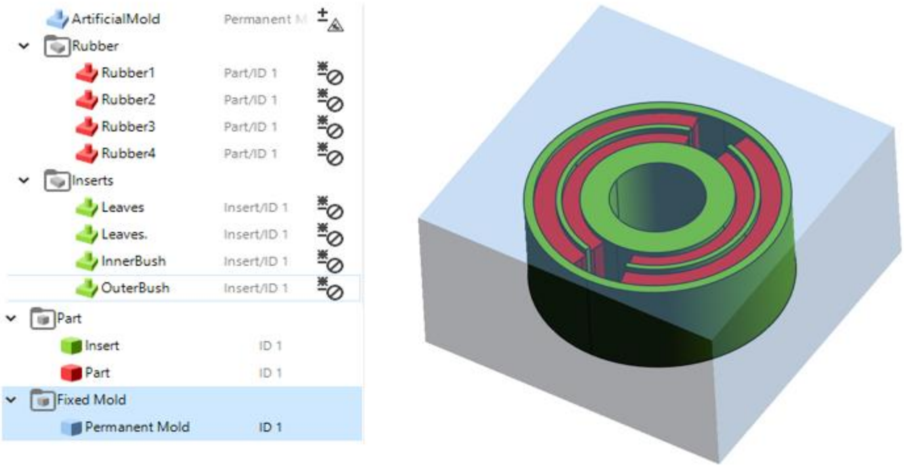
Keywords: injection molding simulation, RFQ, anti-vibration.

Elastomeric elements are used for vibration reduction and noise control in many industries. New part geometries are constantly designed and tailored to fulfil the specific mechanical requirements of each application, with much of the design performed virtually before any physical prototyping. It is advantageous for manufacturers of technical rubber articles to have the tools to accurately and efficiently calculate the costs of production of different geometries with different rubber compounds. This article discusses through an example railway rubber bushing how injection molding simulation software can help the quoting process and quickly responding to market demands, even with limited information.

The main advantage of the simulation is the prediction of curing time with complex geometries in an early stage. High temperatures are needed to initiate the cross-linking reaction of the rubber compound, which leads to the final good mechanical properties of the part. This process has a major impact on cost, as it requires a lot of energy and time in the injection press. With the help of software, a good estimation with good accuracy can be calculated by an experienced user in a short time.

In this article, a step-by-step description is outlined for obtaining a curing time estimation using SIGMASOFT® Virtual Molding simulation software. How to consider the part and mold geometry, process parameters, rubber compound, simulation setup and results evaluation are discussed. With a curing time of 20 min. in the mold, curing degree reaches over 90% throughout the part considering residual heat after demolding in ambient condition. Difference in curing inside and through the cross-section of the part can be visualized and investigated. The software is supplementing traditional curing time estimations with an insider view especially for complex part geometries [1-2].



ArtificialMold Permanent M
Rubber
Rubber1 Part/ID 1
Rubber2 Part/ID 1
Rubber3 Part/ID 1
Rubber4 Part/ID 1
Inserts
Leaves Insert/ID 1
Leaves. Insert/ID 1
InnerBush Insert/ID 1
OuterBush Insert/ID 1
Part
Insert ID 1
Part ID 1
Fixed Mold
Permanent Mold ID 1

Figure 1. Part geometry for curing simulation (green: inserts, red: rubber, light blue: mold).

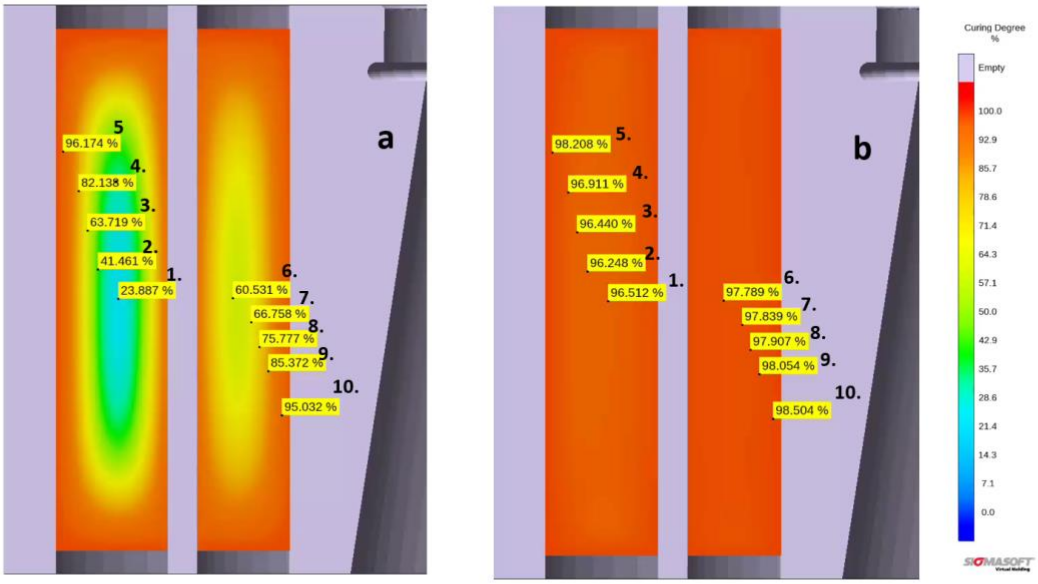


Figure 2. Curing degree distribution at a. Demolding (21 min.), b. After 1hr. cooling down.

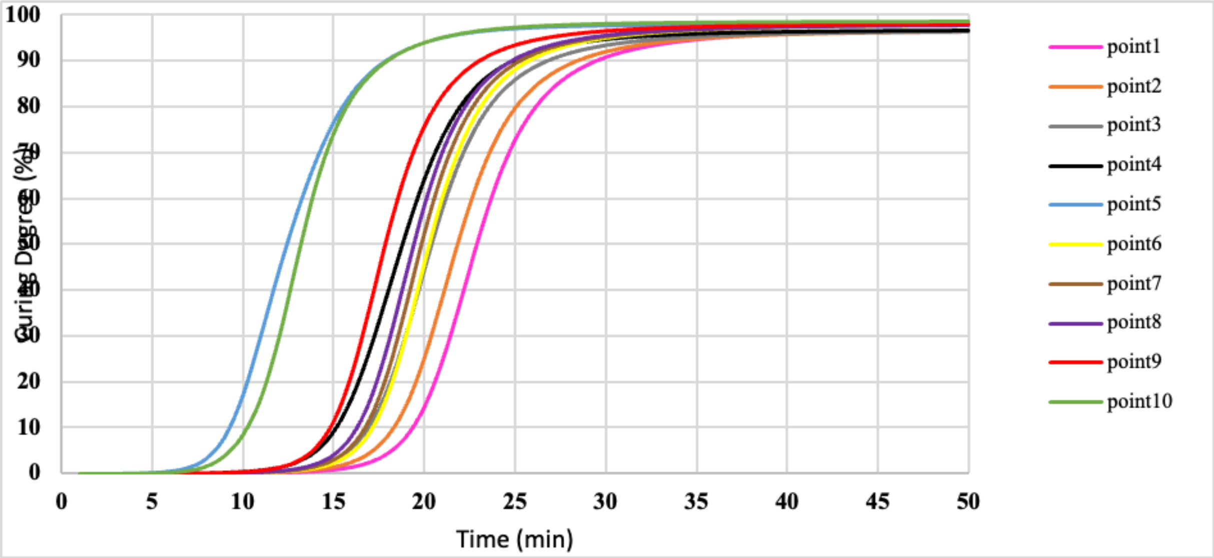


Figure 3. Curing analysis of bushing with 150°C mold temperature (results plotted in points 1-10 shown in Figure 2).

Acknowledgement

Thanks to the Angst+Pfister Group Engineering and Angst+Pfister Advanced Technical Solutions for contributing to the study.

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Predicting 20-year-long mechanical performance of elastomer seals in nuclear environments: a focus on radiation-thermal ageing

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Keywords: sealing performance; irradiation; relaxation; modeling.

Predicting the performance of elastomer seals to ensure tightness over several years presents a significant challenge for industries, particularly within the nuclear field. These seals must maintain their functionality for 10 to 20 years despite undergoing ageing processes under normal and/or accident conditions.

In this study, four EPDM materials were compared over time. Thermal ageing was led during 1000 h at temperatures of 100 °C, 130 °C and 150 °C with intermediate sampling after 24 h, 72 h and 336 h. To fit with nuclear field applications and industrial final users, a 26 kGy dose of gamma ray was applied to samples at room temperature with a rate of 0.1 kGy/h and 1.5 kGy/h. Moreover, radiation-thermal ageing was carried out consecutively at 130 °C and 150 °C and 1.5 kGy/h.

A series of analyses of material parameters were investigated to evaluate their impact on sealing performance. Compression Set (CS), hardness and physico-chemical parameters (mass, volume, glass transition temperature, composition) were studied with a particular focus on CS and Hardness. Different results highlighted the specific evolution of hardness over time observed in the literature[1]. In addition, CS highlights the cumulative impact of ageing in series. However, as the compression set is limited to 100%, the ageing impact cannot be studied beyond this point.

To extrapolate these results in the long term, different models are proposed in the literature[2][3][4]. Three models combined with time-temperature superposition and a life-time criterion were applied to our data to evaluate the ageing and to obtain the activation energy. (**Figure *1***)

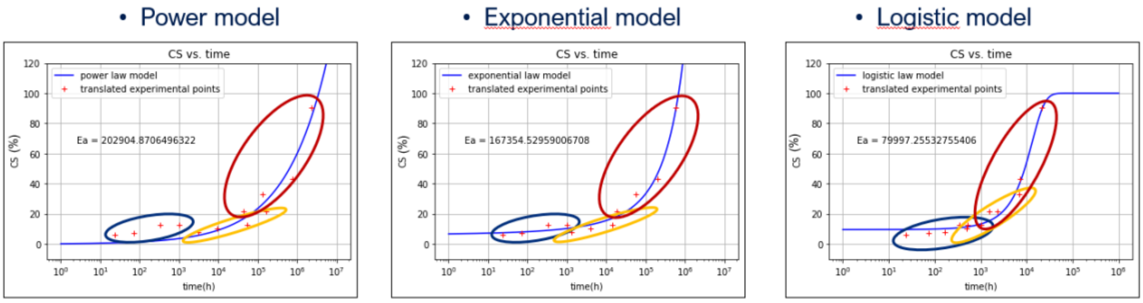

Figure 1: Different models applied on CS data (EPDM1)

The relationship between the mechanical properties and the evolution of O-ring tightness was addressed in the second part of the study. The sealing force of the O-ring which can be associated with the Compression Stress Relaxation (CSR), was measured continuously for 1000 h (**Figure 2**). In parallel, some permeability and sealing tests at 10 bar of helium were led after 0 h, 24 h, 72 h, 336 h and 1000 h at the three temperatures previously studied.

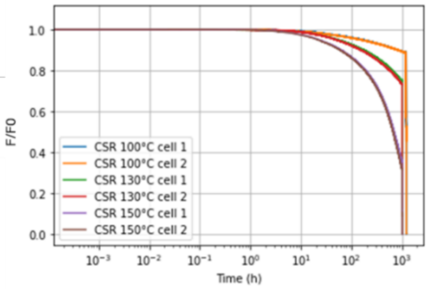

Figure 2 : Sealing force of the O-ring (EPDMl) with ageing temperatures (2 cells).

After analysis of the relaxation, the results are used as input data to evaluate the robustness of our engineering tool enabling to design sealing systems. The improvement of the usual dimensioning of the groove and O-ring is ensured by adding data of relaxation over time. Consequently, it is possible to estimate the evolution of the sealing force and the squeeze to the O-ring with time to improve the prediction of tightness.

Currently, a specific test bench is developed to study the relationship between the sealing force reaction of the O-ring and the sealing performance with a progressive decrease of compression level applied. Through this test, it is possible to determine the minimum compression ratio necessary to ensure tightness. A series of tests is carried out for different states of ageing.

Physico-chemical, mechanical, and dimensional characterizations are conducted to evaluate how ageing affects elastomers. Through the examination of these evolving properties over time, it becomes possible to verify the relevance of the parameters studied for sealing function and improve the knowledge of the ageing mechanisms of elastomers in nuclear environments.

Acknowledgement

Thanks to the industrial partners and all the teams who contributed to the study.

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Nanoparticles Effect on Multiphase Rubber Systems

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Keywords: Blend; Compatibilization; Silica; Sepiolite.

Tyre materials are complex multiphase rubber systems containing different polymers, resins, anti-degradants, curatives, processing aids and reinforcing fillers. The combination of two or more polymers and/or copolymers, comprising at least 2 weight percentage (wt%) of each component, namely polymers blend, is particularly advantageous in the materials formulation. In fact, new materials can be designed without the necessity of synthesizing new and expensive monomers and developing new polymerization routes. It is indeed possible to combine different polymers and, by changing only the blend composition, have access to a wide range of properties. However, potential improvements in the material performances are usually hindered by the polymers incompatibility which not only leads to phase-separated morphologies with poor interfacial adhesion, but also to inhomogeneities in the additives distribution, downgrading the properties of the material.

In this context, extensive research efforts have been undertaken in the compatibilization of these systems with compatibilizing agents such as block or graft copolymers. Nevertheless, their effectiveness as well as their versatility seems to be limited. More recently, the addition of fillers, commonly employed in polymer matrices to impart different functionalities, has been reported to induce morphological modifications in an extensive number of polymer blends. Even though it is now possible to control the localization of the filler and manipulate the resultant morphology, in most of the studies, the reported explanations of these phenomena are often conflicting and sometimes lack of a common view.

In this context, the present study aims to i) analyse the effects of commonly employed reinforcing fillers on technologically relevant rubber blends and ii) propose alternative methods for the control of the filler effect. In detail, in the first part of this study, the selected styrene-butadiene rubber (SBR)/butadiene rubber (BR) blend system compatibility was analysed in relation to the single polymers characteristics, blend composition, blending method and crosslinking process.

Starting from these reference systems, the blend microstructural evolutions in the presence of inorganic fillers were evaluated respect to the filler properties and the compounding processes, by combining thermal, thermo-mechanical and morphological analyses. In detail, since the internal system structure and properties are strictly related to the filler localization and the interactions established among the various constituents, the correlations between these aspects were investigated.

To study the filler effect, at first it was necessary to investigate the SBR/BR system in the absence of any compatibilizing agent, increasing step by step the complexity of the formulation. In this way, the miscibility and compatibility level of the rubber blend was evaluated in relation to i) the single polymer characteristics, ii) the preparation method as well as iii) the crosslinking approach. For the characterization of the polymers miscibility, a combination of thermal, thermomechanical and morphological analyses was established. The immiscibility of the SBR and BR phases increases at higher styrene contents of the SBR and differences in viscosity. However, depending on the blend composition, preparation approach and crosslinking method, differences in the compatibility of the systems can be distinguished. The characteristics of the two polymers and the blend composition have a significant effect not only on the final blend morphology, as observed for the unfilled blends, but also on the filler localization and dispersion. This aspect is particularly important because the filler localization affects in turn the polymer blend morphology, compatibilization and mechanical properties.

Moving to the filler effect, two different silica-based fillers were considered of interest in the context of tyre application: spherical silica nanoparticles (NPs) and anisotropic Sep [1] in light of their different size, morphology, and chemical surface features. In detail, the results of an integrated multi-technique approach show that, at low filler loadings and BR contents in the SBR/BR blend, SiO_2 NPs localize preferentially in the less viscous rubber phase, that is BR, lowering the BR phase availability compared to the unfilled rubber blends. On the contrary, at higher filler quantities and BR content, the filler segregation seems to be limited, with shifts in the Tg values and interphase contributions. The filler kinetically controlled localization and the SBR/BR compatibility seem to be modifiable by altering additional parameters, such as the addition order, the filler morphological and surface features as well as by favouring the filler migration or compatibilization. In all cases, it appears fundamental to favour the particles distribution and polymer-filler interactions to improve the polymers compatibility. At the same time, as expected, it seems not favourable to increase the compatibility of the filler for one phase only except for the BR one. Regarding Sep, the high AR of the filler favours the adsorption of polymer chains and improves the fillers ability to disperse in the polymer matrix thus compatibilizing the two polymers (Fig. 1).

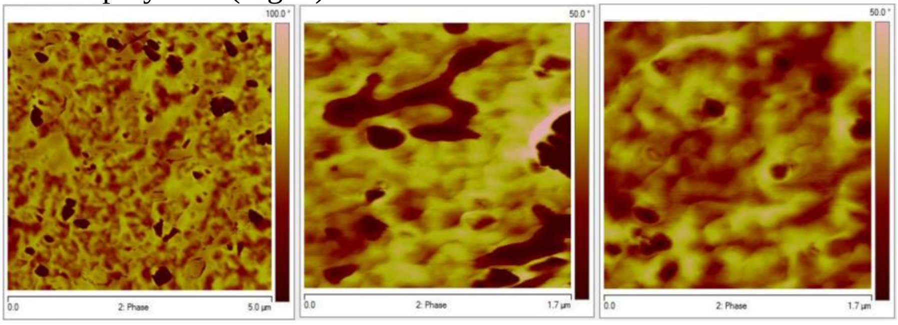

Figure 1. AFM phase images of the SBR/BR blend at 50/50 composition containing modified Sep.

In this context, the employment of oligomeric SBR and BR silanes exaggerates these aspects and gives additional information over the effects associated with both silica and Sep localization and distribution. Furthermore, this study supports the employment of different silane coupling agents to compatibilize NPs as an effective way to control the filler localization and the microstructural evolutions in rubber blends morphology. In any case, further investigations are necessary to apply this approach in tyre manufacturing.

The results confirms that the multiphase rubber blend is a complex system characterized by many variables which would require an extensive statistic evaluation to support the experimental results and the preliminary conclusions reached in this study.

Acknowledgement

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UPM BioMotion$^{\text{TM}}$ Renewable Functional Fillers (RFF): A new and innovative material class for sustainable rubber end-use applications

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Keywords: renewable functional fillers; biobased carbon content; negative carbon footprint; light-weight.

Replacing fossil-based materials with innovative, renewable, and sustainable solutions has been a primary objective of various industries, for example automotive, transportation, building and construction, or sports. Especially in rubber applications, highly CO_2-intensive raw materials are often used and options for producing products with a lower environmental footprint have been limited.

To address these needs, UPM has developed a completely new material class of renewable functional fillers, which enables a switch from fossil raw materials to sustainable alternatives: UPM BioMotion$^{\text{TM}}$ RFF. It will be produced at UPM's award-winning, first-of-its-kind biorefinery in Leuna, Germany, for which start of production is planned at the end of 2024. UPM BioMotion$^{\text{TM}}$ RFF combines a unique set of properties for rubber and plastic applications enabling the next step towards a more sustainable future. It is made from responsibly sourced hardwood from regional, sustainably managed forests and features a negative carbon footprint considering cradle-to-gate boundaries and biogenic carbon.

Renewable raw materials accumulate carbon during plant growth, by sequestration of carbon dioxide from air. The amount of biobased carbon in a product can be measured and certified. UPM BioMotion$^{\text{TM}}$ RFF has been awarded the highest quality level “DIN-Geprüft biobased” certification mark. Its biobased carbon content has been confirmed 100% according to ASTM D6866 test method. Thanks to its low material density of only 1.3 g/cm^3, UPM BioMotion$^{\text{TM}}$ RFF is regarded truly light weight. This combination of properties creates high value in rubber applications, especially at high filler loadings. Both, the increased biobased carbon content, and the reduced weight compared to classical elastomeric compounds are directly measurable in the final articles like profiles, sealings, hoses and many more.

We present a broad range of application examples for truly sustainable rubber compounds with biobased carbon contents of up to 95% and higher. This is realized by using UPM BioMotion$^{\text{TM}}$ RFF in combination with different bio-based rubbers and plasticizers, which are besides functional fillers the other main drivers to increase biobased carbon in elastomeric compounds. In addition to that other sustainable, but not biobased solutions are studied in combination with UPM BioMotion$^{\text{TM}}$ RFF further. In doing so, we will show that UPM BioMotion$^{\text{TM}}$ RFF is a new and innovative material class, designed to increase the sustainability performance of various rubber applications and related industries.

Few-Layer Graphene (GNP) Filled Styrene-Butadiene Rubber (SBR)

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Keywords: Graphene nanoplatelets; Styrene-butadiene rubber; Composites; Carrier systems.

The graphene family of materials possess remarkable intrinsic properties [1], that when combined with the elasticity of synthetic rubbers, results in the production of rubber compounds with potential for use in a broad range of high-performance industrial applications and consumer products [2-3]. However, the utilization of graphene as a filler is accompanied with several technical challenges, including the dispersion of graphene in the rubber compound and its impact on the cure kinetics and network structure of the host rubber. In this work, few-layer graphene nanoplatelets (GNP) was dispersed in solid and liquid wax, followed by its addition to a styrene butadiene rubber (SBR) formulation. Herein, we report the impact of the wax-based carriers on the mechanical, viscoelastic, and cure properties of GNP filled SBR compounds. The structure and morphology of the GNP (prior to and after dispersion in wax) was characterized using X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, X-ray diffraction (XRD), Fourier infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM).

The physical and viscoelastic properties of the resultant GNP/SBR compounds were investigated using a rubber process analyzer (RPA), dynamic mechanical thermal analysis (DMTA), volume swell testing, and tensile testing. Unfilled SBR compounds and carbon black (CB) filled SBR compounds, were also tested as control samples.

The results show that the addition of GNP effectively enhances the tensile strength, hardness, and abrasion resistance of SBR by 166%, 10% and 57%, respectively. This behavior is associated with an increase in crosslink density and the formation of a more robust interconnected filler network, as seen from variation in the Payne effect, and an increase in SBR elasticity demonstrated by a reduction in a tan δ value from 1.84 to 1.40.

The waxes enabled the dispersion of GNP in the SBR matrix, evident from studying the Payne effect, in addition to increasing the elongation at break by 33%. However, inclusion of the wax-based GNP resulted in a reduction of the crosslink density of SBR compared to that observed for neat GNP. This is a consequence of a plasticizing effect associated with the wax carrier systems on the SBR compound. The physical and mechanical properties of all the compounds prepared are compared and summarized in Figure 1. The inclusion of neat GNP in comparison to CB at similar volume fraction results in enhanced abrasion resistance, similar tensile strength, but an increased modulus at 100% strain of approximately 30%. This work demonstrates the effectiveness of GNP as a functional filler for SBR and the potential of using wax based carrier systems to assist dispersion of GNP and processing of SBR formulations.

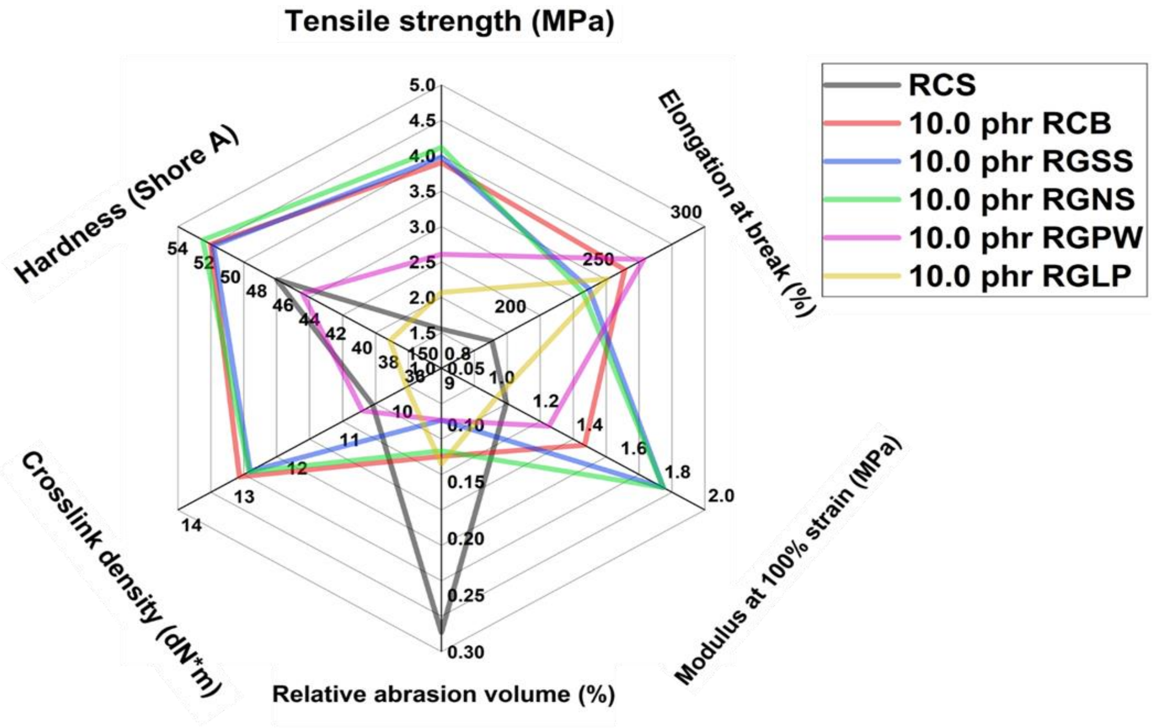

Figure 1. Spider-chart summarizing the mechanical and cure properties of the different SBR compounds. (RCS is unfilled SBR, RCB is carbon black filled SBR, RGSS and RGNS are unmodified GNP filled SBR, RGPW and GLPW are wax modified GNP filled SBR)

Acknowledgement

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New functionalized elastomers for low rolling resistance tyre compounds

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Keywords: sSBR, Low-Cis-BR, functionalization, tyre tread, low RR, high grip.

BACKGROUND

In the present global scenario of industry approaching the carbon neutrality in 2050, also the automotive sector has been actively striving for new solutions devoted to eco-sustainable targets, but always in the enduring perspective of enhanced performances and high efficiency of vehicles. This means being able to introduce eco-environmentally friendly components, manufactured through optimized energy-saving processes and in combination with a responsible use of sustainable and circular feedstocks.

Today different propulsion technologies are possible for the vehicles, due to the increasing penetration of the electrification into the market. Due to this, it is possible to have availability of Hybrid, Plug-in Hybrid, Battery or Fuel Cell EV propulsion systems, in alternative to the conventional IC technology. This is further raising the stakes of performances for EV, as more and more powerful systems are required, in the constant attempt to successfully close the performance gap (especially, in terms of mileage in medium/long distance car journeys) Vs IC vehicles. This is disadvantageously impacting the weight of electric vehicles, with tyres resulting in more severe service conditions and, thus, having to provide outstanding performances, in terms of extremely low rolling resistance coefficients, enhanced traction properties as well as longer mileage life (wear). It is duly remarked how the latter is also negatively impacted by the presence of high instant torques in EV propulsion systems.

All of this implies superior requirements for the tyres destined to the EV-segment, with the consequent necessity for the tyre industry to develop more advanced compounding steps as well as new tyre building solutions. As rubber still tends to represent the major component of tyre compounds, it is straightforward to entail how elastomers are going to play an extraordinary role in this optimization development process of tyres for the EV segment.

MATERIALS

In this study, we discuss about newly developed elastomers and how they can provide excellent performances in low-rolling resistance winter and all-season PC tyre recipes.

Comparative case studies are presented to show the beneficial effect of new generation functionalized solution styrene-butadiene polymers (fn sSBR), with high and low glass transition temperature (Tg) values, with respect to reference polymers.

New generation functionalized low-cis-BR is introduced in combination with sSBR, providing super performance with respect to reference BR elastomers.

Table 1 summarizes the details of the investigated polymers.

On top of performances, the introduction of sustainable feedstocks further contributes to achieve reduction of GHG emissions, through the mass balance approach and ISCC Plus certification.

TABLE 1

Material	Mooney, mu	Styrene, %	Butadiene configuration	Process oil	Tg, °C
Reference sSBR 1	68	21	63% (1,2-vinyl) *	dry	-23
Reference sSBR 2	58	15	48 (1,2-vinyl) *		-50
New gen. fn sSBR 1	61	27	59% (1,2-vinyl) *		-21
New gen. fn sSBR 2	60	15	32% (1,2-vinyl) *		-65
Reference High-Cis-BR	44	-	97% (1,4-cis)		-107
Reference Low-Cis-BR	50		38% (1,4-cis)		-94
New gen. fn Low-Cis-BR	55	-	44% (1,4-cis)		-96

* in sSBR the vinyl content is referred to the butadiene component

EXPERIMENTAL

Compounds are prepared in a laboratory internal mixer, equipped with BY rotors. Physical and mechanical properties of rubber compounds were measured according to ASTM, DIN or ISO standards. The Rolling Resistance Index on vulcanized specimens was determined through strain sweep measurements using a torsional bar specimen (ARES rheometer, 60°C, 10Hz) or, when specifically indicated, using a RPA2000 closed chamber rheometer in order to explore the response of compounds at higher strain level. Temperature sweep tests on vulcanized specimens were carried out with torsional bar geometry at 1 Hz, 0.1% and 2°C/min (ARES rheometer).

RESULTS

In Figure 1 we show compound data about Rolling Resistance predictor, with reference to the investigated set of elastomers shown in Table 1.

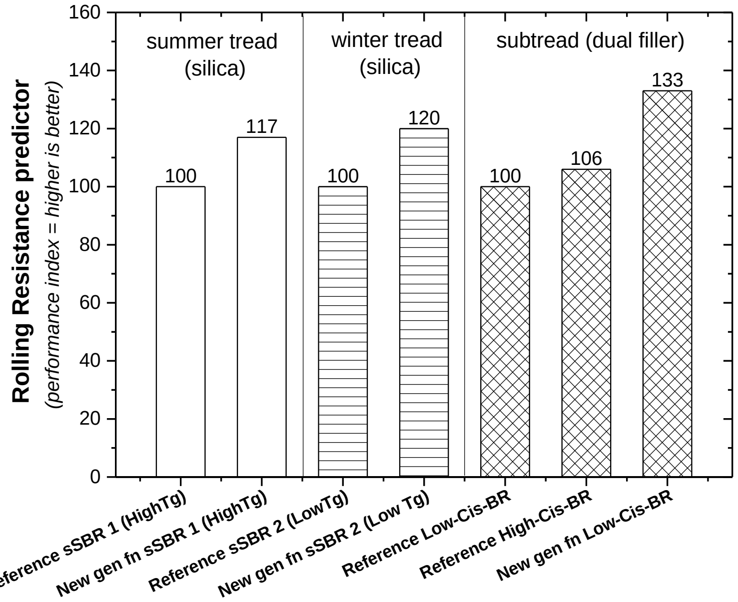

Figure 1. Rolling Resistance index predictor for sSBR and BR: data material comparison is between reference Vs new generation functionalized grades. Indexing of data is applied with regards to performance (“the higher, the better”).

Optimisation of Reversible Sulphur Crosslinked Natural Rubber Elastomers for Recycling

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Keywords: Disulphide Metathesis, Dynamic Crosslinks, Recyclable Natural Rubber, Sustainability.

Natural rubber is typically crosslinked using either sulphur or peroxide to achieve the required properties for high-performance applications, which inherently limits the recycling that is possible without significant loss of mechanical performance. With 15 million tonnes of natural rubber consumed a year as of 2022[1], minimising the loss in performance after each recycling instance is essential to achieve a circular economy amongst a broad range of applications including mining, healthcare and most notably tyres. Through either semi-efficient or conventional sulphur curing systems, naturally occurring disulphide bonds are produced amongst the crosslinks. In recent years, these disulphide bonds have been successfully exploited to promote recyclability through a dynamically reversible crosslink.

Further research has expanded the approach proposed by Kaur, presented at IRC 2021, that won the Best Student Award, whereby labile crosslinks were exploited to provide reprocessable natural rubber. Previous work utilised Copper (II) Methacrylate (CuMA) to suppress the disulphide metathesis allowing for substantial ability to remould natural rubber multiple times. Despite the many benefits, low thermal stability hindered high temperature applications as the suppression was seen to remain up to around 170 °C. Additionally, limited scorch time present for curing of reclaimed/virgin rubber mixtures limits a number of processing methodologies. Further limitations lie in CuMA's relatively high cost.

In this work, a range of alternative chemistries are examined to address these issues. Other commercially available disulphide metathesis inhibitors are explored together with their potential synergistic effects with CuMA. Mechanical characterisation of an array of different cured natural rubber as well as recycled compounds confirmed the ideal optimised disulphide metathesis inhibitor combination. Further investigation into Mooney plots of both the cured and recycled was performed to understand the underlying bond dynamics of the produced compounds.

By incorporating the newly produced compounds into virgin rubber the recyclability of waste streams currently in use is demonstrated. Further investigation into the future of recyclable tyres was also carried out.

Acknowledgements

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Sustainable Rubber Approach: Towards a Greener Future

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Keywords: Sustainability; Innovation; University projects.

Pirelli is deeply committed to advancing high-performance products while continually enhancing their safety and reducing environmental impact.
To this end, Pirelli unveiled a new industrial plan, outlining ambitious targets for raw material sourcing:

- For the entirety of products, bio-based and recycled materials are foreseen growing from 23% in 2023 to 30% in 2025 up to 40% in 2030.

To support this strategic direction, Pirelli embraces an Open Innovation approach, driving R&D initiatives in the following areas:

1. Exploring renewable feedstock materials as plasticizers, protective agents, curing agents, and coupling agents, with the development of a bio-based "universal coupling agent" in collaboration with Politecnico of Milano.
2. Researching new nanofillers with low environmental impact to formulate compounds with exceptional low hysteresis.
3. Investigating biopolymers sourced from renewable materials, with a focus on lignin and cellulose.
4. Initiating studies on the biodegradability of bulk rubber vulcanizate in collaboration with Bicocca university.

Despite previous challenges in utilizing renewable sources as reinforcing agents due to dispersion and compatibility issues, Pirelli is pioneering the use of lignin as a reinforcing filler in tire compounds through a proprietary approach. Extensive R&D efforts are ongoing to enhance the interaction between lignin and the elastomer matrix, demonstrating Pirelli's ongoing commitment to innovation and sustainability in the tire industry.

Utilization of Tire Pyrolysis Oil-Derived Carbon Black for Automotive Sealing Applications

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Keywords: EPDM rubber; carbon black; tire pyrolysis oil; sustainable materials; mechanical properties.

The disposal of end-of-life tires (ELTs) poses a significant environmental challenge due to their resistance to natural degradation. However, recycling of waste ELT provides a considerable opportunity for sustainable development and resource conservation. Pyrolysis is one of the most promising methods as it is an environmentally friendly recycling technique [1]. The pyrolysis of ELT generates Tire Pyrolysis Oil (TPO), which can be utilized as a sustainable and eco-friendly alternative for various industrial applications [2]. A key application of TPO is manufacturing carbon black (CB), a process that contributes to reducing carbon footprint.

In this study, the use of two different TPO-derived CBs as a reinforcing filler in ethylene propylene diene monomer (EPDM) rubber composites for automotive sealing systems were investigated. One of them is a commercial mass balance TPO-derived CB (Ecorax Circular 215) while the other is an experimental product (ExpCB) which has 100% TPO-derived CB (EB 10011). EPDM rubber composites were formulated with varying amounts (100, 110, 120 phr) of TPO-derived CBs and compared to conventional CB (Corax FEF N550) as reference. The evaluation included examining the rheological properties, such as scorch and t90, as well as mechanical properties like tensile strength, elongation at break, and tear resistance. Based on the results, substitution of conventional CB with TPO-derived CBs (Ecorax and ExpCB) had a slight effect on curing time (t90). While Ecorax and reference compound displayed similar curing times, ExpCB showed a tendency to slightly slower curing time. In terms of mechanical properties (tensile & elongation), ExpCB demonstrated the better performance compared to reference and Ecorax. Moreover, EPDM test sheets (plates) were subjected to short-term aging tests. Results revealed that TPO-derived CBs consistently displayed lower permanent set values indicating improvements in the prevention of permanent deformation and shape recovery.

The results highlight the feasibility of TPO-derived CBs as sustainable substitutes for conventional CB (Corax N550) in EPDM rubber composites. This research contributes to the development of eco-friendly rubber materials and offers implications for applications in automotive sector. The adoption of TPO-derived CB as a reinforcing filler is expected to become a dominant trend in automotive sealing systems in the foreseeable future.

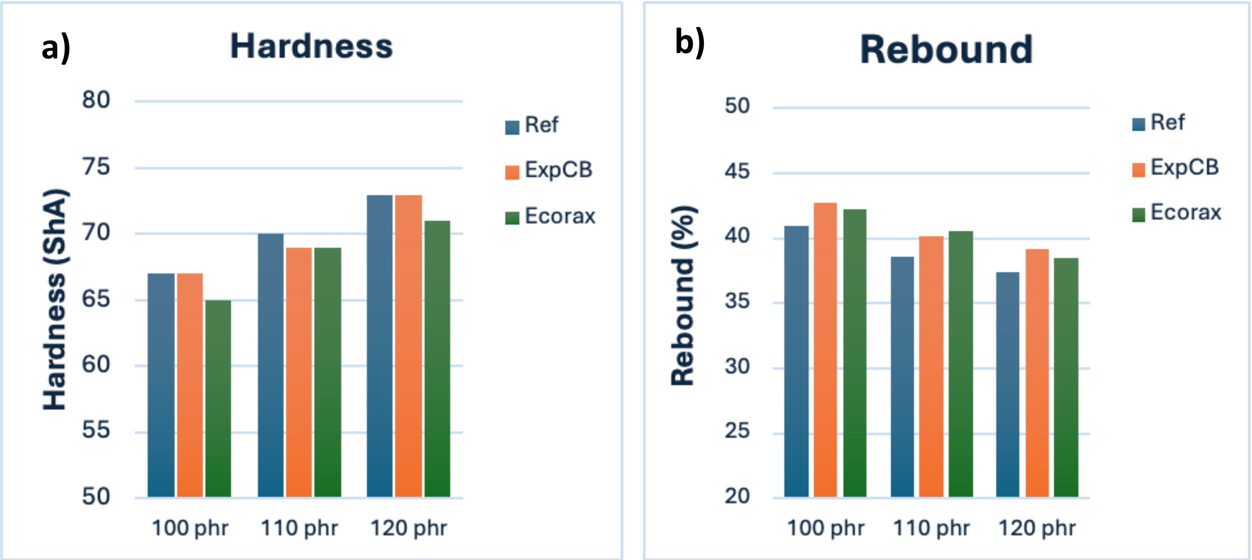

Figure1. (a) Hardness and (b) Rebound change with different types of CB at varying amounts.

Table 1. Sample compositions

(phr)	Ref1	Ref2	Ref3	TPO1	TPO2	TPO3	Ecorax1	Ecorax2	Ecorax3
EPDM	100	100	100	100	100	100	100	100	100
Corax FEF N550	100	110	120	-	-	-	-	-	-
Exp. CB	-	-	-	100	110	120	-	-	-
Ecorax Circular 215	-	-	-	-	-	-	100	110	120
White Filler	45	45	45	45	45	45	45	45	45
Process Oil	60	60	60	60	60	60	60	60	60
Small Chemicals	11	11	11	11	11	11	11	11	11
S+Accelerators	6.5	6.5	6.5	6.5	6.5	6.5	6.5	6.5	6.5

Acknowledgement

Authors would like to thanks Orion Engineered Carbons GmbH for collaborative efforts and supplying Carbon Black materials used in this study.

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Adding Self-Healing Properties to Epichlorohydrin-Based Rubbers With Different Approaches

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The increasing demand for durable materials and the significant environmental impact of plastic and rubber waste, which comprises approximately 40% of non-recyclable and non-convertible waste, highlight the need for innovative solutions like self-healing materials. These materials can autonomously restore their original properties following damage from external or internal stresses through reversible physicochemical processes [1]. Epichlorohydrin-based polymers such as Poly(epichlorohydrin)(CO) homopolymer Poly(epichlorohydrin-co-ethylene oxide) copolymer (ECO) and Poly(epichlorohydrin-co-ethylene oxide-co-allyl glycidyl ether) terpolymer (GECO) is a polyether type polymer with alkyl chloride functionality, is widely used in applications such as fuel hoses, gaskets, and air ducts due to its resistance to oil, heat, fuel, ozone, and its low-temperature flexibility and energy damping properties [2]. The structures of CO and GECO polymers are shown in Figure 1.

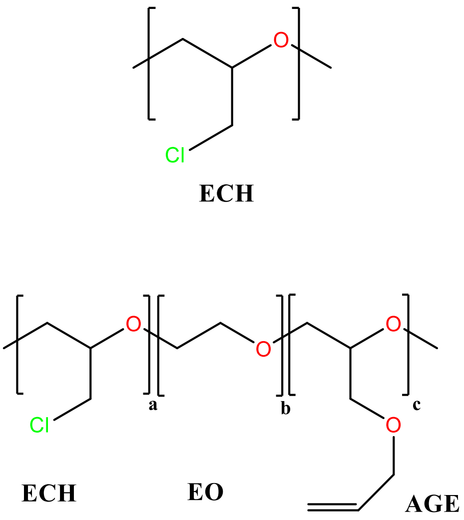

Figure 1. CO and GECO polymers' structures

To leverage these attributes for self-healing applications, In this study poly(epichlorohydrin) (PECH) was transformed into an ionomer by introducing ionic groups such as butyl-imidazole, sodium azide, and hydro borax atoms. This conversion facilitates the formation of reversible cross-links, crucial for self-repair mechanisms [3,4].

We synthesized CO and GECO ionomers and demonstrated their self-healing capabilities through a dynamic network of reversible cross-links formed with inorganic salts. Hydrin rubbers were modified via nucleophilic substitution and controlled radical polymerization NMP. The chloride groups were modified to introduce ionic groups through reactions with metal salts (NaN_3, $B(OH)_4$) or by quaternization with amines like butyl-imidazole and 4-Vinyl pyridine followed by an ionization. The analysis of the obtained polymers was done using Fourier Transform Infrared Spectroscopy (FTIR), a technique that identifies the ionic groups. We also employed Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) to assess the thermal properties and stability of the polymers. Microscopic analysis was conducted to follow the self-healing process. Scanning Electron Microscopy (SEM) was used to observe crack closure before and after healing. The ionic hybrid interface created enables repeated self-repair, thus significantly enhancing the material's durability and extending its functional life.

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Properties of cured products by crosslinking of 1,2-Polybutadiene

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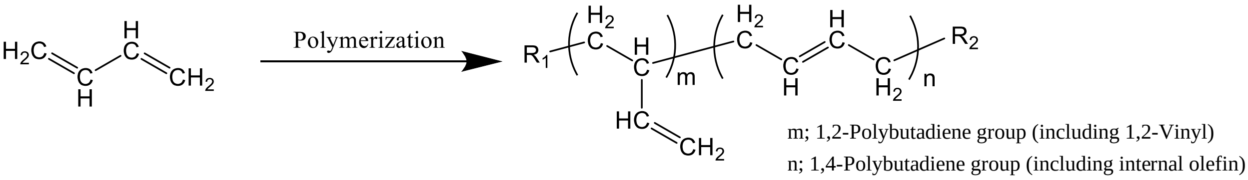
Keywords: Polybutadiene; EPDM; CSM

Introduction

The distinguishing features of Nippon Soda's liquid polybutadiene “NIPPON SODA PB” are: (1) It includes at least 85% branched 1,2-vinyl groups (Fig. 1, m) in its molecular chain, and (2) It has substituents at both terminals of the molecule. These structural features are attributable to unique living anionic polymerization, and NIPPON SODA PB has been used in various industrial applications since 1970, when it was first manufactured and sold.

Polybutadiene has two regioisomers that depend on the polymerization position. There are a number of liquid polybutadienes on the market, but most of products contain a large quantity of 1,4-vinyl groups (Fig. 1, n), so we make a clear distinction between them and our “NIPPON SODA PB”. In addition, we have developed 1,2-epoxylated polybutadiene (1,2-epoxylated PB) which is based on 1,2-polybutadiene (1,2-PB).

By adding NIPPON SODA PB to rubber or resin and carrying out a crosslinking reaction of 1,2-vinyl groups, 3-dimensional network structure is formed in these materials. This makes the effect of improving elasticity and strength, as well as oil/water resistance. In addition, 1,2-epoxylated PB reacts with chlorine in chlorine rubbers, which also contributes to various performance improvements.



m; 1,2-Polybutadiene group (including 1,2-Vinyl)
n; 1,4-Polybutadiene group (including internal olefin)

Figure 1. Structure of Polybutadiene [Poly(1-butene-*co*-2-butene)]

EPDM(Ethylene Propylene Diene Terpolymer) modification

Table 1 shows an example of EPDM rubber formulation using 1,2-PB. Properties of EPDM with Polybutadiene are in Table 2, and it shows that there was a certain correlation between the amount of 1,2-PB and the extent of crosslinking (hardening). Next, we confirmed the relationship between the 1,2-vinyl content in polybutadiene and outcomes of the crosslinking reaction (Table 2). As the 1,2-vinyl content is increased, the mechanical strength and oil resistance are improved. This is due to the increase in crosslinking density. The compression set is also correlated with the 1,2-vinyl content,

Material name	phr
EPDM [1)]	100
1,2-Polybutadiene	0, 10
Zinc oxide	5
Stearic acid	1
Calcined clay	120
Carbon black	5
Paraffinic oil	6
Paraffin wax	5
Dicumyl peroxide (DCP)	7
Dibenzoylquinone dioxime	1.5

Table 1. Example of EPDM modified with 1,2-PB

1) Ethylene content: 42%,
ENB content: 0.7%, ML1+4 (125°C): 27

and the need for adding an appropriate amount was not observed. Therefore, high 1,2-viniyl content of polybutadiene is demanded by EPDM formulations.

Table 2. Properties of EPDM with Polybutadiene

Polybutadiene[1]	phr	Mechanical properties		Oil resistance [2]		Compression set [3]
		Shore hardness	Tensile strength at break [MPa]	Standard oil IRM901		23°C [%]
				Δm [%]	ΔV [%]	
Not added	0	A69	6.69	46	72	17
m/n = 22/78: M_n=2,500	10	A67	7.08	46	70	17
m/n = 48/52: M_n=2,100	10	A69	6.98	44	66	14
m/n = 66/34: M_n=2,500	10	A70	7.24	41	63	13
m/n = 92/8: M_n=3,200	10	A71	7.42	38	58	12

1) m: 1,2-vinyl, n: 1,4-vinyl, 2) Temperature: 70°C±2°C, 72hours, 3) Compression ratio: 25%, 72hours

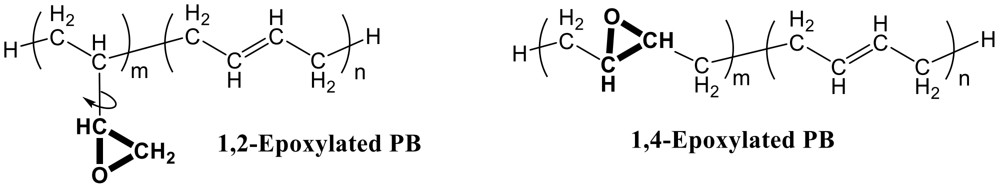
CSM (Chlorosulfonated Polyethylene) modification

1,2-epoxylated PB includes two functional groups: epoxy groups and 1,2-vinyl groups. This polybutadiene can undergo a cross-linking reaction of 1,2-vinyl groups and a ring-opening reaction of the epoxy groups. Reactivities of 1,2-epoxylated PB are different from 1,4-epoxylated PB because of the stereo chemistry of the epoxy group. Physical properties such as Mooney viscosity, hardness, tensile strength, tear strength and compression set could be improved by using 1,2-epoxylated PB for CSM rubber, owing to the crosslinking reaction of the 1,2-vinyl groups. In addition, CSM rubber using 1,2-epoxylated PB showed equivalent or superior acid resistance compared to existing acid acceptors or 1,4-epoxylated PB.

Table 3. Example of CSM modified with 1,2-Epoxylated PB

Material name	phr
CSM [1]	100
1,2-Epoxylated PB	10, 15, 20
Sorbitan stearate	3
FEF Carbon black	30
DOZ	10
Dicumyl peroxide	3
TAIC (Triallyl isocyanurate)	4
Total	165

1) TOSO-CSM TS-530



1,2-Epoxylated PB

1,4-Epoxylated PB

Figure 2. Structural Difference of 1,2-Epoxylated PB and 1,4-Epoxylated PB

Table 4. Volume expansion properties of CRM with 1,2-Epoxylated PB

Solvent	Condition	Unit	MgO	PbO	1,2-Epoxylated PB		
			15 phr	15 phr	10 phr	15 phr	20 phr
20 wt% HCl	80℃ × 7 days	%	174	1	0	3	5
10 wt% HNO_3	80℃ × 7 days	%	181	18	5	2	0

Conclusion

In this presentation, we'll describe the contribution of the 1,2-PB for EPDM and CSM rubbers based on cross linking reaction. It is expected that the findings will be useful for rubber formulation and design.

OIT-DSC: A method to compare real v/s artificial aged rubber in chassis bushes

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Keywords: Oxidation Induction Time-DSC, oxidative aging, chassis bushes, artificial aging.

Hyundai-Kia vehicles are well known for their industry-leading 5- and 7-year warranty respectively. These warranties require a high level of durability and aging resistance for all vehicle parts, including chassis and powertrain bushes. To ensure high aging resistance and identify the optimal balance between aging resistance and bush performance, it is important to correlate and compare the wear of components aged in the field to those from accelerated aging tests in the lab.

At Rubber Con 2023 we have shown how swelling tests and tensile tests of rubber samples cut from the bush could be used to quantify wear in the aged bushes. However, these methods focused mainly on the change of mechanical properties in the rubber and required a complicated sample preparation and produced results with notable scatter.

This paper focuses on the efforts that were made to identify wear parameters in chassis rubber bushes, that can quantify the degree of oxidative aging in the rubber from a chemical point of view.

In order to enable this, the following tests were performed on rubber samples from new, field aged and accelerated, artificially aged bushes: 3-D-Microscopy of the rubber surface, Shore hardness, Thermo-Gravimetric-Analysis (TGA), Differential Scanning Calorimetry (DSC), Oxidation Induction Time- Differential Scanning Calorimetry (OIT-DSC) and gas chromatographic mass spectroscopy (GC/MS) of the Extract.

3D-microscopy of the rubber surface turned out to be a good method to visualize the damage caused by Ozone. OIT-DSC showed the most promising results to quantify the degree of oxidative aging in field aged bushes. The oxidation induction time of aged samples was found to be significantly shorter than for rubber samples from new bushes.

Nevertheless, OIT-DSC and 3D microscopy of the rubber surface indicate that our currently used accelerated aging process may require further optimization to fully reflect the degree of oxidative aging wear in the rubber compared to the filed aged samples, even though this process is able to simulate the change of mechanical parameters. Therefore, OIT-DSC measurements could help to improve artificial aging test specifications.

Curing behaviour, mechanical properties, and the thermo-oxidative resistance of SSBR/silica/ lignin composites

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Keywords: Lignin; SSBR rubber; hybrid fillers; thermos-oxidative resistance

As a bio-mass derived functional material, Lignin has been of interest for a variety of applications, such as the fuels, the nanoparticles and other high-value chemicals, e.g. anti-oxidants. In the rubber industry, lignin materials are also promising as its potential to be the nanofillers and provide strong reinforcements comparable to commercial fillers. In this study, we investigated the feasibility of lignin as both the filler and the antioxidant in the solution styrene-butadiene rubber (SSBR) system. Herein, micro/nano-particles were prepared from the balling milling of the hardwood derived lignin materials and incorporated in SSBR together with silanised silica. The curing behaviour of the composite with hybrid fillers was investigated, and the effect of the partial replacement of silica by lignin in the composite was evaluated. Especially, the effect of thermo-oxidative resistance of the composites was studied by the differential scanning calorimetry (DSC), the accelerated aging test and the fatigue test, and its mechanism of anti-oxidation was analysed. This study shows that lignin micro/nano-particles possess the potential to be utilised as the filler and the anti-oxidant to promote the sustainable development of rubber industry for the carbon neutrality.

Seismic Protection with Rubber Isolators and Challenges for the Applied Rubber Compounds

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Keywords: seismic protection; structural protection systems; rubber isolators.

Seismic protection by isolating structures has a long history and started already serval thousands of years in Greece and Egypt when placing structures on sand to allow horizontal movements resulting in massive decrease of accelerations. Nowadays isolation is often realized with rubber isolators consisting of various horizontal layers of vulcanized rubber. MAURER SE is a worldwide operating company on the field of seismic structural protection systems for hospital, museums, states buildings, industrial structures and apartments with a rubber isolator plant located in Torbali/Izmir. The applied rubber compounds are mostly natural rubber but also sometimes chloroprene rubber. These shall fulfil existing standards like EN, AASHTO, ASCE, etc. The bearing sizes must be designed to safeguard certain performance parameters to achieve proper acceleration reduction in the range of factor 3-5 for the structure. Therefore, specific values for lateral stiffness, lateral damping, high shear deformation capability, vertical load stability even under big shear deformation and durability must be granted. All these parameters have its origin in the rubber compounds itself, which need to be developed for certain tear resistance, elongation at break, rubber-metal bond strength, aging resistance, inner damping, heat and cold resistance. This paper will provide a basic understanding for seismic isolation with various rubber bearing types like low damping, high damping and lead rubber bearings. It will also address the challenges to rubber compound development to meet specific performance parameters to grant for stability, reliability and durability within these lives saving systems.

Development of Mechanical Properties of Ozone Resistant NBR/PVC Rubber Mixtures

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Keywords: NBR , PVC , ozone resistant , rubber mixture.

The automotive industry has a crucial importance in our country's economy with the added value, technological development and employment opportunities [3]. In the automotive industry, rubber hoses are produced for many purposes such as air cooling, cooling-heating water hoses, oil, fuel and vacuum resistant hoses [1-4].

Oil and fuel resistant hoses, NBR (Acrylonitrile butadiene) rubber type with polar properties is preferred. Acyrlonitrile (ACN) content of NBR elastomer provides oil resistance property [1-4]. Ozone resistance is the one of the important requirements for oil and fuel resistant hoses. NBR rubber cannot meets the requirement of ozone resistance when used alone in the rubber mixture [5]. NBR rubber can mixed with PVC (Polivinil chloride) which has high polar properties, and it improves ozone resistance, mechanical, physical and thermal properties of rubber mixture [2-5].

The main objective of this study is to improve the mechanical properties of ozone resistant PVC & NBR rubber mixtures. At the same time, another goal of this study is to meet the needs in different industrial branches, to create a new market and to contribute to the added value of our country by providing production with a PVC/NBR mixtures produced with certain amount of domestic capital, equivalent to the mixture produced with commercially used masterbatch rubber.

Banbury mixing technique which has intermesh rotor type and 3 lt. capacity was used for the production of different rubber mixture formulations prepared by using different blend compositions of NBR rubber, PVC mixture which obtained from domestic supplier and other additives which have constant compositions in blends (Table 1). The preparation of the samples were optimized using Premier RPA test machine with rheometer testing. Ozone resistance properties were investigated using ozone cabinet test machine. Mechanical properties were analyzed in terms of the hardness, density, tensile strength, elongation at break, tear and permanent deformation values were measured. The results of mechanical tests have been evaluated according to the SAE J30 R6 (2012) (Society of Automotive Engineers) standard.

Ozone resistance test showed PVC addittion improves the ozone resistance of NBR rubber mixture. N/P-Masterbatch, N/P-5 and N/P-6 samples has no ozone cracks after the ozone resistance test. High level ozone cracks detected for the rest of the samples. N/P-Masterbatch, N/P-4 and N/P-5 samples meets the hardness requirement which is considered 70±5 Shore A. The hardness values of rubber mixtures measured from the samples increase in direct proportion to the increase in PVC portion in rubber mixture. Tensile strength and elongation at break test results showed all samples meets the requirement which is in the standard SAE J30 R6 (2012). N/P-Masterbatch samples had a minumum tensile strength and permanent deformation value. Density, tensile strength, tear values, permanent deformation were increased and elongation values were decreased when PVC portion increase in the rubber mixture.

Table 1. Rubber mixture formulations

Components [phr]	**Rubber Mixture Formulations**						
	N/P-Masterbatch	**N/P-1**	**N/P-2**	**N/P-3**	**N/P-4**	**N/P-5**	**N/P-6**
NBR/PVC Masterbatch	100	-	-	-	-	-	-
NBR[a]	-	100	90	80	70	60	50
PVC[b]	-	0	10	20	30	40	50
Carbon Black	76	76	76	76	76	76	76
Plasticizer	29	29	29	29	29	29	29
Activators	4	4	4	4	4	4	4
Process additives	3	3	3	3	3	3	3
Antioxidants	3	3	3	3	3	3	3
Additive	4	4	4	4	4	4	4
Accelerator	1	1	1	1	1	1	1
Vulcanization agent	1	1	1	1	1	1	1

NBR[a]: Acrylonitrtrile butadien rubber

PVC[b]: Polyvinylclorur

In conclusion, in this study it was determined that the most successful blend was the N/P-5 when NBR/PVC mixtures which have different blend compositions compared according to the mechanical and ozone properties. It was concluded that properties of the mixture which N/P-5 are compatible with the mixture prepared with commercial masterbatch and can be used as a substitute product. For the further study, functional properties will investigate.

Acknowledgement

Thanks to the grant sponsors and/or people who contribute to the study

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EUDR – The Road to Compliance for Rubber Companies

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Keywords: EUDR; Deforestation; Compliance; Supply Chain

The European Union Deforestation Regulation (EUDR)[1], enacted on 29 June 2023, establishes a new legal framework to prevent commodities linked to deforestation and forest degradation from entering or leaving the EU. Businesses have been given an 18-24 month grace period, in advance of 30 December 2024, to align their supply chain operations with the impending compliance requirements. The deadline is fast approaching, with Natural Rubber being a commodity central to the regulation. Companies throughout the supply chain will be required to capture data, implement new technologies, and optimise their operations to prevent the importation of Rubber products sourced from deforested areas into the EU.

The United Nations (UN) Sustainable Development Goals (SDGs) were created in 2015 with the ‘aim of peace and prosperity for people and planet’[2]. Goal 15 promotes Life on Land with a specific focus on deforestation. One of the targets was, by 2020, to promote the implementation of sustainable management of all types of forests, halt deforestation, restore degraded forests and substantially increase afforestation and reforestation globally. However total tropical primary forest loss in 2023 totalled 3.7 million hectares, the equivalent of losing almost 10 football fields of forest per minute. In response to these goals, deforestation regulation is growing worldwide to support the UN SDGs – EUDR for the EU, UK FRC in the UK, the Forest Act in the US, and many others are in the early stages of consultation.

New research shows deforestation linked to Rubber has been 'underestimated’[3]. Rubber related deforestation has remained consistent across the last 30 years. Despite greater awareness of environmental impacts, many Southeast Asian countries continue to see unchanged deforestation rates per hectare. These persistent issues have led to the inclusion of Rubber within the scope of EUDR.

Under the EUDR, various rubber-based products, from natural rubber and latex to vulcanized rubber items like tires and transmission belts, fall within the regulatory scope. Companies importing to or exporting from the EU must conduct thorough due diligence to ensure their rubber products meet EUDR standards. This requires collecting detailed sourcing information (including geolocation), assessing risks, and mitigating any identified risks across the supply chain. Compliance is required to maintain market access and avoid significant penalties which can be up-to 4% of EU turnover.

The definition of Deforestation within EUDR is taken from the UN Food and Agriculture Organisation (FAO), which defines it as the conversion of forest to agricultural use[4]. Forest Degradation means structural changes to forest cover in the form of conversion to a planted/plantation forest. Therefore, Rubber is considered compliant if it has been grown on land that has not been subject to deforestation or degradation after 31st December 2020.

Compliance requires detailed data for each shipment, including Product Description, Quantity, Geolocations of the plots of land where the commodity was produced, Date or time range of Harvest, and proof of Legality and Deforestation-Free status. EU importers, or 'Operators,' will then need to carry out a risk assessment to ascertain the deforestation risk associated with their products. If significant risks are identified, the Operator will need to undertake risk mitigation which will include independent audits, surveys, and proof of implementation of controls and procedures.

Deforestation risk analysis will leverage satellite data to understand whether the area has been deforested or degraded since 31st Dec 2020. Figure 1 provided an example of an area that has been deforested.

31st December 2020 February 2024

Figure 1. Deforestation Example using Satellite Imagery

Rubber businesses will need to focus on answering these questions to ensure compliance which include: What information needs to be collected, how it can be shared, the sufficiency of evidence, the frictionless trading of Rubber, and ownership of compliance in the supply chain.

Rubber companies trading with the EU face significant commercial risks if they fail to comply with the regulatory standards. However, adopting a proactive approach can provide a competitive advantage. By prioritising sustainability, companies not only enhance their reputation but also attract environmentally conscious talent and appeal to investors who prioritise environmental stewardship.

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Innovative modeling approach enables the quality prediction of rubber parts during a filling and curing simulation

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Keywords: Rubber, Degree of cure, Processing history, Simulated part quality.

This work introduces an innovative modeling approach for the direct calculation of mechanical part characteristics as quality-related figure instead of the commonly employed degree of cure in the context of a filling and curing simulation of rubber materials. First, the drawbacks of existing methods for characterizing the reaction kinetics by means of a Rubber Process Analyzer (RPA), the data normalization, and approximation for simulation purposes were discussed in more detail. One major limitation in the normalization of the reaction kinetics is the neglected difference in the maximum transmitted torque, i.e., between 140°C and 170°C the torque gap reaches 2.65 dNm (17%) for an industrial-scale styrene butadiene rubber compound. This lack of information cannot be resolved by state-of-the-art reaction kinetics models, i.e., Deng Isayev or Kamal and Sourour. Another point is that these models assume that the same degree of cure can be achieved by increasing the vulcanization temperature and at the same time reducing the vulcanization time. As the results of the quality inspection reveal, e.g., for parts being vulcanized to a targeted degree of cure of 80%, an increase in the vulcanization temperature by 30 K almost doubles the compression set values (CS) or leads to an absolute increase in ΔCS by 36%, i.e., to CS values of $41^{+2}_{-1}\%$ at 140°C and $77^{+5}_{-2}\%$ at 170°C.

Moreover, in a modern filling and curing simulation of reactive materials, such as rubber compounds, the part quality is not automatically linked to the degree of cure. Depending on the operator, the calculated degree of cure has to be matched manually with the molded part quality. Another possible option is to transfer the information of the simulated degree of cure to external calculation programs in order to predict the part quality. However, it should be noted here that the processing history is completely neglected and it may occur that one and the same degree of cure leads to a variation in part quality.

To meet these challenges, an innovative modeling approach referred to as the average curing speed (ACS) model has been proposed. This model considers the degree of cure and the average curing speed instead of temperature and is calibrated once with known results from quality tests. Any quality specification of a part, such as information of a tensile test or dynamic-mechanical analysis, can be considered as one-time calibration data. In this work, the compression set was chosen since it is commonly accepted in the industry.

To validate the ACS model, parts were compression molded at 155°C and 165°C, to a targeted degree of cure of 80%. The CS test results are $53^{+2}_{-4}\%$ and $67^{+9}_{-4}\%$. Being provided with the option to consider the ACS model in the simulation routine, SIGMASOFT® v6.0 (SIGMA Engineering GmbH, Aachen, Germany) software has been applied for mimicking the compression molding process for both settings and the part quality was calculated based on the processing history.

Finally, the average part quality obtained from the innovative modeling approach provides an excellent prediction of the real compression molding process. The predicted mean CS values of the evaluation area, i.e., the volume of a CS sample, are 51% and 73% and are within the deviation of the investigated real parts (Figure 1). To assess the vulcanization progress on rubber parts, it is no longer necessary to assume the part quality based on the simulated degree of cure. Instead, the quality can be mapped individually for each volume element, which will enable new optimization strategies for process design in the future.

In conclusion, the validation highlighted the enormous potential of the innovative modeling approach and proved that the average curing speed is a suitable measure for the quality simulation of the compression molding process. In a further study, the authors will discuss the applicability of the innovative modeling approach for the complex injection molding process.

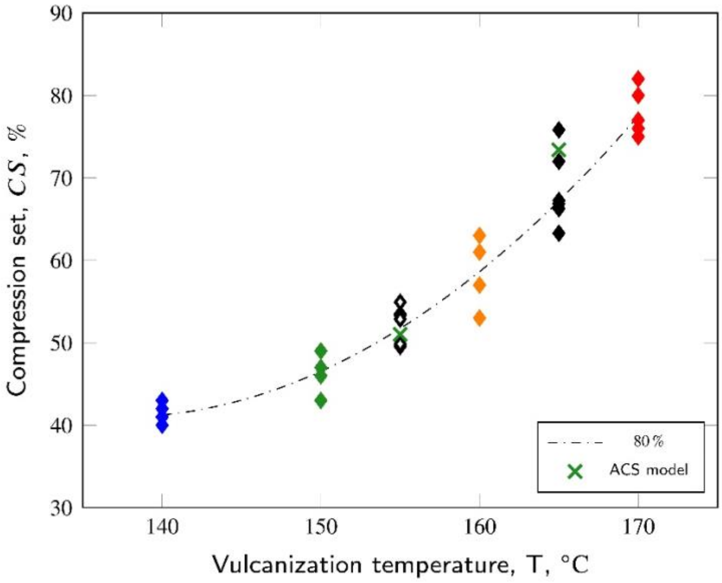

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Figure 1. The innovative average curing speed (ACS) model was applied in the simulation. The results reveal excellent prediction of real part quality (represented by black diamond symbols) compared to the ACS model’s output (mean values represented by green crosses). Colored diamond symbols represent compression set values of other manufacturing temperatures.

Study into the Energy Aspects of Mixing of Filled Rubber Compounds

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Keywords; mixing; energy; formulation; cooling.

Almost all rubber products are compounds created from a formulation, that include one or more polymers and a range of chemicals. In a compound, the chemicals must be finely dispersed and homogeneously distributed within the polymer matrix by mixing. Mixing is typically carried out in an internal mixer. Mass transfer between different components is achieved by imparting rolling, shearing, extensional and squeezing forces. Viscoelastic deformation, bond braking, filler breakdown and creation of new surfaces requires considerably energy that is converted to heat.

Traditionally the temperature rise in mixing is regulated by effective cooling. According to the energy balance approach the heat load in mixing is removed by the cooling system [1]. Compound temperature is a critical process response and is used in process design engineering.

Without high cooling efficiency the only means to add extra work is to revert to wasteful multi-stage mixing.

This paper details an experimental approach, that allows practical determination of the required mixing energy for different production compounds, containing different polymers and reinforced with different filler systems. Elaboration of the data allows quantitative determination of the enthalpic energy and internal energy components [2].

Simultaneous equations, solving for internal energy
Use of points of thermal equilibria and thermal differential gives a new insight into the rubber compound mixing process and allows quantification of the heat load. The information obtained allows design of more energy efficient mixing cycles and smart cooling systems.

The effect of polymer type and filler loading on the thermodynamic of mixing is investigated. The enthalpic component and internal energy are compound and process dependent. The approach is validated with data from production compounds.

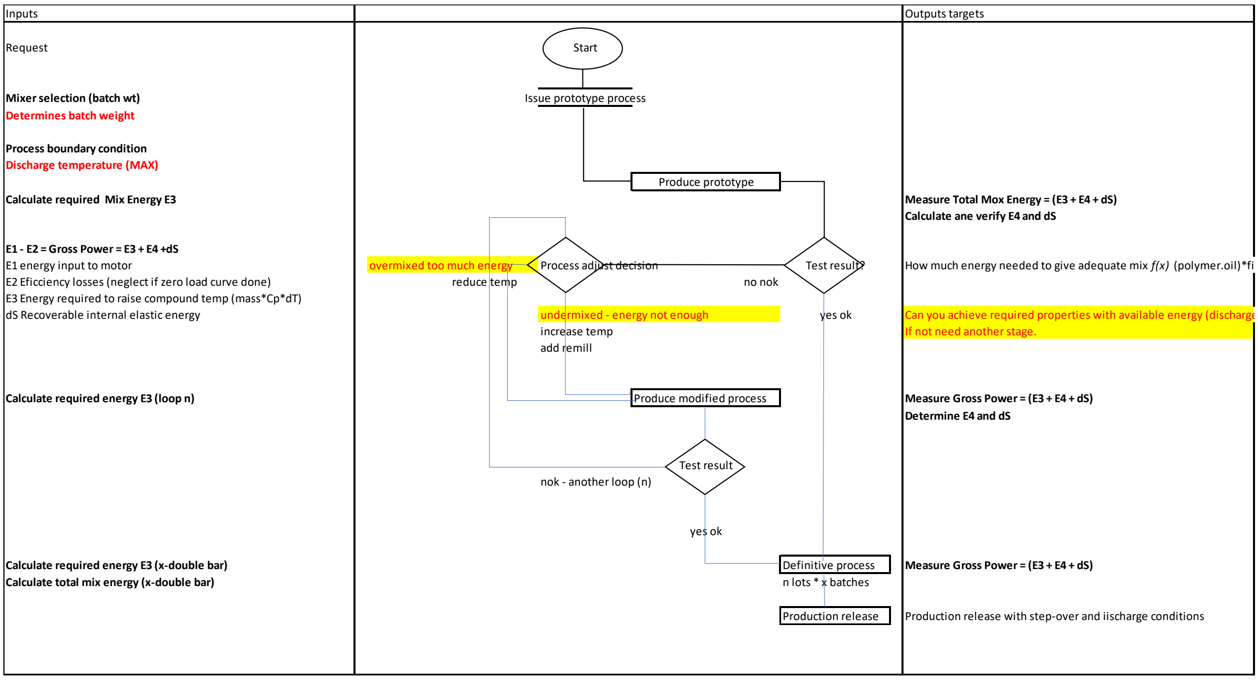

Figure 1. Required Mixing Process Energy Flow Diagram

Acknowledgement

Thanks to HFMG and ADT for providing the experimental data for this work and allowing its publication.

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Different Viewpoints on Sustainability - A Process Additive Perspective

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Keywords: Sustainability, processability, dispersibility, hysteresis.

Process additives are highly active chemicals that are frequently used along the entire rubber production chain. Starting with complex reactive mixing, through down-line processing such as calendaring or extrusion, followed by assembly within a building sequence, culminating in vulcanization during moulding operations. Process additives are typically used at low dosages; these materials provide benefits such as improved dispersion and homogeneity during compound mixing. Throughout rubber processing at higher shear rates rubber flow, tack and green strength can be controlled. During vulcanization mould flow and release can be enhanced.

The drive towards greater sustainability has broadened the opportunities for process additives to contribute towards a circular economy.

Over recent years, the share of sustainable feedstock of rubber process additives has been progressively shifted towards higher amounts of renewable and recycled content. For certain applications such as lubricants designed for highly filled silica compounds, products are available that are now entirely based on sustainable feedstock without a downgrade of the mode of action in the final application. Depending on the end user need, various certifications can be applied.

Similarly, efficiencies in the manufacturing of these products have been achieved, leading to a reduction in emissions. This involves implementation of monitoring systems to track emissions from production, machinery upgrades, and re-design of manufacturing processes to reduce energy consumption and to minimize waste.

This efficiency expands to innovations in the packaging of chemical products. Examples are the use of big bag and Goodpack crate systems which maximize container loading and the use of tailor-made sachets using low melt film allowing for sachet direct inclusion into mixing processes. Both approaches significantly reduce packaging waste.

Process additives provide multiple benefits in the final use rubber application. These advantages extend to both rubber manufacturers and end users. To meet ever more challenging end user demands formulations include material concepts resulting in highly metal-sticking rubber compounds. Key objectives for rubber producers are to reduce the scrap rate and to increase the mixing efficiency, whereas for the end user an improved dynamic property in terms of controlled hysteresis is desired.

One innovative process additive towards this is a novel rubber additive recently developed and called Struktol VP 1797. This product technology does possess two levels of action. Firstly, an improved effectiveness towards silica filler dispersion and secondly a reduced rubber to metal stickiness.

In this example, the novel additive leads to a reduction of Mooney viscosity by 20% which allowed shorter mixing cycles and in turn lower energy consumption during mixing. Additionally, the loss of batch weight could be significantly reduced by the control of the metal to rubber interface using the novel additive resulting in significantly reduced scrap rates during production, minimizing the waste impact. Further, the effective interaction with the filler led to improved energy efficiency of the final compound, as evidenced by reduced hysteresis, substantiated by dynamic mechanical analysis results showing a reduced tan delta at 60°C. This in turn emphasizes the positive impact of the use of process additives on the life cycle assessment of tires, for example.

Peptiser products do not only improve rubber process efficiency but also offer a more sustainable approach towards natural rubber processing. This is reflected in the increased content of sustainable feedstock as well as reduction of zinc and 2,2'-dibenzamido diphenyl disulfide (DBD) content. In contrast to chemical peptisers, a larger Mooney viscosity reduction is achieved with modified products. This in turn allows shorter, less energy consuming mixing cycles as well as minimized material pressures during extrusion. The way this technology works differs from chemical peptisers. The mastication effect is slower; however, the product remains active for a longer period of time compared to conventional peptisers. Preferably the higher molecular weight polymer chains are broken down, resulting in a more uniform molecular weight distribution and better dynamic vulcanization properties. For instance, reduced flexing heat build-up can be observed due to stabilised chain breaking by new modified peptiser and extended blow-out to failure times are measured.

Lignosulfonate filled rubber compounds with applied low molecular weight plasticizers

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Keywords: Rubber; lignosulfonate; plasticizers; compatibility.

Current trend in today's modern society is narrowly linked with utilization of biodegradable and environmentally friendly polymer materials. The main aim to use natural-based sources in polymers is to mitigate the negative impact on the environment and to reduce the carbon footprint. A lot of natural based sources have been tested as potential fillers or components for polymer compounds as starch, cellulose, lignins, lignosulfonates and their derivates.

Lignin is one of the most abundant natural polymers and can be isolated for example from wood. For a long time, lignin has been considered a waste from the pulp and paper industry, but this view is rapidly changing and now it is considered a raw material with a huge potential to produce value-added products. One of its disadvantages is, that it is highly hydrophilic and its complex structure causes strong interactions, which affects its compounding with other polymers. To improve adhesion and compatibility between both components, a combination of lignin with reinforcing fillers, or the application of various physical and/or chemical modification techniques and procedures are required. These procedures have been found to be very promising and clearly have pointed to a high application potential of lignin into rubbers. Materials with high added values have been fabricated. However, it must be noted that a lot of applied modification procedures require additional expenses and/or are time consuming.

In the current work, derivate of lignin - calcium lignosulfonate was dosed to the rubber formulations in constant amount of 50 phr. Acrylonitrile-butadiene rubber served as the matrix. To improve the adhesion and homogeneity between the rubber and the biopolymer, three low molecular weight plasticizers were used, namely 1,4-butanediol, ethylene glycol and glycerol. They are highly available and cost effective. These plasticizers have been chosen due their polarity. The plasticizers were applied into rubber formulations in concentration scale ranging from 5 to 30 phr. The main aim of the work was to show that an improvement of compatibility on the filler–rubber interfacial condition and subsequent enhancement in physical–mechanical properties can be reached by simple addition of plasticizers into rubber formulations filled with lignosulfonate, without any additional modification procedures or change in fabrication conditions. The enhancement in physical-mechanical properties of rubber compounds filled with biopolymer might contribute to the broadening of their potential applications.

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Strategies to improve thermal conductivity and mechanical properties of elastomers using multi-filler systems

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Keywords: Elastomers; Thermal conductivity.

Due to the viscoelastic nature of elastomers, large amount of heat is generated inside elastomer compounds under the dynamic mechanical loading. The heat transfer to the surroundings in elastomers is very slow due to their low thermal conductivities; hence, the overheating of compounds. This results in decline in the performance, thermal stability and life cycle of compounds. Incorporation of conductive fillers into the elastomers plays a very important role in the thermal management and improvement of mechanical performance. However, presence of nanoscopic gaps between filler-filler and scattering of phonons at the polymer-filler interface affect the efficiency of heat transfer in filled elastomers. [1-2] Therefore, developing a hybrid/multi-filler system in which connected filler network transferring heat efficiently is crucial. Herein, we present the potential hybrid and multi-filler systems, which not only give better thermal conductivity but improved mechanical properties and thermal stability by replacing the part of conventional fillers with carbon nanotubes and graphene nano platelets. Compounds of NBR and CNTs, GNPs and carbon black (CB) were prepared in different proportions. Their thermal conductivity and mechanical properties were investigated and were compared with the CB filled compound.

Acknowledgement

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Investigating Pyrolytic Carbon Black in Natural Rubber: Rheological, Mechanical and Dynamic Effects

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Keywords: Pyrolytic Carbon Black; Sustainability; Capillary Rheometer

In the field of sustainable and green chemistry, the traditional role of carbon black has faced significant scrutiny. Due to the various environmental issues associated with the production and use of conventional carbon blacks, there is widespread consensus among industry professionals to explore equally effective alternatives that offer both superior rubber reinforcement performance and minimal environmental pollution [1].

The automotive industry, the primary consumer of carbon black, has established specific targets to integrate effective alternative materials such as pyrolytic carbon black in line with sustainability and circular economy principles [2]. Pyrolytic carbon black is one of the key products of pyrolysis process [3]. It has the potential to replace conventional carbon black obtained from fossil fuels in polymer compounds [1]. Substituting conventional carbon black with pyrolytic carbon black during rubber processing results in a significant decrease in both CO_2 footprint and pollutant emissions (SO_x, NO_x), including polycyclic aromatic hydrocarbons (PAH) produced in conventional carbon black manufacturing. Therefore, it is logical to find ways to introduce pyrolytic carbon black into the commercial carbon black sector without compromising the quality of the final product [4].

This study aims to enhance technical understanding of pyrolytic carbon black as an alternative in the rubber industry, focusing on its effects on processing, rheological, mechanical and dynamic properties. Two types of pyrolytic carbon blacks and two commercial carbon blacks were used. The rubber compound formulations for all recipes are presented in Table 1.

Table 1 Filled Natural Rubber Compounds Formulations in phr*

Components [phr]	**Sample notations**			
	N3	**P3**	**N5**	**P5**
SVR 10	100	100	100	100
Zinc Oxide	5	5	5	5
Stearic Acid	1.5	1.5	1.5	1.5
Processing Aid	2	2	2	2
Antioxidant	3	3	3	3
N330	70	-	-	-
N550	-	-	70	-
Pyrolysis Carbon Black (pCb-3)	-	70	-	-
Pyrolysis Carbon Black (pCb-5)	-	-	-	70
Total	181.5	181.5	181.5	181.5
S 80	2.5	2.5	2.5	2.5
TBBS 75	1.66	1.66	1.66	1.66

*phr = Parts per Hundred Rubber

The complex viscosity values of four compounds were measured using a rubber process analyzer and a capillary rheometer, and it was found that the viscosity results from these two methods were in good agreement. The data obtained from capillary rheometer is essential for understanding and solving processability issues. Despite its importance, there is a lack of studies on the processability of rubber compounds filled pyrolytic carbon black using a capillary rheometer. This study shows how commercial carbon black and pyrolytic carbon black impact processability. According to data from both the rubber process analyzer and capillary rheometer, the viscosity of compounds containing pyrolytic carbon black was significantly lower, indicating that pyrolytic carbon black substantially improves processability. It was found that the use of pyrolytic carbon black increases the scorch time and optimum cure time, meanwhile the maximum and minimum torque decreases. The tensile strength, elongation at break and hardness of the compounds before and after aging were tested and compared. No significant change in tensile strength was observed. Due to the lower modulus in the compounds with pyrolytic carbon black, elongation at break values were higher in comparison to the samples with conventional carbon black. The loss factor (tan δ) at 60°C, which is a recognized a precise predictor of rolling resistance, was also obtained for each NR-based compound. It was observed that compounds with pyrolytic carbon black has lower tan δ relatively. Also thermal conductivity of compounds were measured by using capillary rheometer to determine the effect of different types of filler used. Based on the obtained results, it may be possible to replace conventional carbon black with pyrolytic carbon black in some applications.

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New thermal conductivity and EMI shielding performance in rubber by using optimized carbon additives blends

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Keywords: thermal conductivity; EMI shielding; graphite; conductive carbon black.

Rubber compounds need to meet new specifications to adapt to, amongst others, electric vehicle and electronic applications. Higher density of electric and electronic systems in tight environments require systems to enable heat dissipation. Also the fast growth of wireless communication and car autonomous driving systems [1] means higher risks of crosstalk between electronic systems and electromagnetic waves. Therefore, efficient EMI shielding materials are needed to ensure safe driving.

1/ Thermal Conductivity Improvement

Graphite is providing thermal conductivity in a wide range of polymers. For this study, two high purity graphites were tested in EPDM system:

- TIMREX® KS 44, a synthetic graphite, with d90=90 µm
- TIMREX® C-THERM™ 011, a high aspect ratio graphite, with a d90 close to 100 µm.

Figure 1. SEM of TIMREX® KS 44

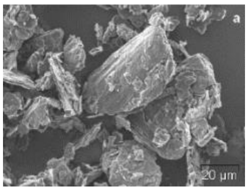
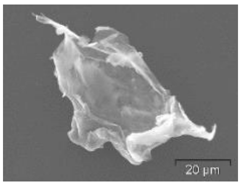


Figure 2. SEM of C-THERM™ 011



The graphite efficiency on thermal conductivity is tested against a reinforcing conductive carbon N550, and a conductive carbon black ENSACO® 250G supplied by Imerys Graphite & Carbon

Table 1 Compositions of EPDM for thermal conductivity evaluation

Components [phr]	Sample notations															
	N550 25	N550 50	N550 75	N550 100	E250G 25	E250G 50	E250G 75	E250G 100	KS44 25	KS44 50	KS44 75	KS44 100	CT011 25	CT011 50	CT011 75	CT011 100
EPDM[a]	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Oil	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
N550	25	50	75	100												
ENSACO® 250G					25	50	75	100								
TIMREX® KS44									25	50	75	100				
C-THERM™ 011													25	50	75	100
Co-agent	1,5	1,5	1,5	1,5	1,5	1,5	1,5	1,5	1,5	1,5	1,5	1,5	1,5	1,5	1,5	1,5
DCP[b] (40% active)	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8
Total	234,5	259,5	284,5	309,5	234,5	259,5	284,5	309,5	234,5	259,5	284,5	309,5	234,5	259,5	284,5	309,5
% carbon additives	11%	19%	26%	32%	11%	19%	26%	32%	11%	19%	26%	32%	11%	19%	26%	32%

[a] EthylenePropylene Diene Mononer
[b] Dicumyl peroxide

Thermal conductivity, measured by Laser Flash, is significantly increased both in-plane and through-plane and can reach up to 8W/m.K.

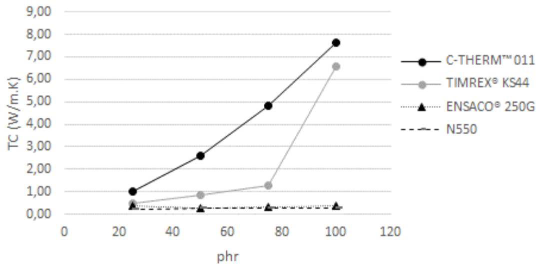


Figure 3. In plane thermal conductivity

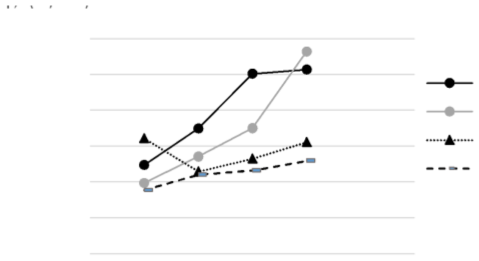


Figure 4. In plane thermal conductivity

TIMREX® KS44 and C-THERM® 011 performance overwhelm the ones of carbon black in thermal conductivity. To maintain a good level of mechanical performance, blends with reinforcing carbon black are needed and were tested. Additional data will be shared in the final paper and conference.

2/ EMI Shielding

To achieve high EMI shielding in far field, i
with high electrical conductivity [2]. The formulatio
and 50 phr ENSACO® 260G carbon black with the
ENSACO® 260G (table 2).

Table 2. Compositions of EPDM for EMI shielding evaluation

Components [phr]	Sample notations			
	75 E260G	100 E260G	50 E260G + 25 CT011	50 E260G + 50 CT011
EPDM[a]	100	100	100	100
Oil	50	50	50	50
N550	50	50	50	50
ENSACO® 260G	75	100	50	50
C-THERM™ 011			25	50
Co-agent	1,5	1,5	1,5	1,5
DCP[b] (40% active)	8	8	8	8
Total	284,5	309,5	284,5	309,5
% carbon additives	44%	48%	44%	48%

[a] EthylenePropylene Diene Mononer

[b] Dicumyl peroxide

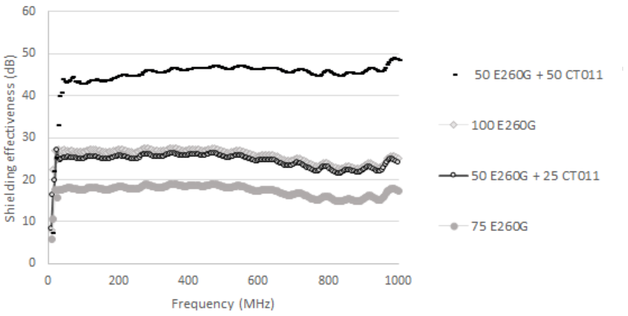


Figure 5. EMI shielding according to ASTM 4935-2 mm

The low resistivity obtained in particular with the blends containing 50 phr ENSACO® 260G and 50 phr of C-THERM® 011 enable this material to perform well in EMI shielding and reach up to 50 dB at 1 GHz (figure 5, as measured on 2 mm plaque using ASTM D4935).

Acknowledgement

Thanks to the Imerys Research and Development colleagues who contribute to the study: Kevin Piirai, Gilles Meli and Victor Hitsch.

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A crosslinking kinetic model considering reversion effect and its application in vulcanization process of heavy truck suspension rubber bearing

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Keywords: crosslinking kinetic model; reversion; curing; finite element analysis.

As the last and key step in rubber production, the vulcanization process plays a decisive role to obtain high-quality rubber goods with long service life; however, few existing vulcanization kinetic models could consider reversion effect and non-isothermal vulcanization conditions [1-3].

The vulcanization kinetic model is shown in Eq. (1). For the induction stage, it is assumed that the degree of curing increases linearly with time. For the curing stage, t_p was introduced to the modified K-S model [3]. For the reversion stage, a new model analogous to the modified K-S model was proposed. In Eq. (1), α is the degree of curing (DOC), t is the time elapsed since the beginning of the reaction, t_i and α_0 are the time and degree of curing at the end of induction stage, t_p and b are the time and degree of curing at the end of curing stage, n_1, n_2, k_1 and k_2 are the temperature-dependent parameters. Typically, α_0=0.05 and b=1.

$$\begin{aligned}&\textit{Induction Stage}: \alpha = t\times\alpha_0/t_i\\&\textit{Curing Stage}: \alpha = b+\left(\alpha_0-b\right)\Big/\left[1+\left(\left(t-t_i\right)\times\left(t_p-t_i\right)\Big/\left(\left(t_p-t\right)\times k_1\right)\right)^{n_1}\right]\\&\textit{Reversion Stage}: \alpha = 1-\left[k_2\times\left(t-t_p\right)^{n_2}\right]\Big/\left[1+k_2\times\left(t-t_p\right)^{n_2}\right]\end{aligned} \tag{1}$$

To apply the new vulcanization kinetic model to practical vulcanization processes and distinguish between the equivalent induction stage, equivalent curing stage, and equivalent reversion stage in non-isothermal vulcanization, two time-related dimensionless parameters known as the induction factor $\overline{t_i}$ and curing factor $\overline{t_p}$ were introduced.

Based on the definitions, we know that the equivalent induction stage comes when $\overline{t_i}<1$, the equivalent curing stage appears when $\overline{t_i}\geq 1$ and $\overline{t_p}<1$, the equivalent reversion stage shows up when $\overline{t_p}\geq 1$. The first ordinary differential equation for rate of curing can be obtained as shown in Eq. (2).

$$\frac{\partial\alpha}{\partial t}=\begin{cases}\dfrac{\alpha_0}{t_i} & \overline{t_i}<1\\[2ex] \dfrac{\left(b-\alpha\right)^2}{b-\alpha_0}\times\dfrac{n_1}{k_1}\times\left[\left(\dfrac{\alpha_0-\alpha}{\alpha-\mathrm{b}}\right)^{\frac{1}{n_1}}\times\dfrac{k_1}{t_p-t_i}+1\right]^2\times\left(\dfrac{\alpha_0-\alpha}{\alpha-b}\right)^{1-\frac{1}{n_1}} & \overline{t_i}\geq 1\,\&\,\overline{t_p}<1\\[2ex] -\alpha^2\times k_2\times n_2\times\left(\dfrac{1-\alpha}{k_2\alpha}\right)^{1-\frac{1}{n_2}} & \overline{t_p}\geq 1\end{cases} \tag{2}$$

Eq. (1) was utilized to fit the normalized curing kinetic curves. The comparison between the fitting data using the new vulcanization kinetic model and the normalized experimental test results at different temperatures are shown in Fig. 1. All the R^2 values exceed 0.995. At 1860 s of the vulcanization process, we found an interesting phenomenon as shown in Fig. 2(a). From the surface to the center of the sphere along the radial direction, the degree of curing increases first and then decreases. At about a quarter of the diameter, the degree of curing reaches its highest value, 100%. The degree of curing values from the center of the sphere to this point and from the surface of the sphere to this point are between 85.3% and 100%. The curing states of the two regions are completely different in terms of departure of torque (DOT) distribution results, see Fig. 2(b) for details. The departure of torque value corresponding to the surface of the sphere is +14.7%, while the departure of torque value at the center position with the degree of curing of 85.9% is -14.1%. This is the phenomenon of "over-cure on the outside surface and under-cure at the inside position" that is often said for the vulcanization processing of thick rubber products. We have quantified this interesting phenomenon of great interest to the rubber industry. The contour plots of temperature and curing states of heavy truck suspension rubber bearing are shown in Fig. 3.

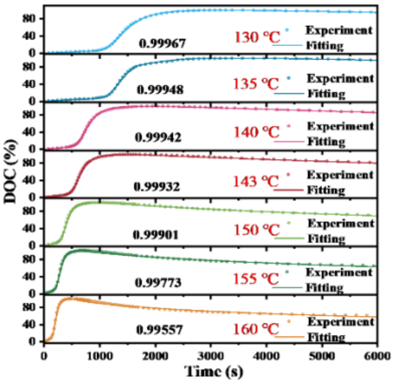

Figure 1. The comparison between the fitting data using the new vulcanization kinetic model and the normalized experimental test results at different temperatures

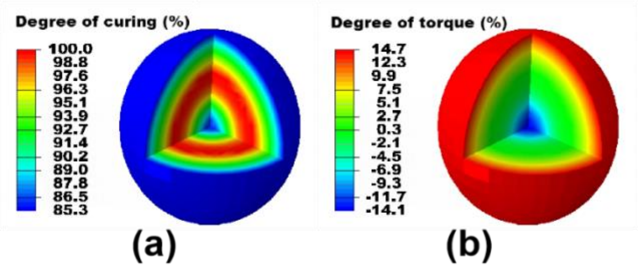

Figure 2. The contour plots of the degree of curing and degree of torque corresponding to 1860 s in the vulcanization process

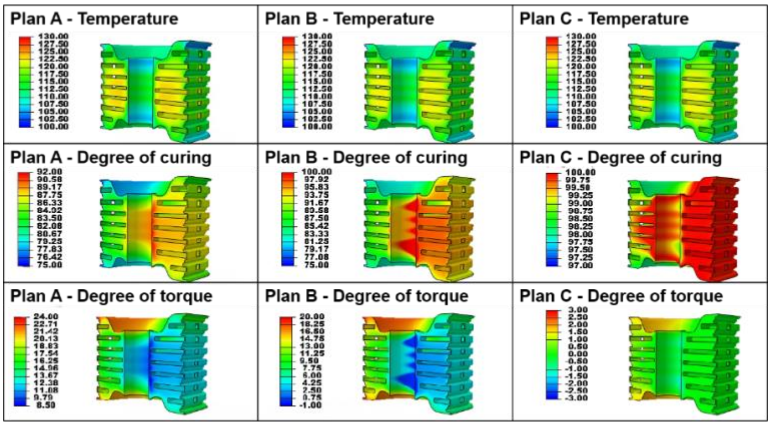

Figure 3. Contour plots of temperature and curing states of heavy truck suspension rubber bearing

Acknowledgement

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Research on the application of modified cashew net oil in tire tread compounds

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Keywords: Bio-based plasticizer; Modified cashew net oil; Sustainable materials.

The demand for sustainable materials to replace petroleum-based materials is becoming increasingly urgent， because of the large consumption of petrochemical base raw materials affect the ecological environment and the petroleum-based materials are non-renewable. Renewable materials such as lignin, cellulose, vegetable oil, rosin, rice husk ash silica, recycled rubber, etc. have been reported to be applied in different rubber products. The rice husk silica showed similar physical and chemical properties as highly dispersible silica, and they have the same macroscopic morphology and microstructure[1]. Recycled rubber is widely used in rubber formulations[2, 3]. Modified cashew nut shell oil is not widely used in tire formulations. The main component of cashew nut shell oil after special treatment is cashew phenols, which have a phenolic hydroxyl structure with high reaction activity. The modified cashew nut oil B106 is a pure bio-based plasticizer, free of polycyclic aromatic hydrocarbons, low pour point, low viscosity, and easy to operational. This paper introduces the application of B106 and TDAE in tire formulation.

Typical PCR tire tread formula was used. Formula 1: Non-oil-filled SSBR(Tg-24.5 ℃, vinyl 63%, Styrene 21%) 75phr, BR9000 25phr, TESPT 6.4phr, TDAE 38phr, S-80 1.88phr, CBS-80 2.25phr, DPG-80 2.25phr. Formula 2: Non-oil-filled SSBR(Tg-24.5 ℃, vinyl 63%, Styrene 21%) 75phr, BR9000 25phr, TESPT 6.4phr, B106 26.6phr, S-80 1.88phr, CBS-80 2.25phr, DPG-80 2.25phr. B106 was provided by Jiangsu Cheeshine Performance Material Co. Ltd., other materials are commercially available raw materials, if not explained. The vulcanization conditions is 160℃ for 20min and curing curve conditions is 170℃ for 30min.

The scorch time and T90 time of B106 are close to that of TDAE，but the mooney viscosity was lower.

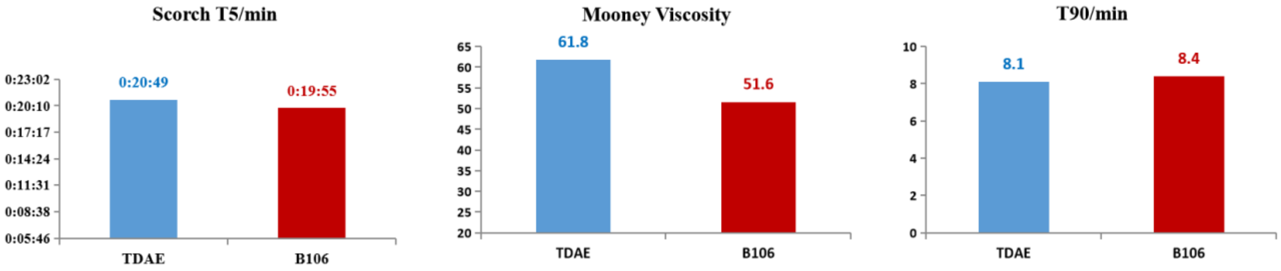

Figure 1. The comparison of processing performance

The hardness of B106 formula after reduction of usage is higher than that of TDAE. B106 formula with lower modulus at specific elongation, but has significantly increased elongation at break. After aging at 100 ℃ for 48 hours, the aging retention rate of B106 formula is close to TDAE formula.

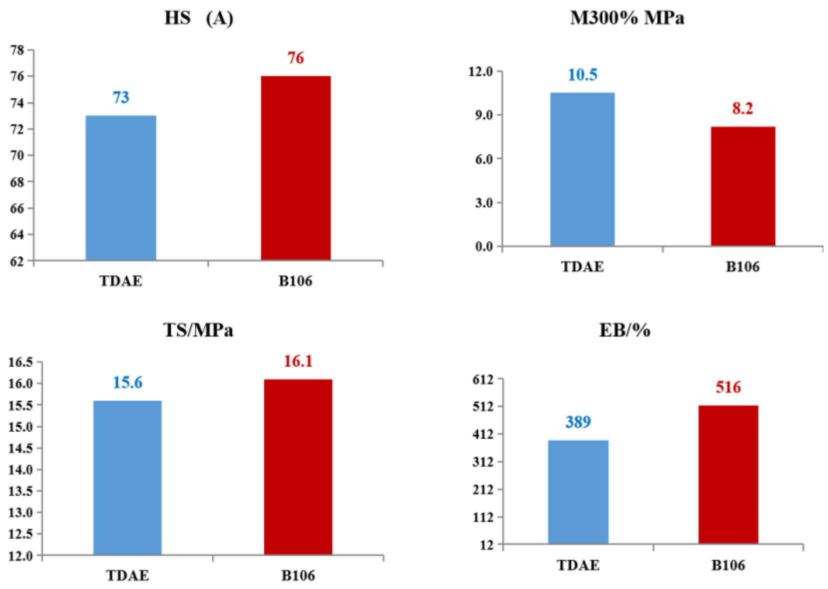

Figure 2. The comparison of physical properties

This work use modified cashew net oil B106 to replace TDAE, compared with TDAE formula, the scorch time, T90 and tensile strength of B106 formula are close to that of TDAE, but the mooney viscosity was lower. The hardness of B106 after reduction of usage is higher than that of TDAE, but has significantly increased elongation at break. B106 has lower wet-grip property but lower Tg, lower low temperature modulus and lower rolling resistance.

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Syndiotactic polystyrene based thermoplastic elastomers

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Keywords: elastomer, syndiotactic, polystyrene.

The styrene-butadiene-styrene triblock copolymer (SBS) is the largest production of thermoplastic elastomers. However, due to the relatively low *T*g of the hard segment of polystyrene in SBS (boiling water can destroy its physical cross-linking structure), resulting in a significant decrease in its tensile strength under high temperature conditions. Syndiotactic polystyrene displays a high crystallinity, a melting point of up to 270 °C, and excellent heat resistance, chemical resistance and electrical properties, making it one of the engineering plastics that can compete with polyester, nylon, and other heat-resistant engineering plastics. Introducing crystalline syndiotactic polystyrene into traditional SBS, replacing the physical cross-linking structure formed by the original glass phase with the crystalline phase of syndiotactic polystyrene, will endow the material with good thermal and chemical stability.

On the other hand, polysiloxanes possess excellent flexibility, low temperature resistance, thermal stability, and biocompatibility. Introducing them into the syndiotactic polystyrene system as intermediate flexible segments to construct harder and softer styrene block copolymers will endow the material with excellent high and low temperature resistance. Herein, we connect the end-functional syndiotactic polystrene to the polysiloxane chain segments to build new type of SBS.

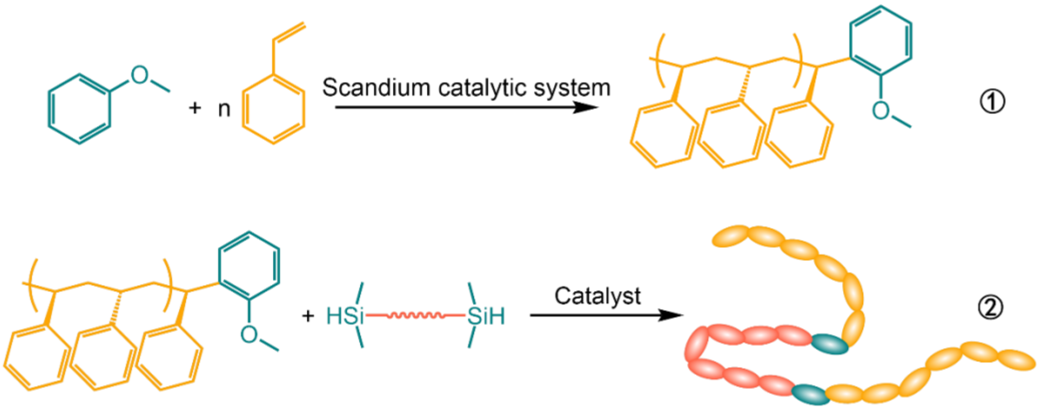

Figure 1. Preparation of polystyrene based thermoplastic elastomers using a two-step method: ① C-H activation chain transfer polymerization to prepare end-functionalized syndiotactic polystyrene ② Building SBS-type copolymers by hydrosilylation reaction .

Table 1. C-H activation chain transfer polymerization to build end-functional polystyrene

Entry	CTA	[St]/[Cat]/[Al^{i}Bu$_3$] /[CTA]	Time (h)	Conv (%)	M_n ($\times 10^3$)	M_w/M_n	T_m (°C)
1	**Anisole**	500/1/1/1	12	>99	174.9	1.64	263
2	**Anisole**	500/1/1/2	12	>99	154.2	1.51	263
2	**Anisole**	500/1/1/5	12	98	34.1	1.81	262
4	**Anisole**	500/1/1/10	12	87	24.6	1.97	262
5	**Anisole**	500/1/1/20	12	84	9.1	2.12	262

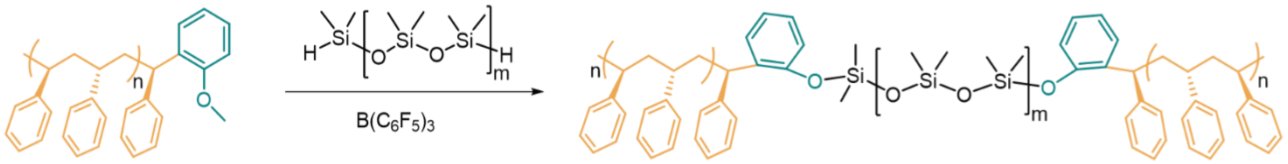

Figure 2. Building SBS-type copolymers by hydrosilylation reaction .

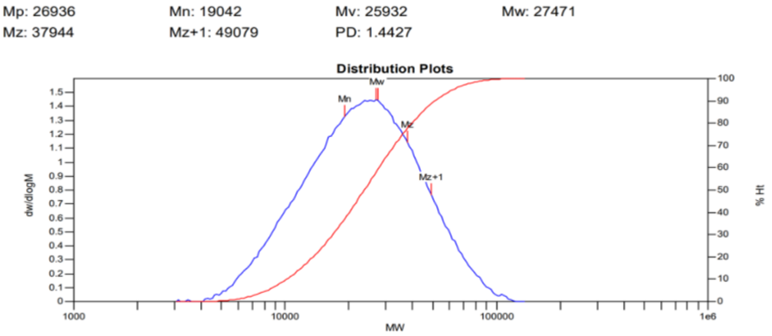

Figure 3. Single peak of molecular weigh distribution of synthesized SBS, Mn=19.0×10^3, PDI=1.44

Acknowledgement

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Characterization of silicone rubber in elastomeric vibration isolators

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Keywords: Rubber characterization, hyperelastic and viscoelastic behavior, parameter identification, elastomeric vibration isolators.

Nowadays, while the usage areas of elastomeric vibration isolators are increasing in sectors such as automotive and aerospace, it is becoming critical to model the behavior of the rubber under static and dynamic loads to provide the desired vibration isolation performance in the devices/platforms. In this study, it is explained how the characterization of the VMQ silicone rubber used in the elastomeric vibration isolator carried out under quasi-static and dynamic loads and how the constitutive models of the material are determined and the parameters of these models are obtained. To determine the hyperelastic and viscoelastic behavior of the rubber, quasi-static and dynamic tests are performed. Using the obtained test data, optimization and curve fitting studies are carried out with the help of the Fmincon solver in MATLAB® software.

There are many types of test performed to determine the hyperelastic properties of the rubber. These are uniaxial tension and compression, volumetric compression, planar shear, equi-biaxial tension and compression, pure shear, and quad lap shear test [1]. The hyperelastic constitutive model that best fits the stress-stretch curve obtained from these tests is determined and the constitutive model parameters are obtained. Within the scope of this study, data obtained from uniaxial tensile test and equi-biaxial tensile test are used simultaneously to obtain the hyperelastic constitutive model parameters. The 3-Parameter (3P) Yeoh model, one of the invariant based hyperelastic constitutive models, is used in the optimization and curve fitting study. Then, the hyperelastic behavior is modeled analytically with the constitutive model that adapts to both deformation modes. The strain energy density function of the 3P Yeoh model can be formulated as given in Eq.1 [2]:

$$W = C_{10}(I_1 - 3) + C_{20}(I_1 - 3)^2 + C_{30}(I_1 - 3)^3 \tag{1}$$

Creep, stress relaxation, and Dynamic Mechanical Analysis (DMA) tests are performed to determine the viscoelastic properties of the rubber. Tests are performed in DMA to determine the viscoelastic behavior of the rubber, depending on temperature, frequency and dynamic amplitude.

Viscoelastic rheological model is expressed as a function of time or frequency and obtained by using different combinations of linear elastic and viscous part in series or parallel [3]. While the Maxwell Model, one of the viscoelastic rheological models, is used with the data obtained from stress relaxation test, the Kelvin-Voight viscoelastic rheological model is used with the data obtained from the creep test [4]. In this study, Generalized Maxwell Model (GMM) is used to model the viscoelastic behavior of the rubber [5,6].

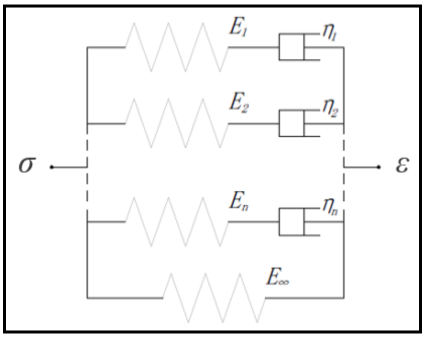

Figure 1. Generalized Maxwell Model (GMM) [5,6]

Frequency sweep tests are carried out at nine temperatures: -50, -25, 0, 25, 50, 75, 100, 125, and 150°C, with an amplitude of 60 µm and frequency range of 0-50 Hz. The frequency-dependent storage modulus and loss modulus of the material can be formulated as given in Eq.2 and Eq.3 [6]:

$$E'(\omega) = E_\infty + \sum_{n=1}^{N} \frac{\omega^2 E_n \tau_n^2}{1+\omega^2\tau_n^2} \tag{2}$$

$$E''(\omega) = \sum_{n=1}^{N} \frac{\omega E_n \tau_n^2}{1+\omega^2\tau_n^2} \tag{3}$$

As a result of the study, hyperelastic and viscoelastic constitutive models of the VMQ silicone rubber are determined and model parameters that would provide input to finite element analysis are obtained. It has been shown that the hyperelastic characteristic of the rubber is compatible with the 3P Yeoh Model, and the viscoelastic characteristic is compatible with the GMM. Following this study, an elastomeric vibration isolator with the device can be analyzed using the Finite Element Method and the optimum elastomeric vibration isolator design can be completed, which ensures that the device remains within the vibration envelope specified in the design requirements.

Acknowledgement

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Sustainable Lightweight Biocomposites derived from Biobased Thermoplastic Polyurethane Reinforced with Nanosized Biochar

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Keywords: Bio-based TPU; Biochar; Ball-Mill.

Environmental considerations along with the technological challenges have led to search for green and energy-efficient processes for advanced manufacturing of materials. In this aspect, the strive for utilization of green fillers in polymer composite has increased focus on application of natural biomass-based fillers. In line with this, Biochar has garnered a lot of attention as a filler material and has the potential to replace conventionally used inorganic mineral fillers. However, aggregation and heterogeneous dispersion of biochar due to its nonuniform micro/macro size distribution limits its reinforcing capability. [1-3] Therefore, in this work a green method has been adopted to prepare nano-sized biochar as a better reinforcement using a planetary ball mill and the ball milled-biochar has been melt-blended with a biobased thermoplastic polyurethane (TPU) for the fabrication of bio-nanocomposite. The effect of the addition of ball-milled biochar on the melting temperature and crystallinity of biobased-TPU nanocomposites was analyzed by differential scanning calorimetry (DSC). A significant enhancement in the mechanical properties for TPU/Ball-milled-biochar composites was observed compared to TPU/Biochar composites. Further, Electrical and thermal conductivity, thermal stability of the prepared TPU/Ball-milled biochar bio-nanocomposite were investigated together with the characterisation of ball-milled biochar using various techniques like XRD, Raman, XPS and scanning electron microscopy (SEM) imaging etc. As biochar is highly cost-effective, the proposed biobased-polymer nanocomposites could become a valid substitute for non-biodegradable nanocomposites in various applications.

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Malaysian Rubber Industry Initiatives Towards EUDR Compliance

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Keywords: Natural Rubber; Sustainability; Regulatory framework; Deforestation.

EU Regulation on Deforestation-free Products (EUDR) is a legislation in European Union nations, designed to establish new regulations with the aim of reducing the effects of deforestation and agricultural practices on sustainability, globally. This new rule emphasised in EUDR is regarding deforestation and intends to guarantee that goods and products imported into the European Union (EU) originate from sustainable sources and are not a consequence of deforestation and forest degradation. The cut-off date for deforestation and forest degradation under this new law is 31st of December 2020 and it came into force on 29th June 2023, directly repealing the EU Timber Regulation (EUTR). EUDR prioritises due diligence, requiring traders and operators to gather information on the geographical coordinates of the land plots where the commodity was produced, as specified in Article 9. Consequently, the Malaysian Rubber Board (MRB) has developed the Malaysian Sustainable Natural Rubber (MSNR) regulatory framework to recognise locally produced natural rubber as sustainable. The MSNR regulatory framework will be implemented under the MRB Act 1996 (Act 551), which gave the MRB the authority to recognise and certify the sustainability of locally produced natural rubber. This means, only the MRB is authorised to assess and recognise if rubber production in Malaysia complies with sustainability principles outlined by the MSNR Standard Operation Procedure. The MSNR incorporates five key principles: no deforestation for rubber cultivation, rubber cultivation regulated by national land law, environmental sustainability, social compliance, and supply chain traceability. MSNR is EUDR compatible, where the cut-off date for deforestation in Principle 1 of MSNR, i.e., no deforestation for rubber cultivation, has been set to the same cut-off date as EUDR. Principle 5 of MSNR, also known as supply chain traceability, is crucial in ensuring transparency and accountability mandates the recording of the geographic coordinates of the land plots where the relevant natural rubber production occurred, in accordance with the EUDR. For instance, when recording rubber hectares larger than 4 hectares, it is necessary to record a minimum of 4 geographic coordinates. The EUDR-operated country benchmarking system and the criteria for identifying the risk status of countries or parts thereof are defined in Article 29 of the Regulation. The EU Commission will determine Malaysia's country benchmarking under EUDR based on the risk of deforestation in the country. The unique nature of the Malaysian rubber industry lies in its ability to produce a variety of products using either imported or locally sourced raw materials. Thus, country profiling should consider various aspects related to the environmental and economic sustainability of its industries. The profiling of the Malaysian rubber industry is quite complex, given that the primary product exported to the EU is NR gloves; however, the raw materials are primarily sourced from Thailand. Thus, the risk is associated with Thailand benchmarking.

The MSNR compliance pilot study was conducted from 6th November 2023 to 26th April 2024. A total of 2,381 smallholders were surveyed for compliance with MSNR in four locations: Bentong, Pahang, Felda Teloi Timur, Kedah, Serian, Sarawak and Tuaran, Sabah which involved a total of

5,780.66 hectares of rubber areas. The ArcGis123 application marked the detailed location of each smallholder's rubber plantation polygon in Figure 1 during the MSNR Compliance Pilot Study. From the survey, 99.8% of smallholders adhere to MSNR, whereas only 0.1% do not comply as of 26th April 2024. This finding suggests that a significant proportion of rubber plantations in Malaysia adhere to sustainability standards and expectations for responsible sourcing of natural rubber. Such a substantial compliance rate indicates that Malaysia has successfully enforced measures and regulations aimed at promoting sustainable practices in the rubber sector. This could potentially facilitate Malaysian rubber products' entry into markets, particularly where sustainability is a significant concern for both consumers and businesses.

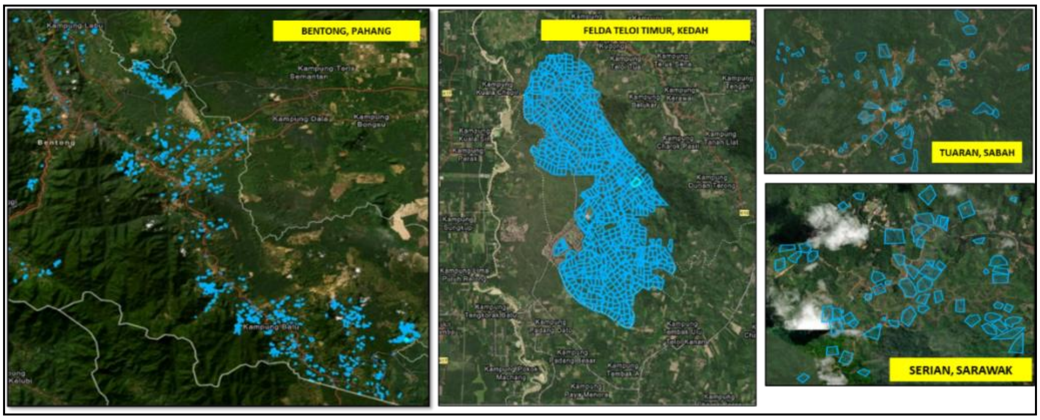

Figure 1. Polygon mapping of smallholder rubber plantations in selected four locations, identified using ArcGIS technology with survey data collected from 6th November 2023 to 26th April 2024.

Acknowledgement

I express our gratitude to the members of the MRB Board for providing funding to conduct the MSNR pilot study. I would like to express my gratitude to Dato' Dr. Zairossani Mohd Nor for his unwavering support, guidance, valuable comments and insightful recommendations throughout the duration of this project. Additionally, I would like to extend my heartfelt appreciation to the MRB Sustainability Taskforce team for our collective work and cooperative endeavour in gathering and analysing data. I would like to express my gratitude to the MRB enumerators for their active involvement and commitment in the study.

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Tyre emissions from battery electric vehicles: effects on wear rates and toxicity

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Keywords: Tyre wear; emissions; Euro 7; 6PPD.

Should we be worried about the additional tyre emissions that will come from our shift to battery electric vehicles, with their greater mass and torque? Concern has been growing in recent years about the environmental effect of tyre emissions since a preservative in tyres was linked to the mass die-off of coho salmon in the USA. Experiments by multiple organisations, including Emissions Analytics, has shown that increased weight due to a vehicle battery can lead to an increase of 20% or more in tyre mass emissions. However, this is not the whole story, as greater wear in terms of mass emissions, does not necessarily correlate with greater toxicity, tyre companies are innovating with new tyre formulations to carry the extra weight, and mitigations such as torque control can be implemented by the vehicle manufacturers.

This presentation will bring together original test results from Emissions Analytics on the links between tyre mass emissions and toxicity, placed in the context of the latest ‘EV specialist’ tyre models that have been brought to market. This will draw on Emissions Analytics’ innovative benchmarking database from its independent EQUA test programme that measures tyre emissions in real-world conditions and performs chemical analysis on a wide range of tyres on the market.

The headline findings are that the switch the electric vehicle creates a material risk of higher wear and greater toxicity, but this does not have to be the outcome if industry and regulators establish an effective framework for evaluating tyre emissions. These findings will be used to interpret the likely effects of the proposed Euro 7 regulations as well as the California 6PPD rule.

Celanese™ Vamac® : A reliable and sustainable elastomeric material for automotive applications

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Keywords: High-temperature resistant, Low-temperature flexibility, Pfas solution.

Vamac® ethylene acrylic elastomer (AEM) was introduced in 1975 and has been successfully used for many years in automotive applications where excellent resistance to heat, engine fluids, and low temperature flexibility is required. An update on Vamac's supply situation will be given. Necessary measures have been taken in the recent years to improve productivity and capacity significantly to allow our customers to continue developing solutions for new challenging applications like in E-Mobility, where AEM allows an interesting and broad variety of compounding possibilities to meet most new requirements.

Vamac is free of substances challenged by the ECHA's PFAS proposal and can be considered an alternative for FKM in applications where no resistance to direct, intense contact with solvent / fuel or extreme heat above 1008h at 175°C is required. The Vamac HyPR 5000 series pre-compounds would be a unique offering in sealing applications with a 10-15°C higher heat resistance over conventional carbon black filled AEM compounds. Sustainability is finally a topic with high priority. Results with recycled compounding ingredients and renewable, bio-sourced materials are presented that might support our customers to reduce the CO2 footprint for AEM compounds.

An overview of the above topics will be given, highlighting that Vamac remains a key candidate for future demanding applications.

An alternative to Hevea Brasiliensis Natural Rubber: Taraxacaum kok-saghyz (TKS)-Dandelion Rubber

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Keywords: Taraxacum kok-saghyz (TKS); natural rubber (NR); dandelion; mechanical properties

Natural rubber (NR) obtained from *Hevea Brasiliensis* (abbreviated as HB-NR) is widely used in fields such as automotive industry, railway and aviation applications. Currently, the production and development of natural rubber worldwide are facing numerous challenges [1-2]. Consequently, the increasing global demand for rubber and the environmental impacts of traditional rubber production necessitate the exploration of sustainable and renewable resources. At present, more than 2.500 plant species capable of biosynthesizing natural rubber have been reported globally. However, most of these are not commercially viable. TKS rubber comes from a plant called *Taraxacum kok-saghyz (TKS)*, which contains rubber mainly distributed in its roots. TKS rubber has a chemical structure similar to HB-NR, with cis-1,4-polyisoprene as its main component. Therefore, TKS rubber is an important alternative source to natural rubber latex. Extracting rubber from TKS with high quality, low cost, and low pollution is also commercially significant [3].

In this study, firstly, the TKS rubber samples obtained from the European supplier were characterized. To determine the viscosity of the samples, Mooney viscosity testing was performed; to understand the composition, Fourier Transform Infrared Spectrophotometry (FTIR) was utilized; and to characterize the molecular weight and distribution of the composition structures, GPC-SEC testing was conducted. The Mooney viscosity results are presented in Table 1. The TKS rubber samples showed lower Mooney viscosity compared to the HB-NR sample.

Table 1. Mooney viscosity test results

Unit	HB-NR	230318_B	230308_Ac_3	230308_2
Mooney Test ML (1+4) MU	60.8	20.6	19.6	20

When the FTIR spectra of the TKS rubber samples were examined, it was observed that the chemical structure of TKS is the same as HB-NR. Additionally, the GPC-SEC results indicated that the TKS samples have a relatively lower molecular weight compared to the HB-NR. The characteristics of the main polymer, as well as the type and amount of filler material, significantly effect the mechanical and dynamic properties of the final product. The compounds including HB-NR and TKS rubber were mixed by using laboratory scale mixer separately. The formulations of the prepared compounds are presented in Table 2.

Table 2. Compound formulations

Components [phr]	**Sample notations**	
	HB-NR	**TKS Rubber**
SVR 10	100	-
TKS Rubber	-	100
Zinc Oxide	5.0	5.0
Stearic Acid	1.5	1.5
Antioxidant	2.0	2.0
Carbon Black	70.0	70.0
Antiozonants	2.0	2.0
Processing Promoters	2.0	2.0
Antioxidant	1.0	1.0
TOTAL	183.5	183.5
Vulcanization Systems	2.8 1.66	2.8 1.66

Phr: Parts per hundred rubber

When the rheological properties of the two compounds were examined, it was observed that curing properties as ts2 (scorch time) and t90 (optimum cure time) were similar, but there were some differences in the mechanical properties. It was observed that the hardness was the same in both compounds. The tensile strength was lower in the TKS rubber compound compared to the HB-NR compound. It was observed in dynamic testing, tanδ value was higher in the TKS rubber compound in comparison to HB-NR compound. The dynamic properties of the samples were analysed by DMA (Dynamic Mechanical Analyser) frequency sweep test. In addition, the effects of TKS Rubber on other mechanical properties were examined through Stress Relaxation and Compression Set tests.

Table 3. Mechanical properties of compounds

	HB-NR	**TKS Rubber**
Tensile Strength (Mpa)	22.4	16.2
Elongation at Break (%)	502	521
Tand @3 Hz (unitless)	0.204	0.311
Dynamic Stiffness @3 Hz (N/m)	1.72E+05	1.74E+05

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AFM Nanomechanics on Filled Rubbers

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Keywords: atomic force microscope; Mullins effect; stress network; nanorheology.

Atomic force microscope (AFM)-based nanomechanics [1] is a powerful tool to investigate a wide variety of topics in rubber science and technology, which gives maps of Young's modulus, adhesion *etc.* at nano-scale resolution. The authors have been devoted themselves to developing the method and applying it to various problems, some of which will be reviewed in this presentation as described below.

For a long time, it has been difficult to reach a consensus on the physical origin of the "Mullins effect" because of the limited capabilities for visualizing microscopic structures. This work investigates the microscopic mechanism of the Mullins effect in carbon black (CB)-filled styrene-butadiene rubber (SBR) after application of cyclic uniaxial tension [2]. The stress-softening behavior of CB/SBR was directly observed at the nanoscale as shown in **Figure 1**. The rubber matrix and interfacial region exhibit different softening behaviors at different elongations, which provides insight into the microscopic mechanism of the Mullins effect.

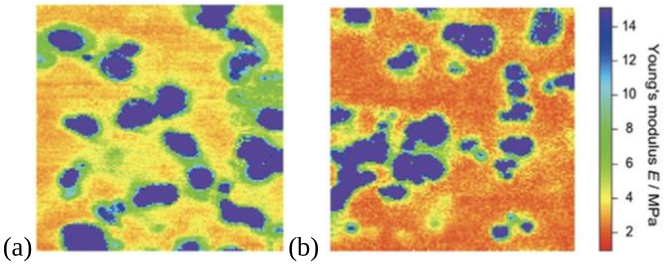

Figure 1. Young's modulus mappings for 10 vol % CB/SBR of (a) the original and (b) the sample after 250% stretching. The scan size was 1.0 μm.

Furthermore, an in-situ AFM nanomechanical technique was used to directly visualize the micromechanical behaviors of CB/isoprene rubber (IR) during compressive strain [3]. We found that CB/IR exhibited heterogeneous local microscopic deformations as shown in **Figure 2**, which were related to the dispersion of CB particles in IR matrices. The local stress distributions of the rubber composites showed heterogeneity, and the stresses were concentrated in the regions near the CB particles during compression. The area of stress concentration gradually expanded with increasing strain and eventually formed a stress network structure. This stress network bore most of the macroscopic stress and was considered the key reinforcement mechanism of CB-filled rubber. Based on the image data from the AFM experiments, we also used finite-element method (FEM) simulations to reproduce the microscopic deformation process of CB/IR.

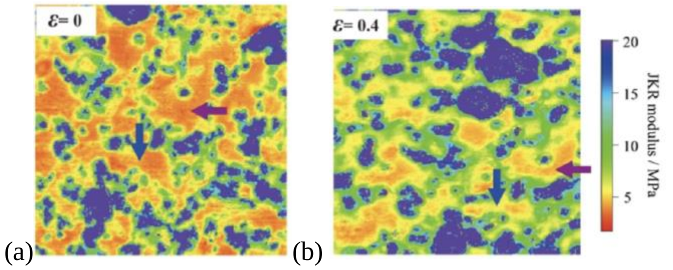

Figure 2. In situ AFM JKR modulus images of CB-filled IR at macroscopic compressive strains (a) ε = 0 and (b) 0.4. The scan size is 3.0 μm.

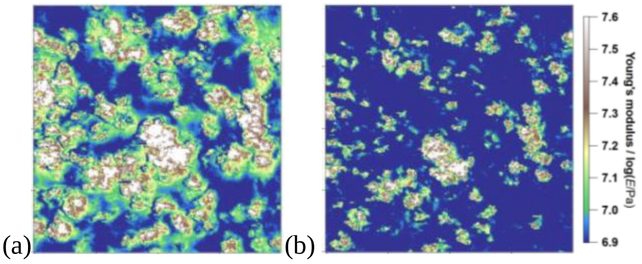

Figure 3. Young's modulus images of silica-filled SBR at (a) 35°C and (b) 65°C. The scan size is 2.0 μm.

The temperature effect on filler reinforcement is of great importance. This study focuses on the temperature dependence of the Young's modulus of silica-filled SBR and aims to elucidate the reinforcing mechanism at the nanoscale. The elastic modulus images of the samples at 25°C-75°C were obtained as shown in **Figure 3**. It was observed that an overall decrease in modulus of elasticity occurred with increasing temperature. It was also found that the loosely bound rubber (LBR) phase, which interacts weakly with silica, was present at 35°C but almost disappeared at 65°C. Thus, it can be inferred that the decrease in the macroscopic elasticity of this specimen with increasing temperature is due to the decrease in the volume fraction of the LBR phase.

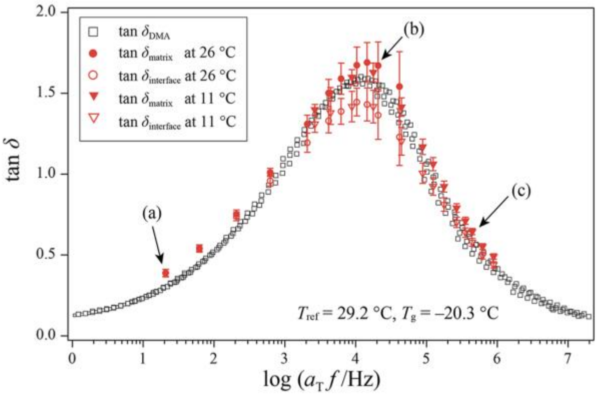

Figure 4. Frequency dependence of loss tangent separated into matrix and interfaaial rubber regions. Open symbols indicate matrix rubber region and closed symbols interfacial rubber region. The bulk loss tangent is also superimposed.

Nanorheological AFM is a measurement technique that maps dynamic viscoelasticity with nanoscale spatial resolution [4]. The technique combines dynamic measurements with quasi-static force curve measurements, allowing quantification of the contact area using a theoretical model of contact elasticity and, therefore, the dynamic modulus. We applied this technique to silica-filled SBR to investigate the nature of the interfacial rubber region [5]. The master curve obtained by this technique perfectly coincided with that by bulk DMA. Furthermore, it was found that the behaviour of bulk loss tangent could be predicted by the contributions from both matrix and interfacial rubber regions as shown in **Figure 4**. We also found that the glass-rubber transition does not occur uniformly but inhomogeneously depending on spatially heterogeneous polymer segmental dynamics.

Acknowledgement

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The Effect of Smear Wear Layer on Wear Performance of Tyre Tread Compounds

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Keywords: Rubber Abrasion; Smear Wear; Tyre Wear Performance.

Rubber wear is typically categorised into three different processes known as abrasive wear, fatigue wear, and smear wear. The mechanisms of the abrasive and fatigue wear have been extensively studied in the past [1,2]. There are much fewer reports into the smear wear mechanism. It is known that a smear wear layer which is a “sticky” degraded layer of rubber can be observed on the rubber surface when smear wear occurs [3,4]. However, the effect of smear wear layer on wear performance has not been fully elucidated. The aim of this study is to investigate how the smear wear layer influences wear resistance of tyre tread compounds and to understand the generation and removal process of the layer during rubber abrasion.

Six different tyre tread formulations were investigated, two were synthetic polyisoprene rubber (IR) compounds and four were styrene butadiene rubber (SBR) compounds as presented in Table 1. A blade abrasion machine (Figure 1(a)) was used to form a smear wear layer on the rubber wheel [3,4]. The thickness of the smear wear layer was calculated based on the weight loss before and after solvent wiping of the rubber surface. Surface abrasion (Figure 1(b)) tests were performed to evaluate the effect of the smear wear layer on total wear rate using the samples on which smear wear layer has previously been formed before the measurement using a blade abrasion machine. Surface abrasion was also used to investigate the removal process of the smear wear layer as well as the effect of adding drying powder on a silicon carbide grinding block. Additional, LAT100 (Figure 1(c)) measurements were performed with different rates of powder supply to also evaluate the smear wear layer removal process.

Table 1. Sample compositions

Compound	Polymer	Filler
IRN220	IR	70phr N220
IRVN3	IR	65phr Ultrasil VN3 + 5phr N220
SBRN220	SBR	70phr N220
SBRVN3	SBR	65phr Ultrasil VN3 + 5phr N220
SBRN134	SBR	70phr N134
SBR9100GR	SBR	65phr Ultrasil 9100GR + 5phr N220

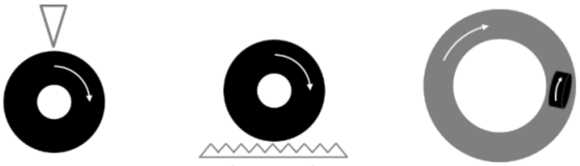
(a) Blade Abrasion (b) Surface Abrasion (c) LAT100

Figure 1. Schematic of wear measurement machines

Figure 2 shows the total wear rate as a function of smear wear layer thickness. The wear rate decreased with increasing smear wear thickness below 6 µm, indicating that a thin smear wear layer works as a protective layer while in contact with the road surface. On the other hand, above 6 µm, the wear rate increased with an increase in the smear wear thickness. This means that the degraded physically weak smear wear layer is more easily peeled off at a higher thickness.

Figure 3 shows LAT100 results which were obtained by changing the rate of drying powder supply. Under the “no powder” condition, the sample surface was “sticky” meaning that a smear wear layer was formed on the surface during the measurement. Supplying powder during the measurement, greatly increased the wear rate. The powder was attached on the sample surface and the surface was not “sticky”. This indicated that the smear wear layer was removed by interacting with powder resulting in an increase of total wear rate. In real tyre operating conditions, there are typically some sand particles present on the road. Therefore, in order to elucidate the effect of the smear wear layer on wear resistance, it is important to understand the balance between the smear layer generation rate and the smear wear layer removal rate. Based on these results, tyre wear performance could be improved by decreasing smear wear layer generation rate, while leaving a certain amount of smear wear layer on tyre surfaces.

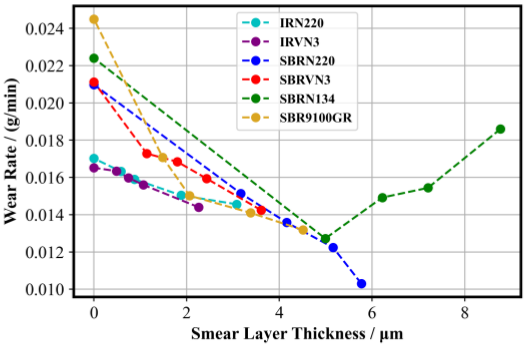

Figure 2. Effect of smear wear layer thickness on wear rate

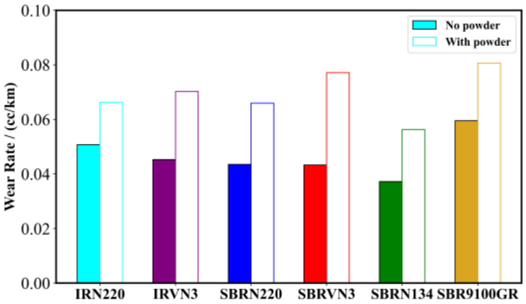

Figure 3. Influence of powder on wear rate measured by LAT100

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Evaluating the Impact of Crosslinker Amount and Pre-Strain Level on the Electromechanical Characteristics and 3D Printing Potential of Functionalized Liquid Isoprene Rubber Dielectric Elastomer Actuators

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Keywords: Dielectric elastomer actuator, HRMAS NMR spectroscopy, interactive fiber rubber composites, and 3D printing of elastomers.

Liquid rubbers are promising for dielectric elastomer actuators due to their adjustable mechanical, dynamic, and dielectric properties. In this study, we developed a dielectric elastomer from a cross-linkable functionalized liquid rubber and examined its electromechanical performance by varying compositions and pre-strain levels. Liquid isoprene rubber (LIR) was crosslinked through esterification reactions with a crosslinker, verified by high-resolution magic angle spinning nuclear magnetic resonance (HRMAS NMR) spectroscopy. Surface morphology was analyzed using scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX). We tested the bending deformation characteristics of LIR-based shape memory alloy incorporated interactive fiber rubber composites. The 3D printability of the developed LIR system was optimized via direct ink writing. The new isoprene elastomer is soft, resilient, and adaptable, offering a wide range of stiffness and strains through network adjustments, making it an attractive material for soft actuators and robotics applications [1-2].

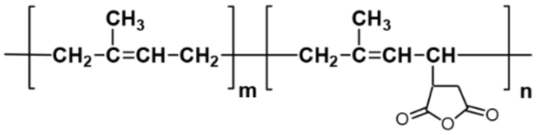

Figure 1. Chemical structure of functionalized liquid isoprene rubber

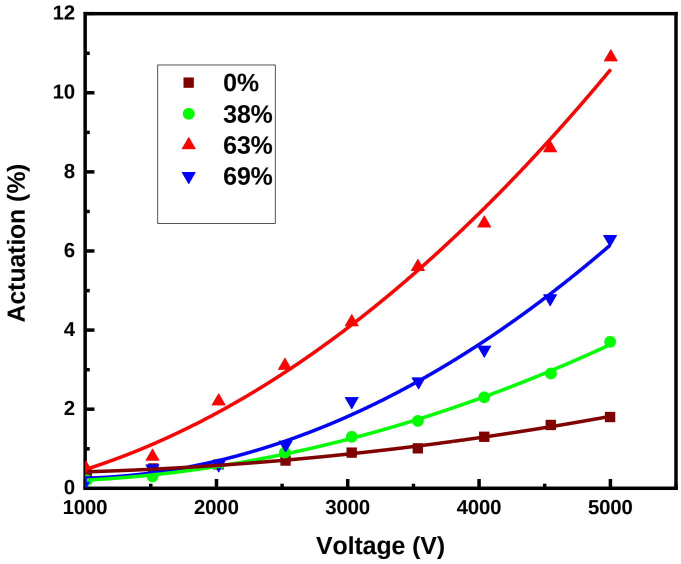

Figure 2. Effect of pre-strain on actuation performance of LIR

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The study on the correlation distance of aggregate of silica in SBR using time-resolved ultra-small angle X-ray scattering

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Keywords: X-ray scattering, correlation distance, silica, SBR.

Introduction

Addition of filler to rubber results in the improvement of the mechanical properties in the rubber/filler systems. The rubber/filler systems have been used widely in our daily life, such as tires, rubber insulators, and so on. Especially, the car tire is famous production used this system. Recently, from the viewpoint of the environmental problems and the depletion of fossil fuel resources, the high performance of tire is required. To achieve higher performance, it is important to investigate the relationship between the dispersion of filler in the rubber/filler system and the improvement of the mechanical properties.

To investigate the dispersion of fille, scattering techniques is useful. Takenaka [1] reported the various scattering methods in detail. X-ray and neutron scattering are widely used to investigate the filler structure in the rubber/filler system. By using various scattering methods, the filler structure can be observed over a wide range of length scales. In the previous studies, Koga et al. [2,3] investigated the dispersion of carbon black (CB) in Styrene Butadiene Rubber (SBR) systems using combined scattering method, including ultra small angle neutron scattering (USANS), ultra small angle x-ray scattering (USAXS) and small angle x-ray scattering (SAXS). They successfully combined USANS, USAXS and SAXS data and found that the filler consists of the hierarchical structure. “Aggregate” comprise approximately nine fused primary CB particles and “agglomerate” formed by the aggregate with mass fractal dimension. Moreover, they analyzed the size of aggregate and agglomerate, the surface dimension of the primary CB particles and the mass-fractal dimension quantitatively by using the theoretical scattering profile expressed by unified Guinier/power-law equations [4,5,6].

In this study, we focus on the correlation distance of aggregate of silica in SBR. The correlation distance of aggregate can be estimated by a polydisperse Born-Green Approximation (PBG) [7]. Using this method, the correlation distance of aggregate is obtained from the USAXS profiles and the relationship between the correlation distance of aggregate in SBR and the mechanical properties is investigated. In addition, we investigate the change with the correlation distance of aggregate of silica in SBR under uniaxial elongation by using in-situ USAXS.

Experimental

The rubber, which we used in this study, is Styrene-Butadiene Rubber (SBR, weight average molecular weight M_w = 500,000), and the filler is silica. To investigate the effect of silane coupling agent, we prepared two samples, which contain and don’t contain silane coupling agent (CA). Silica contents are 5,10,15,20,25 vol% and the weight fraction of the silane coupling agent is 8% of silica weight. These samples were prepared by using Banbury mixer. Oscillatory uniaxial elongation is imposed to the samples. Maximum strain is 100%, Frequency is 1.0Hz. X-ray experiment was conducted at BL03XU, SPring-8, JAPAN to experiment in-situ under uniaxial elongation.

Results and Discussion

From the 2D scattering image obtained at ultra-small angle X-ray scattering, circular averaging was performed to obtain a 1D scattering profile. PBG analysis was performed on the profile to estimate the correlation distance $\langle\xi\rangle_{PBG}$ and its standard deviation σ. Figure 1 shows the $\langle\xi\rangle_{PBG}$ and σ of SBR/silica (a) with and (b) without silane coupling agent to the amount of silica added. The results show that both the $\langle\xi\rangle_{PBG}$ and σ decreased as the amount of silica added increased. This indicates that the inter-aggregate distance became smaller as the amount of silica added increased, because the silica became denser. This trend is similar even without silane coupling agent.

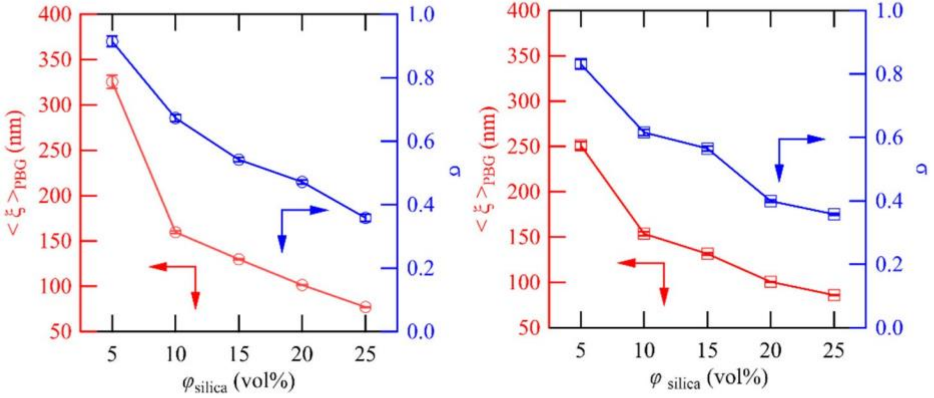

Figure 1. the correlation distance $\langle\xi\rangle_{PBG}$ and its standard devation σ of SBR/silica (a) with and (b) without silane coupling agent as a function of silica contents.

Figure 2 show that the change of $\langle\xi\rangle_{PBG}$ of parrallel and perpendicular direction under uniaxial elongation. When cyclic deformation is applied, the $\langle\xi\rangle_{PBG}$ also changes in a cyclic manner with and without silane coupling agent. In addition, the sample with silane coupling agenet also shows a larger change. By comparing these results with mechanical properties, the correlation between structure and properties was further discussed. The detailed results will be presented on the day of the presentation.

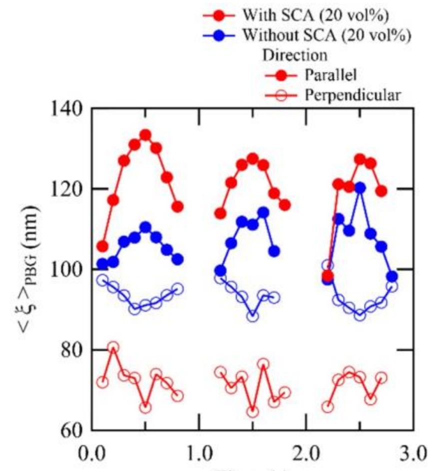

Figure 2. The change of $\langle\xi\rangle_{PBG}$ of SBR/silica with and without silane coupling agent as a function of time.

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Evaluating the effects of carbon black surface functionality on tyre tread performance

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Keywords: carbon black surface functionality; polymer-filler interaction; energy dissipation; tyre tread performance

The technique to control the polymer-filler interaction is the most factor for tyre tread compounds in solving the trade-off between rolling resistance, wet grip and wear properties. The formulation of tyre treads focuses on the interaction between fillers and elastomers. Carbon black and silica [1] are currently used for passenger tyre tread compounds as reinforcing fillers. The utilisation of a silane coupling agent in silica tyres [2] can enhance the polymer-filler interaction in rubber, as well as improve tyre tread performance, notably in terms of rolling resistance and wet grip properties. This work aims to elucidate the effects of carbon black with different surface chemistry when incorporated into natural rubber. The carbon blacks N234 with three different surface treatments, graphitised, oxidised and non-modified were prepared. The graphitised N234 was prepared by deactivating the surface functionality through a 1500°C heat treatment process, and the oxidised N234 enhanced surface activity via a chemical oxidation process. Each compound the viscoelastic properties and abrasion resistance were measured using the dynamic mechanical tester and the laboratory wear tester, respectively.

This is an important finding to help understand the viscoelastic properties through the polymer-filler interactions. Figure 1 shows the loss modulus (E") of rubber at 0°C and tan δ at 60°C for each rubber. The loss modulus at 0°C, represents the wet grip properties; at 0.1-1.0 % strain, the result shows that graphitised N234 exhibits the highest value, followed by the non-modified N234, half oxidised N234, while full oxidised N234 shows the lowest. This result indicates that the filler-filler interaction decreases with the increase in filler surface functionality [3]. The similarity is that the phenomenon of tan δ at 60°C represents the rolling resistance of tyre tread performance. This loss of energy should be the lowest possible value. Hence, the fully oxidised N234 shows the best rolling resistance.

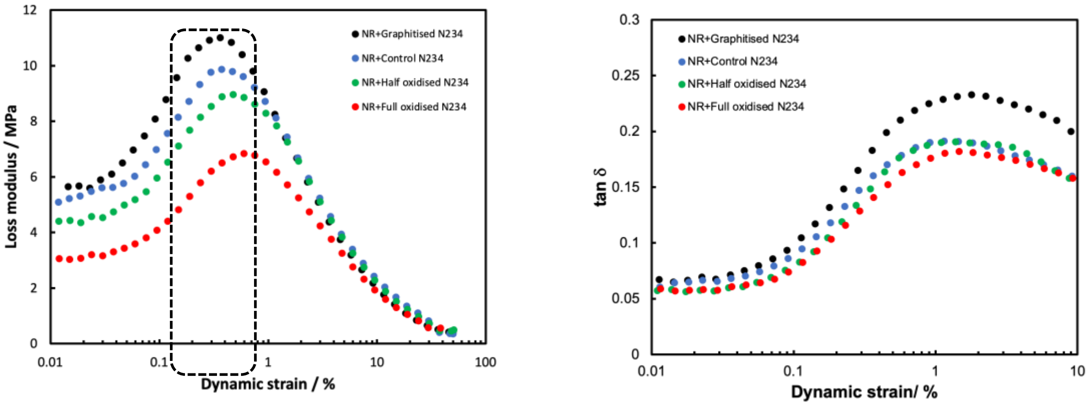

Figure 1. Loss modulus (E") at 0°C (left) and tan δ at 60°C (right) of rubber with strain sweep.

This can be associated with the filler-polymer interaction controlled by the surface treatment of fillers. The deactivated surface functionality, as represented by the graphitised N234, can reduce the filler-polymer interaction and get the highest energy dissipation. On the other hand, the activated surface functionality, as represented by the half and full oxidised N234, can enhance the filler-polymer interactions and give the lowest energy dissipation.

Figure 2 shows the magic triangle of tyre tread rubber compounds, it was also found that rolling resistance efficiency and wear resistance increase with increasing the filler surface functionality, which can be represented by the oxidised N234. On the other hand, the deactivated filler, represented by graphitised N234, can be ranked from the laboratory test results, which show the best results for wet grip properties.

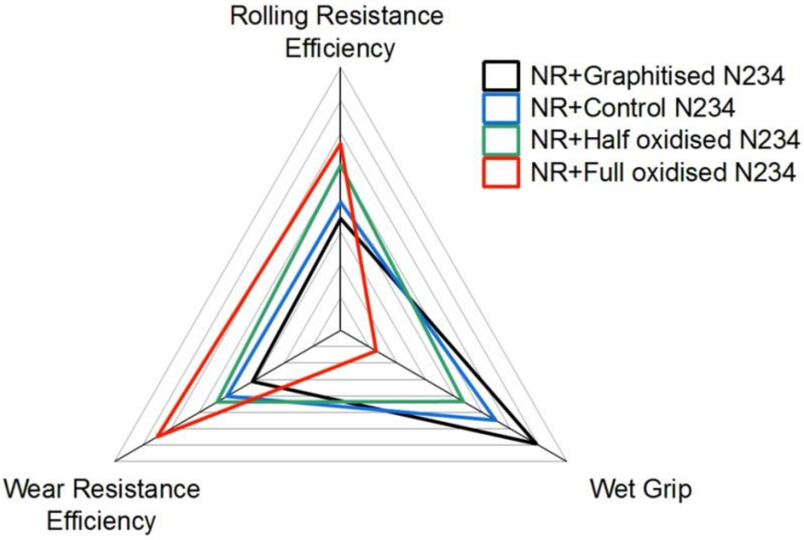

Figure 2. Magic triangle of rubber with carbon black with different surface functionality

Next generation fillers will have to exhibit both sets of properties to enhance the magic triangle further.

Acknowledgement

The authors would like to thank the Royal Thai Government for supporting student scholarships and Birla Carbon for contributing materials.

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Sustainable Solutions for Rubber Crosslinking

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Keywords: rubber crosslinking, sustainability, Rhenocure®.

The search for sustainable alternatives to replace today's fossil-based compounds is progressing rapidly. Currently, it is possible to work with several 'green' rubbers, fillers and oils. However, the pressure on the last 4-10% of a typical recipe, which includes antioxidants and the crosslinking system, is increasing.

Even before the recent societal push for sustainable solutions in all aspects of life, LANXESS was already developing alternatives to replace known hazardous chemicals.

A group of chemicals which back in the day was “repurposed” to serve the search for nitrosamine free crosslinking was the Dithiophosphates. Combined with amines for an extra kick or zinc or as complexes of both they serve today as one of the choices for accelerators in sulfur crosslinked applications.

A new chemical recently patented by LANXESS for the use in diverse rubber applications is Polyethyleneimine. Under its brand name Rhenocure® DR/S this is a new crosslinker and versatile secondary accelerator for different types of rubbers.

In NR based compounds[i] Rhenocure® DR/S offers all the advantages of a secondary accelerator such as concentration dependent reduction of incubation time, sharpening of the vulcanization onset and little to no influence on crosslink density. At the same time, DMA measurements show that it also influences dynamic damping properties probably by improving carbon black dispersion.

A further use of Rhenocure® DR/S is in crosslinking of acrylate rubbers. In focus are HT-ACM types [ii] which have the carboxyl crosslinking group and are typically crosslinked by hexamethylene diamine [iii]. Rhenocure® DR/S can cure HT-ACM alone, without the need for any accelerator.

Ethylene/Acrylic terpolymers (AEM) can also exhibit a carboxyl crosslinking group as described in [ii]. In a similar way as seen in the previous section, this group can be exploited by Rhenocure® DR/S either as accelerator or to initiate crosslinks. A concentration of 3 phr DR/S was sufficient for cured compound to reach the torque level of HMDC+DOTG, which is quite remarkable. Onset of cure is faster than the reference as well. Similar to HT-ACM, AEM compounds can also be cured by Rhenocure® DR/S alone. Care must be taken due to the high reactivity which can induce scorch.

Initially developed as a secondary accelerator and replacement for guanidines in carbon black filled natural rubber compounds, it has also found its place with polyacrylates and ethylene acrylic polymers. Furthermore, its use in combination with white fillers and coupling agents is still under research and shows very promising results.

The aim of this contribution is to show an overview of the use of dithiophosphates in nitrosamine free sulfur crosslinking and to focus on the introduction of Rhenocure® DR/S by showcasing its many advantages such acceleration of sulfur vulcanization, crosslinking and acceleration of carboxyl modified ethylene acrylic and acrylic copolymers and last and foremost, activation of silanization reaction in silica filled rubber compounds. This all will be portrayed in the bigger picture of LANXESS' initiatives regarding sustainability as it strives every day to make work with chemicals safer.

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Effect of Two Types of Feedstocks on Carbon Blacks

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Keywords: CT; FCC; SHINE50ULSR; Feedstock.

Differences are found for carbon blacks produced using different sources of feedstocks. Carbon black (CB) produced using a coal tar (CT) feedstock formed particles with amorphous cores. In contrast, the carbon black produced from fluidized catalytic cracker (FCC) decant oil as feedstock formed particles with a single nucleated core possess. These structural dissimilarities is premised on differences in fuel composition, specifically component classes as found by saturate, aromatic, resin, asphaltene analysis.

In this study, for simplicity, two types of carbon blacks are compared for their physical and chemical properties. These carbon blacks are formed under similar reactor conditions in furnace process, with feedstock composition being the only significant variable. One carbon black is formed using coal tar as the feedstock (referred to as CT-CB), while the other carbon black is formed using fluid catalytic cracking decant oil (referred to as FCC-CB).

CT-CB is derived from a coal-tar based feed. Coal tar is an extremely complex mixture, containing 4, 5, 6, and even 7-ring aromatics, as well as methylated and poly-methylated derivatives with different contents of saturates and aromatic. Other components can include heterocyclic compounds such as pyridine, benzene-toluene-xylene (BTX) compounds, cumenes, and naphthalenes [1].

FCC-CB is derived from fluid catalytic cracking of decant oil. Analysis results highlight the key differences relative to the CT material as higher saturate and lower aromatic content. FCC decant oils can contain an aromatic distribution ranging from single to 4-ring compounds, potentially including some naphthenic rings. Reflecting catalytic origins, the lighter aromatic fraction may bear varied alkyl groups as reflected by the SARA analysis [2].

Table is being summarized with the results of the analysis for saturates, aromatics, resin, and as phaltene content for these feedstocks. The sulfur content for the CT was 0.7 wt.% and 3.0 wt.% for the FCC material.

Conclusion :

Two feedstocks, CT and FCC form “SHINE 50 ULSR – a special carbon black” carbon black using similar reactor conditions. The main compositional difference is the prevalent content of methylated aromatics, heavy to light in the CT. And, these have different rheometric properties of rubber compounds made with SHINE 50 ULSR carbon black giving room for formulation adjustment before use.

Acknowledgement

Thanks to M/s. Shine carbon and Chemical Pvt. Ltd., who allow me to publish the study

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Electrical Conductivity Behavior of Rubber Composites with Varying Crosslink Density Under Cyclic Mechanical Deformation

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Keywords: conductive polymer composite; mechanical deformation; crosslink density; conductive pathway.

During the last decade, conductive polymer composites (CPCs) have been considered to be relatively cost-effective materials for many engineering applications, such as sensors, antistatic coatings and films, conducting adhesives, and electromagnetic interference shielding materials. For any possible application, the intimate relationship between the conductivity changes and external stimuli, such as electrical, thermal, mechanical, and chemical stresses, must be understood [1]. From this point of view, mechanical deformation can be expected to be the most important factor affecting the electrical properties of flexible conducting composites. Although the practical application of this knowledge is clear, the mechanism of conductivity changes during mechanical deformation must be understood in detail to get reliable product. Investigating both electrical conductivity and mechanical properties in parallel using online measurements seems to be of particular interest. Moreover, to date, no investigation has been done to evaluate the effect of vulcanization time on the electrical conductivity of styrene-butadiene rubber (SBR) and ethylene-propylene-diene terpolymer (EPDM) rubber composites under mechanical tensions.

Herein, this contribution is focused on understanding the mechanism of conductivity changes during mechanical deformation for conductive rubber composites based on SBR or EPDM vulcanized for various times. The rubber compounds were prepared with the same ratio of sulfur and other ingredients to rubber, while the amount of CB was kept constant at 70 phr or 40 wt%. The composition of rubber compounds is summarized in Table 1.

Table 1. Composition of rubber compounds in phr and their designation.

Components	Concentration (phr)
Rubber (SBR or EPDM)	100
Carbon black	70
ZnO	3
Stearic acid	1
CBS[a]	1
Sulfur	1.75

[a] N-cyclohexyl-2-benzothiazole sulfenamide

The physical and mechanical properties and static conductivity were evaluated. Furthermore, both the electrical conductivity and stress-strain curves were recorded in parallel using online measurements (Figure 1).

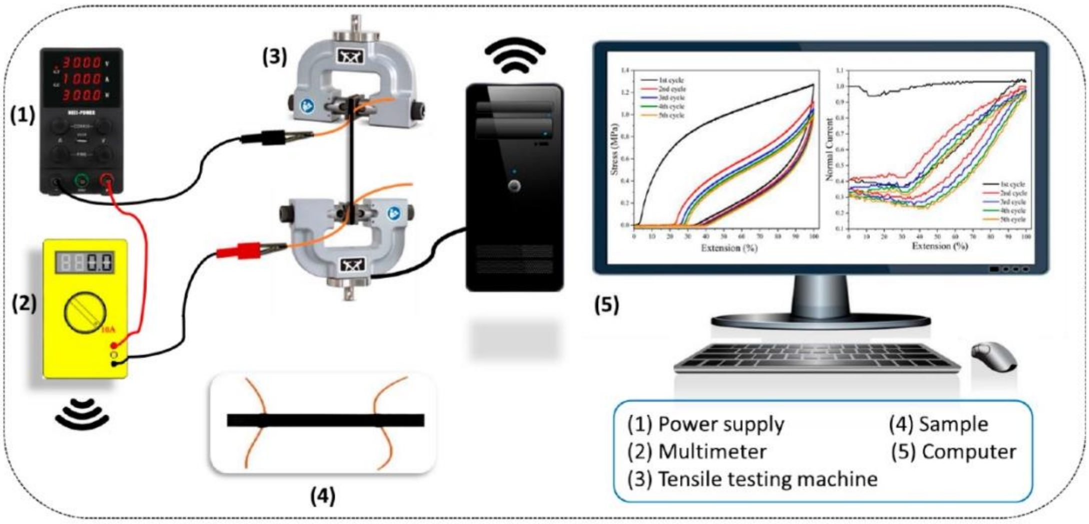

Figure 1. Online measurement of conductivity changes during cycling mechanical deformation [2]

Higher tensile strength, Young's modulus, and static conductivity values of the composite were observed with the increase in vulcanization time. The electrical conductivity during five runs of repeated cyclic mechanical deformations for SBR composites increased permanently, although not linearly, whereas EPDM composites showed a slight increase or at least a nearly constant current, indicating healing of minor defects in the conductive pathways or the formation of new conductive pathways. For the SBR composite, the current value starting from the second cycle increased with rising vulcanization time in the SBR composite, while the current values were nearly constant for all cycles in the EPDM composite.

Acknowledgement

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The relationship between wear morphology and fatigue crack growth in tire tread compounds

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Keywords: Tire Tread Compounds; Fatigue Crack Growth; Wear Mechanisms; Abrasion.

Evaluating tire tread compound performance with laboratory benchtop tests has been a topic of great interest for tire manufacturers and researchers. Specifically, the nature of how wear morphology develops during service has been a focus to understand the degradation process in tread compounds. The two primary types of abrasion mechanisms generated during deformation are known as thermo-mechanical wear and tribo-chemical wear, which has been elucidated as “smear wear” [1-2].

There are numerous factors which contribute to the degradation process including aspects such as the driving style, the type of vehicle and the road surface. However, the nature of these abrasion mechanisms can be more easily studied by examining the change of temperature and frictional force generated during deformation. To understand the change in the type of wear mechanism, a combination of test methods must be used to create a more integrated theory on the governing factors which influence these two primary types of degradation. To study this, a laboratory set-up has been configured to emulate the dynamic loading process a tire experiences and replicate a more realistic abrasion process [3-4].

Using a fracture mechanics approach originally proposed by Southern and Thomas, a comparison can be drawn between the abrasion process and an independently measured cyclic pure shear fatigue crack growth test [5]. This is accomplished by evaluating the crack growth rate versus the tearing energy from both experimental set-ups. Both the abrasion and pure shear fatigue crack growth tests are carried out on one machine with bespoke components fitted to conduct the different experiments. Shown in Figure 1, the laboratory test bench and the abrasion process used to replicate tire loading are shown alongside one another.

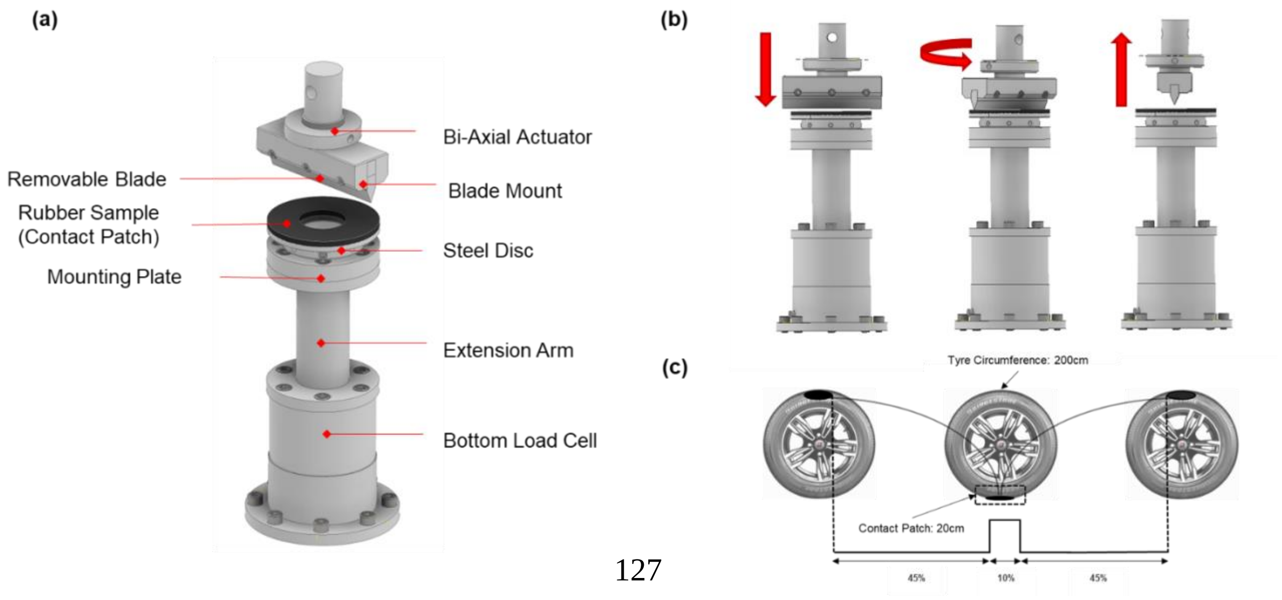

Figure 1. **(a)** Annotated diagram of friction-wear rig and respective components **(b)** Abrasion process illustrated in several stages to emulate dynamic contact of a tire during rolling-conditions **(c)** Loading stages for a single contact patch of a tire

Aspects such as the transition between mechanical degredation and chemical degredation can be understood by carefully comparing the results from these two testing methods. Using the abrasion set-up provides insight into the wear debris and surface wear morphology formation. Figure 2 illustrates how the change of load and temperature leads to a transition in the wear mechanism for a filled styrene-butadiene tread compound.

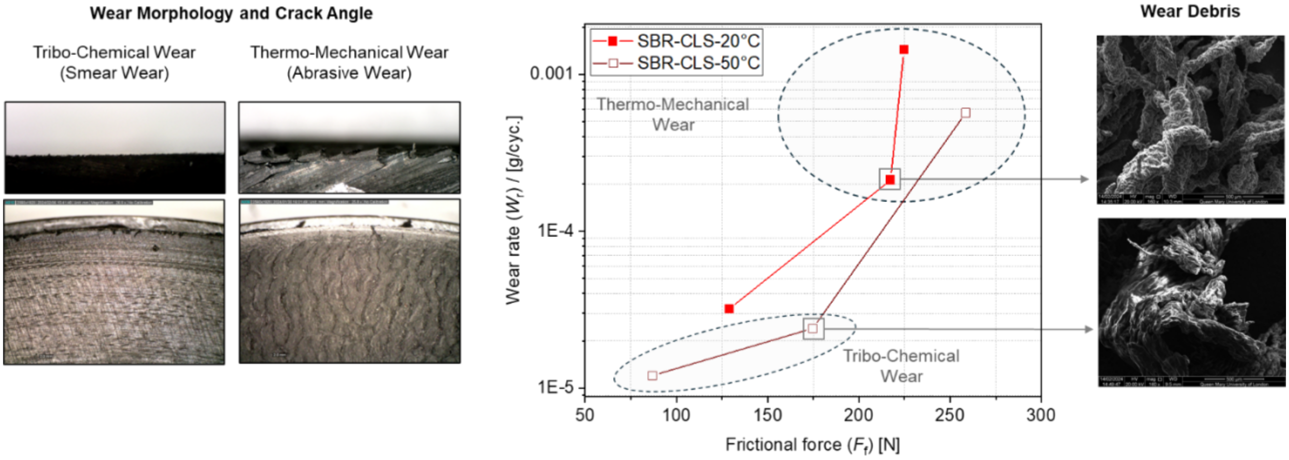

Figure 2. The effect of wear rate versus frictional force for a filled styrene-butadiene tread compound at different temperatures plotted alongside of images of the crack angle opening, surface wear morphology and wear debris

Input conditions are carefully controlled in this study to investigate the transition in the wear mechanisms. As a result, further insight into the phenomena behind wear morphology and fatigue crack growth mechanisms can be better understood.

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The ageing and degradation properties of nanocellulose/carboxylated nitrile butadiene rubber (XNBR) latex films

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Keywords: carboxylated nitrile butadiene rubber, nanocellulose, biodegradation, crosslinking system, ageing.

Carboxylated nitrile butadiene rubber (XNBR) is widely used in glove manufacturing due to its excellent mechanical properties, chemical resistance, and elasticity. Despite these advantages, XNBR gloves pose environmental concerns because they are difficult to degrade, contributing to long-term waste [1]. This has increased the urgency to develop more sustainable materials that can reduce environmental impact. Recent studies have demonstrated that integrating cellulose-based fillers can enhance the biodegradation process of synthetic polymers [2,3]. In this project, nanocellulose (NC), extracted from oil palm empty fruit bunch (OPEFB) is utilized as a filler in XNBR latex to improve its biodegradability. The work focused on understanding the impact of NC in different crosslinking systems. The methodology involved compounding NC with XNBR latex in both sulphur and non-sulphur crosslinking systems. The resultant films were subjected to thermal ageing and soil burial procedures to simulate environmental conditions and assess biodegradation. For the biodegradation experiment, the films were buried in soil and assessed at intervals of 2, 4, and 8 weeks. The Fourier transform infrared (FTIR) analysis, tensile test for mechanical properties and swelling index to assess the degree of crosslinking were performed to the XNBR latex films.

The results indicated that incorporating NC significantly improved the biodegradation rate of the XNBR latex films. Films with NC showed increased mass loss over time compared to those without NC, suggesting enhanced microbial activity and breakdown of the polymer matrix (Figure 1). The XNBR films after 8 weeks of soil burial indicate the signed of biodegradation of CNF as carbon source in XNBR films. After 8 weeks of soil burial, the XNBR films exhibit signs of CNF biodegradation (Figure 2). This indicates that the cellulose nanofibers are serving as a carbon source for soil microorganisms, leading to the breakdown of the films. This biodegradation process highlights the potential for creating more sustainable materials by combining synthetic polymers with natural, biodegradable components like CNF. In conclusion, the addition of nanocellulose from OPEFB not only enhances the biodegradation of XNBR latex films but also indicates that the crosslinking system plays a crucial role in determining the degradation rate. These findings provide valuable insights into the development of more sustainable and environmentally friendly XNBR gloves, potentially reducing their environmental footprint.

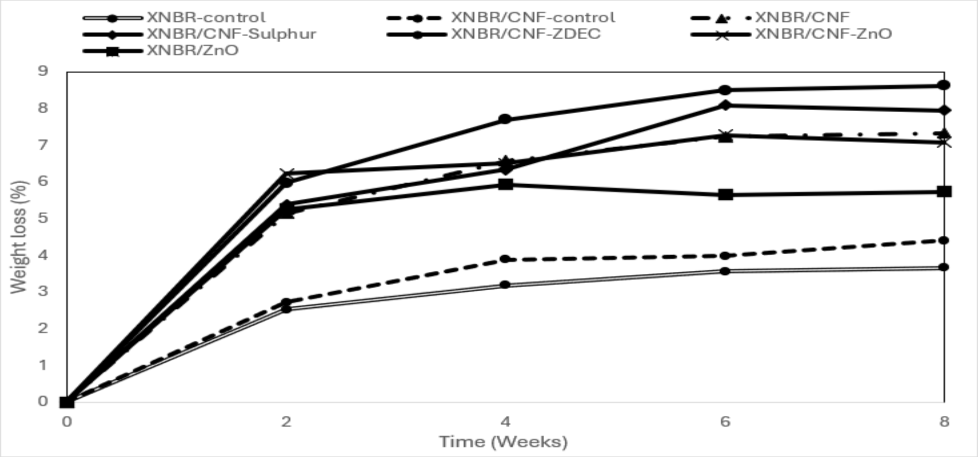

Figure 3. Weight loss of XNBR/NC in different crosslinking systems.

Figure 4: Biodegradation of XNBR/NC in different crosslinking systems.

Acknowledgement

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Rheology and Properties of Hybrid-Filler Rubber Compounds

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Keywords: Hybrid Fillers; Morphological Synergy; Payne Effect; Final Properties.

Energy dissipation in large-strain dynamic loadings is a concern in many rubber products, especially tires. This loss of energy is mainly due to breakage and reformation of filler secondary network in highly-filled rubber compounds, known as the Payne effect [1]. Dispersion of reinforcing fillers in rubber compounds is an important factor determining this nonlinear viscoelastic property in rubber compounds [2]. Other than common methods of improving filler dispersion, i.e. modification of filler surface or elastomer microstructure [3,4], application of hybrid fillers has been under attention by researchers [5,6].

Our recent works show that adding (rather than replacing) small concentrations of a secondary filler, with different chemistry, size, or shape than the primary filler, has been promising as an inexpensive method of obtaining morphological synergy and controlled nonlinear behavior in rubber compounds [7,8]. Other than disspiation related properties, final properties of rubber compounds such as abrasion resistance and coefficient of friction are also affected in hybrid-filler compounds. In this talk, few hybrid-filler rubber compounds and their rheology and final properties will be discussed. For instance, Figure 1 shows adding just 0.25-0.5 phr graphene (in a masterbach form) to styrene-butadiene rubber compound cotaining 80 silica reduced low-strain storage modulus and loss modulus, as measures of the Payne effect.

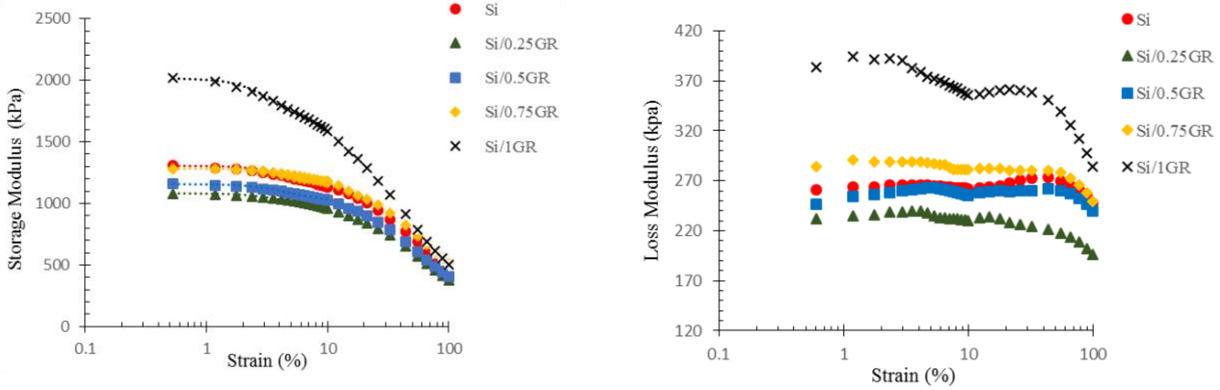

Figure 1. Strain sweep dynamic storage and loss moduli for silica-graphene rubber compounds

The source of this phenomenon was explained based on the morphological synergy obtained by reduced flocculation of the primary filler in the presence of the secondary one.

Final properties of rubber compounds such as heat build-up and abrasion resistance were also affected by the presence of the secondary filler. Figure 2 shows the effect of graphene on these two properties of silica-filled styrene-butadiene rubber. As shown, adding 0.25 phr graphene reduced heat build-up more than 30% and improved abrasion resistance to more than 50%.

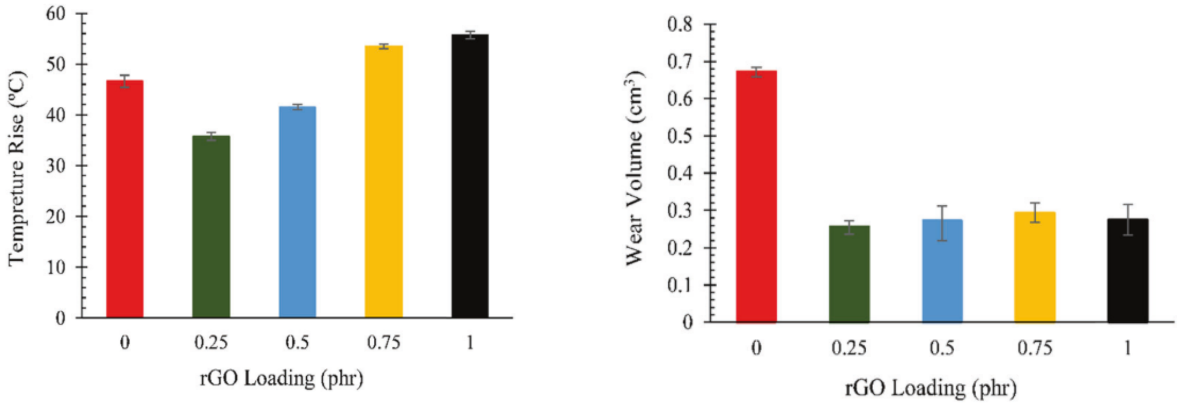

Figure 2. Heat build-up and abrasion rate of silica-graphene hybrid SBR compounds

Similar behavior and properties has been observed for other hybrid filler compounds such as carbon black-silica, silica-nanocarbon black, carbon black-crystalline nanocellulose, which will be presented in this paper.

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New generations of sustainable ZnO activators: a path to low carbon footprint with new properties

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Keywords: Zinc oxide, carbon footprint, environnement.

Vulcanization is a cross-linking reaction that occurs when a vulcanizable polymer is exposed to a vulcanizing agent (usually sulfur) and thermal energy. This thermal energy is necessary to establish chemical bonds between the vulcanizing agent and the reactive sites of the polymer's molecular chains, forming a three-dimensional network. To activate the vulcanization reaction between the polymer and the vulcanizing agent, a vulcanization activator such as a divalent metal oxygenated compound is commonly used, with zinc oxide (ZnO) being the most prevalent.

With global warming and the need for a new energy paradigm, our industries face new challenges. In 2010, the ISO organization published ISO 26000, a guideline on social responsibility. Within this guideline, section 6.5 addresses sustainable resource use (6.5.4) and climate change mitigation and adaptation (6.5.5).

The need to reduce the carbon footprint has driven the search for new, more environmentally friendly materials through new sources of raw materials, reduced energy requirements, and a return to the basics of vulcanization.

Seven years of research have led to the development of a new generation of vulcanization activators, ActiECO+ and ActiECO+ Green. These activators offer additional advantages, making them the preferred choice for formulators as they do not alter the rheology and mechanical properties of the rubber blend. They bring new benefits such as higher circularity through recycling, energy efficiency, and blending to reduce the carbon footprint by up to 90%. They also feature a modified surface for improved blending efficiency, reduced mixing time, and extended shelf life. Additionally, they are non-toxic to the environment and of high purity.

New features never (seldom) described in the literature have also been observed, a complex between a biobased material and the ZnO has drastically reduced the leaching out of the rubber blend by 50% and even totally with a specific formulation.

Component	phr
TSR 10	80
BR 1220L	20
N347	55
S. naph. oil	7
6PPD	2
TMQ	1
CBS	0.8
Sulfur	2.3
Stearic acid	2.5
ZnO	5

	ZnO 5 phr	Acti^{ECO+} 5 phr
Tmin	2.38 ±0.01	2.44 ±0.02
Tmax	17.04 ±0.06	16.12 ±0.02
Delta	14.67 ±0.05	13.68 ±0.02
Ts2	1.05 ±0.01	1.01 ±0.01
T50	1.52 ±0.01	1.45 ±0.01
T90	2.68 ±0.04	2.50 ±0.03

TS (MPa)	19.3 ± 1.5	19,9 ± 1.3
El (%)	355 ± 21	357 ± 7
Mod 100	2.3 ± 0.2	2.6 ± 0.2
Mod 200	7.8 ± 0.4	8.0 ± 0.6
Mod 300	14.8 ± 0.6	15.4 ± 0.8
Hard (Sh-A)	61 ± 1	61.5 ± 1

CFP parameters

- ISO 14067 based
- Sphera LCA related
- “Cradle to gate”
    - Scope 1 & 2
    - Scope 3 upstream
- Elemental allocation (co-products)

Product	CO_2 eq/kg product	Remark
Gold seal	3,90	Sphera
Silox 2C - Actif	3,58 – 3,46	Sphera
ActiECO+	1,57	Sphera Industry (ingredients)
ActiECO+ Green	1,36	Sphera Industry (ingredients)

Dielectric and Mechanical Response of Carbon Black Filled NBR: Frequency-Temperature Relationships

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Keywords: Dielectric Spectroscopy; Dynamic Mechanical Analysis; Carbon Black; Nitrile Butadiene Rubber

High-frequency testing is crucial for evaluating the performance of elastomers required across a range of engineering applications, including tires, shock absorbers, and dynamic sealing. The frequencies required for these applications exceed the capabilities of a standard dynamic mechanical analyzer (DMA). To address this limitation, time-temperature superposition can be adopted but this introduces additional processing errors associated with using appropriate shift factors[1]. This becomes particuarly complex when dealing with filled elastomers. Broadband dielectric spectroscopy (BDS) is a non-destructive technique which can assess a material's response to an alternating electrical current across a broad range of electrical frequencies. A standard impendence spectrometer is capable of accessing significantly higher frequencies compared to those attained by DMA but this technique comes with limitations when measuring highly filled conductive carbon black samples.

This work evaluated both the mechanical and dielectric properties of a series of carbon black filled nitrile butadiene rubber (NBR) compounds to investigate the electrical and mechanical aspects of polymer relaxation. The role of carbon black structure and surface area, as well as volume fraction, was investigated to determine whether these measurements provide additional information pertaining to filler reinforcement. The colloidal properties of the six species of carbon black selected for this study are given in Figure 1. The fillers were added to analogous NBR-based compounds at three filler loadings, an additional unfilled compound was also tested. The formulations of these compounds are given in Table 1.

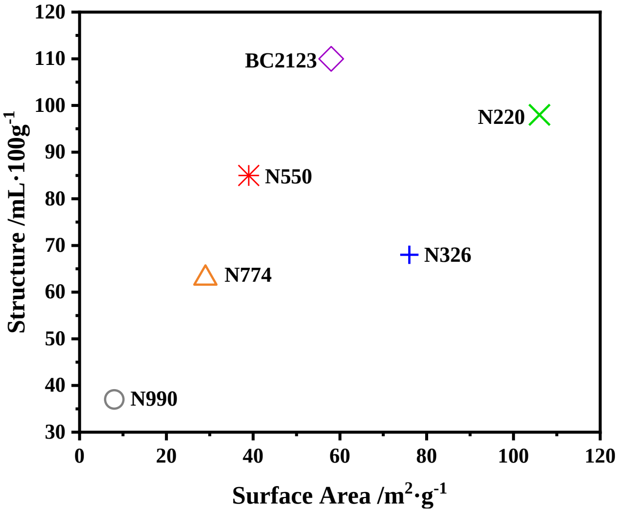


Figure 1. Colloidal plot of selected carbon blacks

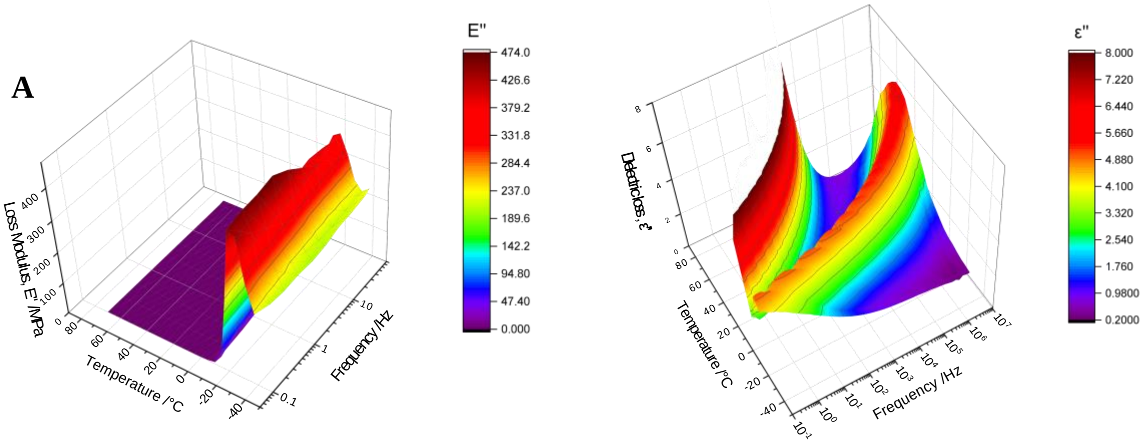
Table 1. Compound formulations

Components [phr]	Details	Sample notations			
		1-6A	**1-6B**	**1-6C**	**UF**
NBR	Krynac 3345 F[a]	100	100	100	100
Carbon black	Various grades	60	25	10	0
Crosslink	Sulphur	EV	EV	EV	EV

[a] 33 % acrylonitrile content

The 3D plots given below show the relationship between frequency, temperature and dielectric/mechanical loss. An α-relaxation peak, which has been confirmed through a Vogel-Fulcher-Tammann-Hesse equation, is visible using both techniques[2-4]. An additional relaxation process is seen in the high temperature/low frequency region of the dielectric loss. This can be attributed to low frequency DC conductivity and Maxwell-Wagner-Sillers polarization, associated with the conductive filler. The role of carbon black colloidal properties on the segmental relaxation is also investigated using these combined techniques.

Figure 2. Relationship between frequency, temperature and dielectric/mechanical loss for N990 filled NBR



Acknowledgements

One of the authors, K. Rutherford would like to thank EPSRC for the iCASE studentship (EP/V519583/1) and SLB, who in combination are responsible for the funding of this research project.

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Polyisoprene and random isoprene-norbornene copolymers with unique microstructure obtained with tailored titanium(IV) phenoxyimine catalysts

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Keywords: polyisoprene, isoprene-norbornene random copolymers; highest monomeric friction coefficient, titanium(IV) phenoxyimine complexes; additive polymerization, norbornene.

The stereospecific polymerization of isoprene has been an appealing topic for academic and industrial research since the discovery of heterogeneous Ziegler-Natta catalysts in 1954. However, later the research focus has moved to homogeneous processes, since they allow to have more precise control over polydispersity and the microstructure of resulting polyisoprene and they enable the synthesis of copolymers with unique microstructures [1,2]. Ti(IV) phenoxyimine complexes, first introduced by *Fudjita et al* [3], are a promising class of precatalysts for 1,3-diene polymerization reactions due to their modular structure allowing to fine-tune their catalytic properties.

In styrene-isoprene rubbers (poly(isoprene-*r*-styrene) copolymers) typically the styrene monomer (thermoplastic, polystyrene T_g ~ $100^{o}C$) is responsible for adjusting the T_g to the desried level, while isoprene (elastomer) is accountable for flexibility and elasticity. Currently, styrene is the monomer with highest monomeric friction coefficient (MFC) commonly used in industry for tire elastomers. To achieve the required properties for rubbers, it is necessary to incorporate more than >10 wt% of styrene into the styrene-isoprene copolymer. Nowadays, cyclic olefins are excellent and, what is important, cost effective candidates for high MFC monomers, as they should result in a cyclic structure constraining polymer chain mobility. Specifically, norbornene has been shown to undergo additive polymerization resulting in materials with a T_g as high as $280^{o}C$, thus inducing 3 times higher T_g shift as compared to styrene. The theoretically calculated shifts of T_g for poly(isoprene-*r*-norbornene) copolymers should be higher than that of poly(isoprene-*r*-styrene) copolymers at similar monomers ratios. *Thus, the replacement of styrene with norbornene, therefore, should result in a new class of the resulting random copolymers*.

In this work, we have prepared a series of tailored homo- and heteroligand Ti(IV) phenoxyimine complexes (Fig. 1A), bearing substituents of various bulkiness and different electron donor/acceptor properties. These fine-tuned complexes, when activated with $Al(\mathit{i}Bu)_3/Li[B(C_6F_5)_4]$, were capable to homopolymerize isoprene and copolymerize it with norbornene in a random manner (Fig. 1B).

The synthesized *polyisoprene homopolymers* were obtained in high yields (>99%) and were characterized with molecular weights up to 654 000 $g\cdot mol^{-1}$ and, in general, sufficiently narrow M_w/M_n = 2.4-3.8. More important, these polyisoprenes possessed unique microstructures, consisting exclusively of cis-1,4-isoprene and 3,4-isoprene units with ratios ranging from 2.2:1 to 7.8:1 correspondingly. The substitution of $Al(\mathit{i}Bu)_3/Li[B(C_6F_5)_4]$ activator with more industry relevant

MMAO resulted in a decrease both in yield of the polymers (62-80%) and in their molecular weight (46000-62000 $g\cdot mol^{-1}$).

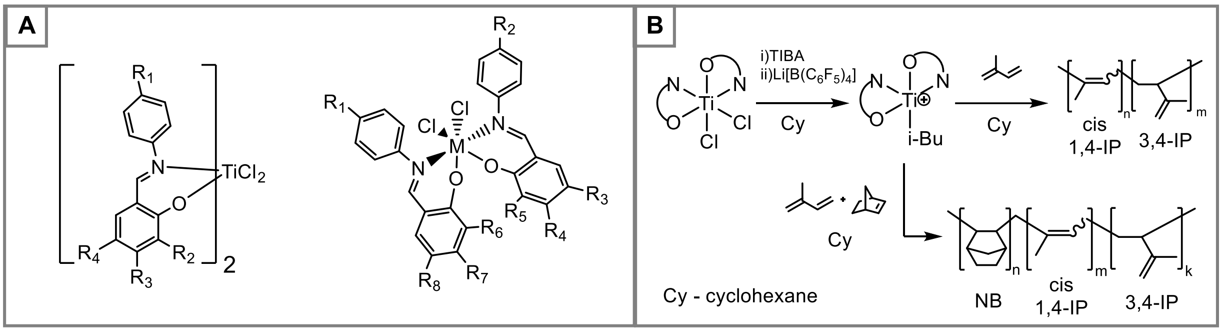

Figure 1. (A) Generic structures of Ti(IV) phenoxyimine complexes, used as precatalysts for isoprene homo- and copolymerization; (B) Activation of Ti(IV) complexes and subsequent polymerization processes.

The selected catalytic systems (Ti(IV) complex/ $Al(i\mathrm{Bu})_3/Li[B(C_6F_5)_4]$) that exhibited the best performance in isoprene homopolymerization were further employed for copolymerization of isoprene with norbornene. The resulting copolymers possessed high molecular weights (250 000-850 000 $g\cdot mol^{-1}$) and satisfactory M_w/M_n = 2.4-3.8. The incorporation of norbornene units was as high as 18% and the distribution of norbornene and isoprene units along the chain was statistical. The copolymers also consisted of exclusively cis-1,4-isoprene and 3,4-isoprene units with ratios between 4.5:1 and 7.8:1 correspondingly. For the first time random isoprene-norbornene copolymers were obtained with controlled microstructure and comonomer ratio that significantly affects all their properties, including glass transition temperature, that varied in the range of -35.4 to -38.9^{o}C for the 10 mol% of incorporated norbornene units.

In conclusion, we have shown that Ti(IV) phenoxyimine complexes can be used as a versatile platform for tailoring catalysts for diene polymerization and copolymerization. They possess both high catalytic activity and ability to produce statistical (co)polymers with unique microstructures. Moreover, their modular structure allows to fine-tune the catalytic properties to produce tailored polymers according to the industrial needs.

Acknowledgement

This work was in part supported by the Luxembourg National Research Fund (FNR) through the IPBG project TireMat-Tech (Grant No. 16/11514551).

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Modeling study of tensile strength of filled and strain-crystallizing elastomers

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Keywords: strain-induced crystallization, filler reinforcement, tensile strength, modeling.

The objective of this work is the investigation of reinforcement of elastomers by filler and strain-induced crystallization (SIC) in terms of tensile strength. The model for SIC in elastomers by Plagge & Hentschke [1] is combined with the model for filler by Viktorova et al. [2] and extended for the simulation of rupture.

The Morphology Generator (MG) developed by Viktorova et al. [2] enables the generation of various filler dispersions like fine and coarsely. Thus, the impact of both the filler volume fraction and the filler dispersion on the tensile strength of filled model networks are analyzed. The results are compared to experimental data. In addition, tensile strength of non-strain-crystallizing model networks is compared to that of strain-crystallizing model networks. Reinforcement by filler and by SIC are compared.

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Does it fatigue? A feasibility study on the fatigue testing of NBR and PUR in the dynamic mechanical analysis for damage prediction

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Keywords: elastomer; dynamic mechanical analysis; damage prediction**.**

For damage prediction of dynamically stressed elastomers, state of the art complex component tests are performed to characterize the load cycle dependent material behavior. To reduce the testing effort, material tests are occasionally carried out on suitable specimen geometries. Nevertheless, the aim is to further simplify and standardize the test series. Dynamic Mechanical Analysis (DMA) is a measurement method that can dynamically stress small test geometries under variable temperature and frequency (0.1 to 100 Hz). The aim of this study is to investigate whether the fatigue behavior of elastomers can be mapped using standard DMA methods and whether the material characteristics can be used to predict damage.

For this study, single stage dynamic tensile tests were performed at constant temperature and frequency using the DMA on a carbon black filled nitrile butadiene rubber (NBR) and an elastomeric polyurethane (PUR). Dynamic tensile tests on paraboloid specimens are used as a reference. The fatigue behavior of elastomers is reflected in a change in dynamic stiffness. This can be modelled using the reference dynamic tensile tests. In the DMA, the change in dynamic stiffness cannot be modelled by conventional methods. Stiffening occurs and the damping of the NBR and PUR decreases. Due to the stiffening effects, damage criteria based on a change in dynamic stiffness cannot be applied.

Effect of wollastonite on adhesion and gas barrier properties of epoxidized natural rubber-based tyre inner liner compounds

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Keywords: Butyl rubber; Epoxidized natural rubber (ENR); Gas barrier properties; Tyre inner liner; Wollastonite

Tyre, which provides contact between road and the vehicle, is a composite material produced by vulcanization of several rubber compounds at the same time to meet different performance requirements. As an important part of the tyre body, the liner is expected to exhibit high gas barrier properties to keep the compressed air inside the tyre. In addition to having excellent gas barrier properties, tyre liner compounds must also exhibit sufficient adhesion to the cord coating compound (usually natural rubber based), which is in direct contact with the liner during vulcanization. This is essential for the integrity and durability of the tyre, especially under highly dynamic conditions. Butyl rubber is the most preferred raw material for preparing tyre inner liner compounds due to its superior gas barrier properties. Despite this, incompatibility and poor adhesion to the other rubbers and inherently low mechanical properties of butyl rubber can be counted as shortcomings for its use in tyre components.

In this study, it was aimed to develop epoxidized natural rubber (ENR) based rubber compounds as an alternative to butyl rubber to use in tyre inner liner compounds. A compatible vulcanization system with approximate cure behaviour and a filler system that can improve both physical and chemical interaction between NR and ENR matrices were investigated. The primary filler considered for this purpose was wollastonite, which could provide a strong physical bonding between the two rubber phases with its low aspect ratio. Rubber compounds were prepared by using three different types of surface-modified (with amino, epoxy, and vinyl silane) wollastonite. Besides, amino silane modified wollastonite, which was found to be most promising, was also evaluated in terms of its aspect ratio and three different aspect ratios (1:1.15, 1:3 and 1:8). All the compounds were studied regarding their rheological and physico-mechanical properties, adhesion performance, gas permeability, and morphological properties. Significantly improved adhesion and mechanical properties along with the competitive gas barrier properties could be obtained with the compound prepared with ENR and 1:3 aspect ratio of amino silane modified wollastonite. It was concluded that the developed compositions in this study could be successfully used as an alternative to butyl rubber-based tyre inner liner compounds.

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Effect of zinc oxide on curing polychloroprene

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Keywords: Chloroprene rubber, Vulcanization, Zinc oxide

Zinc oxide (ZnO) is an inorganic compound that is insoluble in water, white, in powder form, and has a tetrahedral structure. It is used in a wide range of applications, especially in the rubber industry, plastic, ceramic, glass and cement industries, and in the production of lubricants, paints, adhesives and sealants. It is used as an activator together with stearic acid to increase the effectiveness of the vulcanization. Although the presence of zinc oxide in sulphur vulcanization slightly increases the scorch time and the total cure time, it is effective in determining the position where sulphur will be attached on the rubber chain and thus directly affects the cross-linking efficiency. Since it causes the formation of short crosslinks (mono- and di-sulphide), the density of stable crosslinks in the rubber matrix is higher and thus high thermal resistant rubber vulcanizates can be obtained. Chloroprene rubber (CR) is among the rubbers that are resistant to oxygen, ozone and lots of chemicals and have high abrasion and tear resistance. It is highly reactive due to the presence of chlorine atom and can therefore be efficiently vulcanized using metal oxides (MgO and ZnO). CR exhibits relatively high resistance to hydrocarbon-based oils and fuels thanks to the polarity provided by the chlorine atom. The high bonding energy of chlorine and carbon atoms positively affects its flame resistance. However, its working temperature is limited to the range of -35℃ and 100℃. CR is used in a wide range of applications including high-pressure hoses, conveyor belts, cable sheaths, adhesives, gaskets.

In this study, the effect of different types and amounts of zinc oxide to the performance of CR based high temperature hose applications was investigated. Rheological, physical, mechanical, thermal stability, dynamic-mechanical and temperature-scanning stress-relaxation properties of the compounds were studied. It was observed that the rubber compounds prepared with MELOS active ZnO gave significantly higher original tensile strength values than that prepared with competitor (Gold), regardless of the zinc oxide amount, however, caused a higher change in tensile strength after thermal aging. This was simply associated with relatively poor dispersion. With MELOS active ZnO, higher elongation values at break could be achieved compared to Gold ZnO, even when used in lower amounts. However, retention in elongation after aging was found to be higher for MELOS active ZnO. When the active ZnO types are compared in terms of their non-isothermal relaxation behaviour, it was seen that MELOS active ZnO exhibits significantly higher modulus compared to Gold ZnO in a wide temperature range at both concentrations (2.5 and 3 phr). When all the findings were evaluated together, it was observed that MELOS zinc oxide grades with different properties were generally equivalent and besides their effects on mechanical strength of the rubber vulcanizates were positive when used at the same or different amounts, compared to the competitors' products. However, it should be noted that the competency of all zinc oxide types should be considered depending on the basic performance criteria expected from the rubber material, and by this means the efficiency from the zinc oxide can be reached to the highest possible level.

Correlative Characterization of High-Performance Elastomers using Microscopic and Spectroscopic Methods

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Keywords: NBR; activators; fillers; correlative microscopy.

Rubber-based paper roll coatings usually consist of multi-component systems, which, during the past decades, have experienced significant changes due to constantly shifting needs of the paper industry. The resulting complexity of those formulations, however, pose challenges in the effective integration of new functionalities / materials for high-performance materials, often demanding a trial-and-error approach. In order to facilitate the incorporation of new functionalities, we are opting for a systematic, non-heuristic approach in collaboration with industry. This involves dissection and recombination of existing formulations, distinguishing essential from optional components by analyzing their effects on the overall performance at micro – and macroscopic levels.

To fulfil the manifold requirements for final products, the complex multi-component formulations are systematically broken down (bottom-up approach), and analyzed on their chemical, structural and morphological peculiarities of the bulk and the surface. For that, however, a systematic correlative microscopy and spectroscopy approach is indispensably needed as used here. Depending on the targeted information, we apply transmission electron microscopy (TEM), electron energy loss spectroscopy (EELS), scanning electron microscopy (SEM), X-Ray diffraction (XRD), atomic force microscopy (AFM) and quantitative nanomechanical mapping (QNM). The relevance of these methods and related preparation procedures (e.g. cryo microtomy) are also discussed. The data correlation from all these methods makes it then possible to go beyond topography and, in particular, focus on the interface between different polymer phases (polar/nonpolar), the type of reinforcement by different fillers and activators to understand their implications on the final performance (see Figure 1 and 2).

The long-term scope of these activities is the exploration of new functionalities and synergy effects between individual components. In Figure 1 an example for the distribution of one type of methacrylate in the NBR matrix and the EPDM phase (carrier material) is given. Despite the polarity differences between those two phases, the activator is found in both phases. Further, the interlayer phase is showing low content of carbon and nitrogen. The possible microstructures of the activators are described elsewhere. [1,2] Figure 2 gives an example of a highly filled NBR/EPDM batch (f.e. carbon black, silica, aluminosilicate, glass, polyethylene, pumice) with higher EPDM content. The different phases are well separated and the fillers are presumably located in the more polar NBR phase.

By complementary macroscopic measurements, the gap between micro- / nanoscale peculiarities and physical-mechanichal properties at large scales can gradually be closed for a consistent understanding, which paves the way for the on-purpose integration of new properties.

Hence, the overarching goal is to shift the design appraoch more and more towards a decutive path, which also reduces time intensive trial-and-error development strategies and reduces the number of components to the absolute minimum, adressing long term sustainbility goals as well.

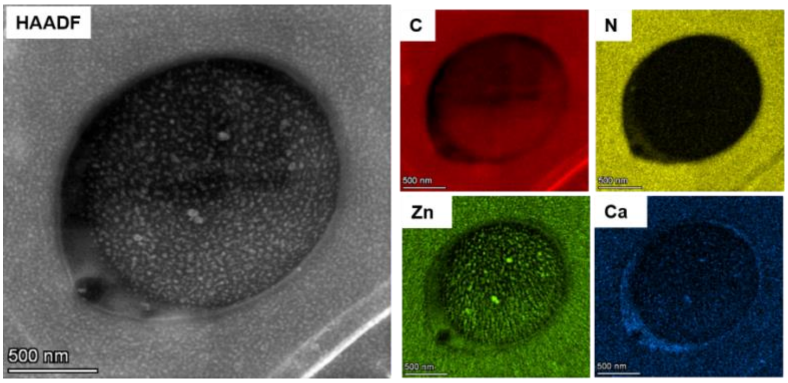

Figure 1. TEM-HAADF image showing the in-situ formed nanoparticles from the activator in the NBR (bright) and EPDM (dark) phase.

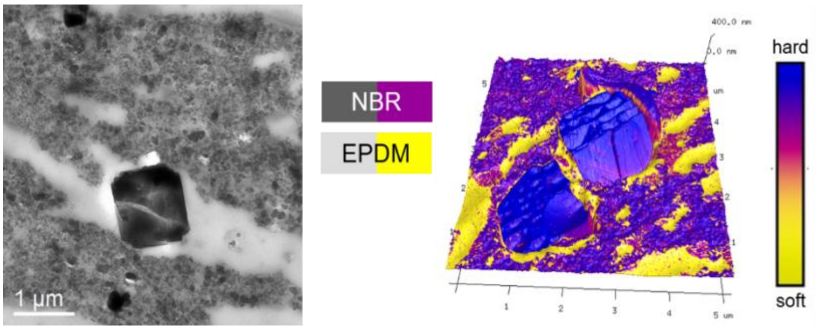

Figure 2. TEM-BF (left) and AFM 3D height & phase (right) images display the distribution of nano-sized fillers within the more polar NBR phase. The surface structure of a large aluminosilicate filler in the EPDM phase is nicely resolved by the AFM.

Acknowledgement

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Constructing strong chemical interface in graphene oxide/rubber composites exhibiting high-abrasion resistance for eco-friendly green tires

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Keywords: Rubber; Graphene oxide; Interface; Abrasion resistance.

The abrasion properties of rubber composite used in tire not only concern on the lifetime of the tire tread, but also are related to the small abrasion particles emitting to the atmosphere. Therefore, developing high abrasion properties of rubber composites is always an important research topic. To enhance the abrasion properties, the strong interfaces between fillers and rubber macromolecules are required. Herein, we reported different strategies to build the interface between graphene oxide (GO) and rubber macromolecules. The contributions of the microstructure in the rubber composites on the abrasion properties were revealed.

First, two different ionic liquids, including1-allyl-3-methylimidazole chloride (IL-1) and 1-aminopropyl-3-methylimidazolium chloride (IL-2), were used to modify GO by π-cation interaction between IL and GO. Furthermore, an IL-GO/natural rubber (NR) masterbatch possessing fine dispersion of GO was prepared by the emulsion compounding method, and thereafter, a further compound with solution polymerized styrene butadiene rubber (SSBR) was fabricated for the tread rubber composite. Results showed that the an elevated interfacial interaction between the IL-modified GO and the rubber macromolecules was built. Compared with silicon dioxide (SiO_2)-filled NR/SSBR composites, the wear resistance of the IL-1-GO/SiO_2/NR/SSBR composites was improved by 17.3%. The wear resistances of IL-2-GO/NR/SSBR improved by 8.6%, ascribing to the strong interface between IL-GO and rubber macromolecules.[1-2]

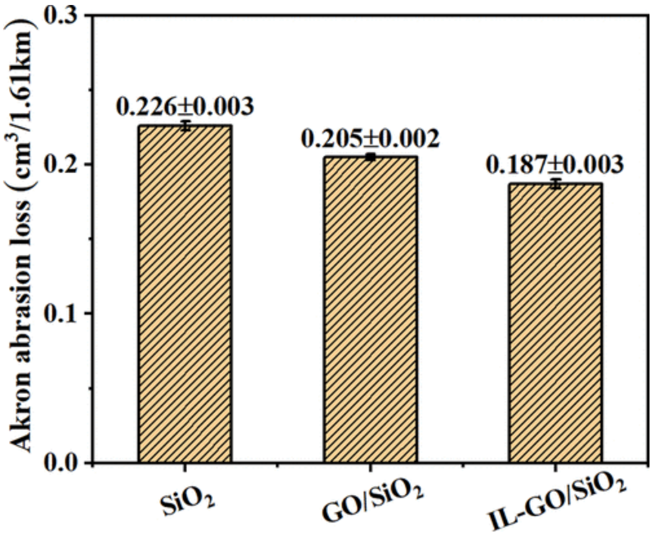

Figure 1. Akron abrasion of NR/SSBR composite filled with different fillers.[1]

Second, γ-mercaptopropyltrimethoxysilane (MPTMS) with thiol groups was introduced to react with GO. A modified GO/natural rubber (MGO/NR) masterbatch with a fine dispersion of

MGO was then introduced into solution-polymerized styrene butadiene rubber (SSBR) to create an MGO/SiO_2/SSBR composite. During the crosslinking process at high temperatures, a strong chemical interface interaction between the MGO and rubber molecules was formed by the thiol-vinyl click reaction. The MGO sheets also act as crosslinks to enhance the crosslinking network. The results showed that the rolling resistance of the MGO SiO_2/SSBR composite was superior by 19.4% and the energy loss was reduced by 15.7% compared with that of the base SiO_2/SSBR composite. Strikingly, the wear performance and wet skid resistance improved by 19% and 17.3%, respectively.[3]

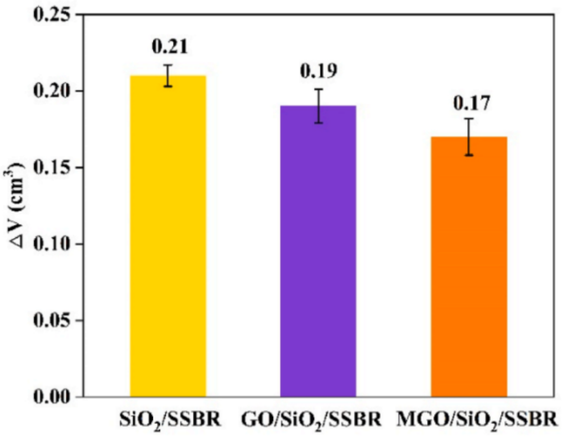

Figure 2. Abrasion performance of SiO_2/SSBR, GO/SiO_2/SSBR, and MGO/SiO_2/SSBR composites.[3]

Third, γ-aminopropyltriethoxysilane (APTES) was used to modify GO and SiO_2 to obtain GO and SiO_2 with positive charges (NG and NS). Furthermore, NG and NS were electrostatically self-assembled by using maleic anhydride (MAH) hydrolysis, thereby obtaining composite particles (NG-NS) with “bridged structures”. Also, the NG-NS/styrene butadiene rubber (SBR) compounds possessing fine dispersion of NG-NS were prepared by the aqueous compounding method. During the crosslinking process, the vinyl groups in NG-NS reacted with the vinyl groups of the SBR molecule chains, thus forming strong chemical interfacial interactions between the NG-NS and rubber macromolecules. Compared with an SiO_2/SBR composite, the abrasion resistance of the NG-NS/SBR composite was improved by 83.3 %. [4]

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Material Selection for Enhanced Durability of Elastomeric Battery Mounts in Electric Vehicles

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Keywords: Durability, Rubber Materials, Fracture Mechanics, EVs.

This research addresses the material selection challenges[1] for a better durability of rubber components in electric vehicle battery mounts, which must withstand typical vibrations and shock loading. We conducted a comparative study of two typical rubber materials: a filled natural rubber and a filled EPDM. The study aims to evaluate their performance under typical SAE norms for electric battery loads (**Figure 1**) and determine which material offers better durability.

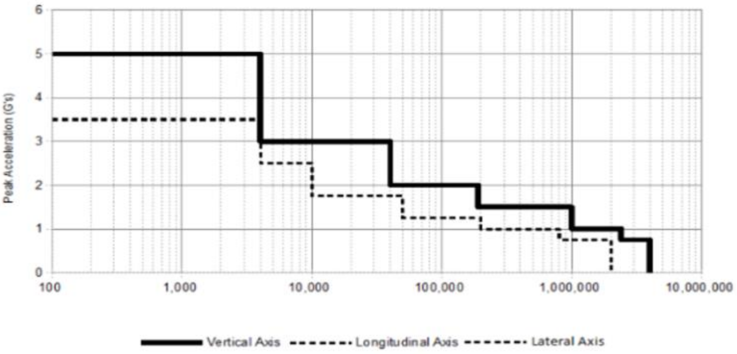

Figure 1. Cumulative Vibration Envelopes.

The approach used in this project is called block cycles analysis[2]. Block cycle analyses are composed of one or more blocks. A block is defined by a strain history that is repeated some number of times. The combination of strain histories and the associated repeats defines the block schedule. The fatigue life is reported as the number of repeats of the entire schedule. The hyper-elastic law (**Figure 2**) and the crack growth law (**Figure 3**) [4] are the two main properties that are needed for simulating the mounts material behaviors, and values were obtained from the literature.

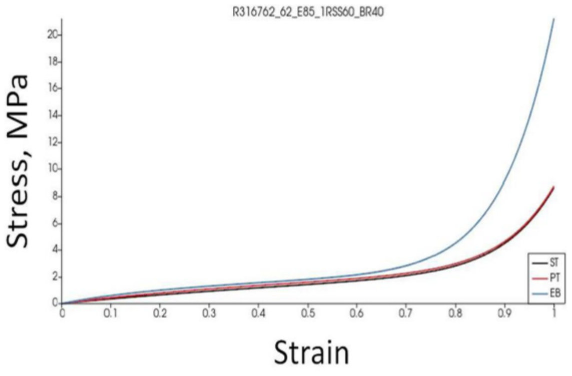

Figure 2. Hyper-elastic Law

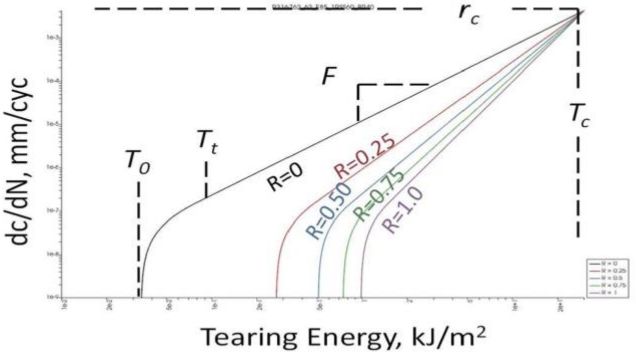

Figure 3. Crack Growth Law

This study is expected to provide guidelines for selecting rubber materials for battery mounts in electric vehicles, contributing to the development of more durable and reliable EV components. It will offer insights into the fatigue life and fracture mechanics of Natural Rubber NR[3] and EPDM, helping manufacturers choose materials that enhance the lifespan and performance of battery mounts. Furthermore, this research will support the development of electric vehicles by ensuring that critical components, such as battery mounts, are designed for longer life and better performance, thereby contributing to the overall sustainability and efficiency of EVs. Additionally, it will demonstrate the effectiveness of Endurica software in delivering reliable solutions for the automotive industry, with a particular focus on the EV sector.

Acknowledgement

Thanks to the grant sponsors, ENDURICA LLC and FE-TECH Innovative & Advanced Engineering Solutions , For Their Contributions to this Study.

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Effect of phenolic resin on the mechanical properties of Poly (epichlorohydrin-co-ethylene oxide-co-allyl glycidyl ether) (GECO) based elastomers

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Keywords: Epichlorohydrin; GECO, phenolic resin; mechanical properties

Poly(epichlorohydrin-co-ethylene oxide-co-allyl glycidyl ether) or GECO is a terpolymer that consists of epichlorohydrin (ECH), ethylene oxide (EO), and ally glycidyl ether (AGE) monomers. ECH monomer has a chloromethyl group, while the AGE monomer contains a side group with a double bond, both of which allow for the use of various vulcanization systems. GECO can be produced with differing ratios of monomers and molecular weights, which affect its mechanical and chemical properties. The ability to adjust monomer ratios and molecular weights allows GECO to be used for various applications in the elastomer industry such as production of hoses, gaskets, vibration mounts, and laser printer rolls [1,3]. The structure of the GECO polymer is shown in Figure 1.

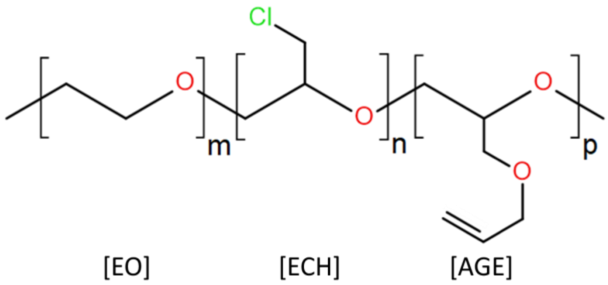

Figure 1. GECO polymer structure

Phenolic resins are important additives that are used to enhance various properties of elastomers, such as plasticization, adhesion, filler dispersion, and processability [4]. In a recent study Şen et al. [5] investigated the effects of using various resin types in one type of GECO elastomer on the damping properties. In this study, we investigated effects of phenolic resin (specifically SMD 31144) on curing, mechanical, and damping properties of four different grade GECO base elastomers. The used polymers and some of their structural properties are given in Table 1. The compound formulations of prepared GECO elastomers are given in Table 2.

Table 1. Monomer ratios and weight average molecular mass of GECO polymers

GECO type	ECH [wt%]	EO [wt%]	AGE [wt%]	Mw (g/mol)
T3108	49.7	43.1	7.2	652.835
T3000LL	64.3	30.7	5.0	763.050
T3100	74.2	14.8	11.0	2.043.920
T3102	75.8	20.5	3.7	2.154.850

Table 2. Recipes of the prepared GECO elastomers

Compound (amounts given in phr)	0 phr resin (ref)	5 phr resin	10 phr resin	20 phr resin
GECO (T3108, T3102, T3100, T3000LL)	100	100	100	100
TESPT-Silica	20	20	20	20
Naphthenic Oil	5	5	5	5
Phenolic resin (SMD 31144)	0	5	10	20
TDQ (2,2,4-trimethyl-1,2-dihydroquinoline)	1	1	1	1
6PPD (N-(1,3-Dimethylbutyl)-N'phenyl-*p*-phenylenediamine	1	1	1	1
MgO	3	3	3	3
StrAcd (Stearic Acid)	1	1	1	1
DPG (Diphenyl Guanidine)	0.5	0.5	0.5	0.5
TMT (2,4,6-Trimercapto-*s*-triazine)	0.8	0.8	0.8	0.8

Results show that phenolic resin significantly affect the cure characteristics (as shown in Figure 2), cross link density, mechanical, and damping properties of various types of GECO elastomers. The MDR data suggest that phenolic resin act like a plasticizer and reduce the viscosity of the elastomers while also decreasing the crosslink efficiency. Mechanical tests showed that phenolic resin increased the viscous character of the elastomers and improved the damping properties.

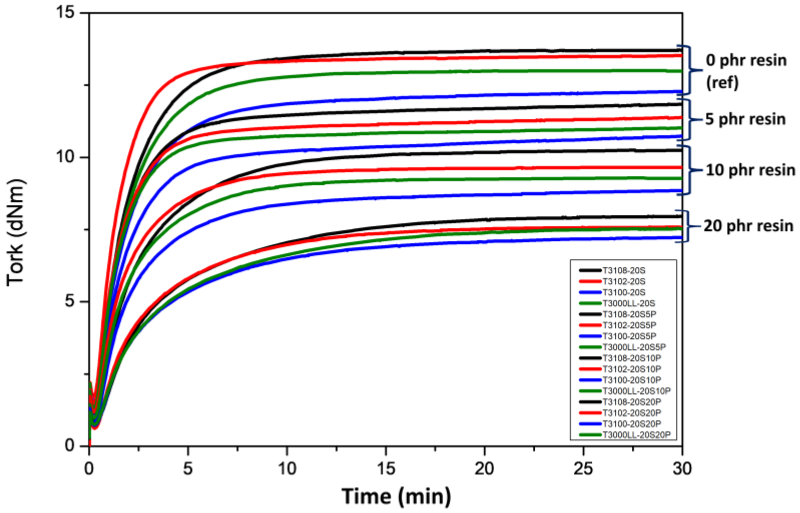

Figure 2. MDR curves of GECO elastomers

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Polymer Electrolyte Membrane with Nanomatrix Channel Prepared by Graft-copolymerization of Ethyl *p*-styrenesulfonate onto Natural Rubber Followed by Hydrolysis

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Keywords: Polymer electrolyte membrane, Nanomatrix channel, Natural rubber, Graft-copolymerization.

1. Introduction

Polymer electrolyte membrane with the nanomatrix channel [1] may have a potential to achieve efficient proton conductivity useful for polymer electrolyte fuel cell to generate green electrical energy. This may be achieved by forming the nanomatrix channel consisting of hydrophobic polymer particles with a diameter of about 1 μm and nano-channel of hydrophilic polymer that possesses a proton conductivity. In our previous studies [2], the polymer electrolyte membrane with the nanomatrix channel was prepared by graft-copolymerization of styrene on the surface of natural rubber particles followed by sulfonation with chlorosulfonic acid. The resulting membrane accomplished high proton conductivity of 0.095 S/cm, which was higher than that of Nafion [3]. However, the membrane was brittle since chlorosulfonic acid resulted in not only sulfonation but also cyclization of natural rubber. The cyclization may be avoided by graft-copolymerization of styrene substituted with sulfonic acid precursor. In the present study, polymer electrolyte membrane with the nanomatrix channel was prepared by graft-copolymerization of ethyl *p*-styrenesulfonate (SSEt) onto the surface of natural rubber particles in latex stage followed by hydrolysis with NaOH.

2. Experiment

Natural rubber latex used in this study was deproteinized natural rubber (DPNR) latex. Graft-copolymerization of SSEt onto DPNR was carried out in latex stage with *t*-butylhydroperoxide/tetraethylenepentamine as an initiator. DPNR latex adjusted to 20 w/w% DRC was charged with N_2 gas for 3 h at 30 °C. The initiator (2.0×10^{-2} mol/kg-rubber) and SSEt (1.0 mol/kg-rubber) were added into the latex, respectively. The reaction was carried out by stirring the latex at about 300 rpm for 3 h at 30 °C. As-cast film of the graft-copolymer (DPNR-*graft*-PSSEt) was prepared by casting the gross polymer latex into a Petri-dish, and it was dried under reduced pressure at 50 °C. The homo-polymer, poly(ethyl *p*-styrenesulfonate) (PSSEt), was removed from the gross polymer by extraction with acetone/2-butanone 3:1 mixture in a Soxhlet apparatus for 24 h. The hydrolysis of DPNR-*graft*-PSSEt latex (ca. 2 w/w% DRC) was carried out with 0.1 mol/L NaOH solution at 85 °C for 3 h. The homo-polymer, poly(*p*-styrenesulfonic acid) (PSS), was removed from the gross polymer by immersing the as-cast film into 1 mol/L HCl solution for 24 h.

NMR measurements were carried out with a JEOL ECX-400 spectrometer equipped with a field-gradient/magic angle spinning (FG-MAS) probe. The graft-copolymer was swollen with acetone-d_6 or DMSO-d_6 for 3 days in a sample tube with a outer diameter of 3.2 mm and it was analyzed by ^{1}H-NMR spectroscopy with a pulse repitition time of 7 sec at a spinning rate of 8 kHz.

3. Results and Discussion

Figure 1 shows ^{1}H-NMR spectra for SSEt, PSSEt, DPNR-*graft*-PSSEt before and after acetone extraction, and DPNR-*graft*-PSS, respectively. In the spectrum (a), signals appeared at 5.4, 6.0 and 6.8 ppm, which were assigned to vinyl protons of SSEt. In the spectrum (b), the signals characteristic of SSEt disappeared, whereas the broad signals appeared at 4.0 and 6.6-7.8 ppm, which were assigned to methylene protons of ethyl ester and phenyl protons of PSSEt, respectively. In the spectrum (c), signals appeared at 1.8, 2.1 and 5.1 ppm, which were assigned to methyl, methylene and unsaturated methine protons of *cis*-1,4-isoprene unit, respectively. In the expanded spectrum, broad signals characteristic of PSSEt appeared at 4.0 and 6.6-7.8 ppm, and small signals characteristic of SSEt appeared at 5.4 and 6.0 ppm. After acetone extraction of DPNR-*graft*-PSSEt, the signals characteristic of PSSEt appeared as shown in the spectrum (d), suggesting that the graft-copolymerization of SSEt onto natural rubber proceeded. The conversion of SSEt in the graft-copolymerization was estimated from the intensity ratio of the signals, as in the following equation:

$$\text{Conversion of SSEt} = \frac{I_{6.6\text{-}7.8} - I_{6.0} \times 5}{I_{6.6\text{-}7.8}} \times 100 \qquad (1)$$

where I is the intensity of the signals and subscript numbers represent chemical shift (ppm). The estimated conversion of SSEt was 98%. The grafting efficiency estimated from the PSSEt content before and after acetone extraction was 39%.

In the spectrum (e), the broad signals assigned to phenyl protons of PSS appeared at 6.5-7.7 ppm, whereas the signal at 4.0 ppm assigned to methylene protons of ethyl ester disappeared. This is the strong evidence that DPNR-*graft*-PSS is prepared by graft-copolymerization of SSEt onto natural rubber followed by hydrolysis with NaOH.

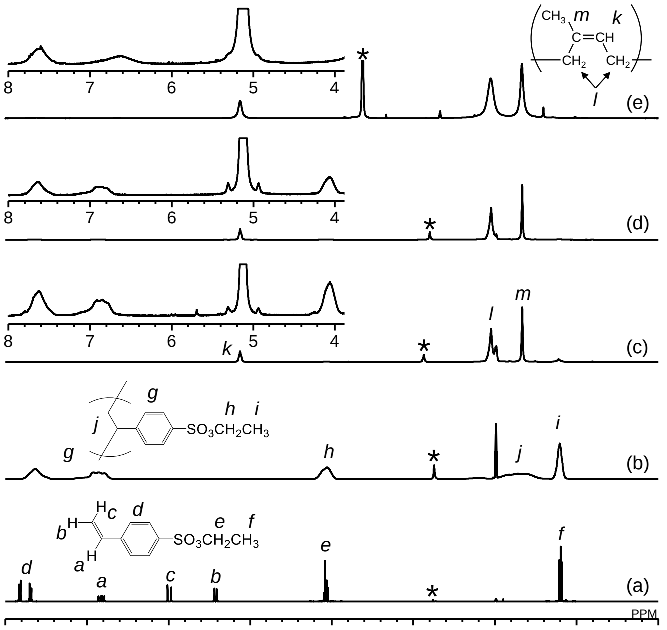

Figure 1. ^{1}H-NMR spectra of (a) SSEt, (b) PSSEt, (c) DPNR-*graft*-PSSEt, (d) DPNR-*graft*-PSSEt after acetone extraction, (e) DPNR-*graft*-PSS. (*H_2O in acetone-d_6 or DMSO-d_6)

Acknowledgement

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Developing and producing piezoelectric rubber composite materials for various industrial applications

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Keywords: Piezoelectric, rubber, polymer composite, $BaTiO_3$.

Nowadays, with the increasing importance and value of smart materials, their use in many sectors is becoming widespread. A material is said to be intelligent if it can react to changes in and around itself and perform the behavior expected of it in an optimal way throughout its entire lifetime. One of the types of smart materials is piezoelectric materials. Piezoelectricity works on the principle that certain crystals create an electric charge when directly subjected to mechanical pressure or tension, called the piezo effect. When these crystals are exposed to an electric field, they undergo a controlled deformation, exhibiting a behavior called the reverse piezo effect [1]. Piezoelectric materials can convert mechanical energy, such as vibration and impact forces applied to the material, into electrical energy, such as electrical voltage and electric current. Rubber materials are used in many sectors, especially due to their superior sealing and anti-vibration properties. Thanks to the fact that rubber materials with piezoelectric properties generate electrical signals during operation, the forces on them and the life of the material can be determined instantly. At the same time, when an electric field is applied to this material, it undergoes a controlled deformation because of the reverse piezo effect, so that the mechanical properties of the material can be changed in a controlled and instantaneous manner. From the literature, there are very limited studies on the investigation of the piezoelectric properties of rubber materials [2] [3] [4]. The aim of this study is to develop piezoelectric $BaTiO_3$ filled natural rubber polymer composites that are environmentally friendly and do not contain toxic elements, improve their properties, and produce the composite with industrial production methods.

In the first phase of the study, natural rubber-based rubber mixture has been produced in the form of plates at High Performance Compounds Kaucuk A.Ş. For the rubber mixture produced, open mill and rubber extrusion in the Angst & Pfister Advanced Technical Solutions A.Ş. has been used and piezoelectric additives at different rates (30-50 vol.%) have been added to ensure homogeneous mixing (Table 1). Within the scope of the study, the composite has been produced with the determined industrial production methods. Piezoelectric properties and the electrical current of the composite under force has been examined, its mechanical properties have been characterized and the connections between these properties have been determined. The piezoelectric rubber composite material to be developed in this study will be produced and shaped quickly and cost-effectively with industrial production methods, and an industrial-ready material will be obtained for sensors, actuators and active-variable suspension bushing and Electric Drive Unit engine mount applications for electric cars.

After the polarization process of composite under different rate of electric fields, piezoelectric coefficient (d_{33}) of composite is increased up to 3 pC/N according to loading of $BaTiO_3$ filler and the rate of applied electric field. Hardness of the rubber composite is increased from 53.6 ShA to 81.4 ShA and tensile strength of the rubber composite decreased from 25.6 N/mm^2 to 1.55 N/mm^2 for the composite which has 50 vol% $BaTiO_3$ filler loading.

Table 1. Sample compositions

Components [vol%]	**Sample notations**			
	B00	**B30**	**B40**	**B50**
Rubber Mixture	100	100	100	100
$BaTiO_3$	00	30	40	50

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Study on the interface of fluorine rubber composites reinforced by functionalized carbon nanotubes based on a two-step process

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Keywords: Fluoroelastomer, carbon nanotubes, nanocomposites, PVDF.

Fluoroelastomer is a highly stabilized polymer fluorine-containing elastomer with a highly stable molecular chain, which is used in various sealing environments under harsh conditions due to its unique stability[1]. In recent years, with the development of automobile, building materials and petroleum extraction industries, and the improvement of energy, aerospace and electronics technologies, new fluoroelastomer materials have been put forward with more stringent requirements.

In the preparation of Viton nanocomposites, carbon nanotubes (CNTs) have attracted a lot of attention for their excellent nanoeffects, and CNTs are susceptible to entanglement or agglomeration due to the presence of strong van der Waals forces, leading to a significant decrease in the properties of composites[2]. Therefore, regulating the amount of CNTs and optimizing their dispersion state in the rubber matrix become the key to obtain high-performance CNTs/rubber nanocomposites[3]. The preparation of high-performance CNTs/polymer composites significantly depends on the interfacial bonding between CNTs and polymer matrix, the dispersion of CNTs in the matrix, and the preparation method of composites[4].

In this paper, we optimize the dispersion effect of the reinforcement in the rubber matrix by using the methods of modification, hybridization and content regulation. Firstly, carbon tetrafluoride (CF4) was used as a fluorine source, and fluorinated carbon nanotubes were obtained by low-temperature plasma treatment of the surface of CNTs. Poly(vinylidene fluoride) (PVDF) was grafted onto fluoride-modified carbon nanotubes (F-CNTs) by using C-F bond as the initiation site. The results showed that the interfacial interactions were enhanced by covalent functionalization, and the Payne effect between the reinforcements was reduced, which was conducive to their uniform dispersion in the rubber matrix. In addition, we examined the effect of CNTs dosage on their dispersion state in the rubber matrix.

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Enhanced mechanical and thermal properties of POSS-FEPM composites using R-group modulation of POSS

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Keywords: Fluorine Propylene Rubber, POSS, crosslinking agent, structure–property relations.

The C-F bond in the structure of Fluorine Propylene Rubber (FEPM) determines its good resistance to high temperature and chemical stability, which makes the rubber widely used in the petrochemical industry [1]. Compared with other rubbers, FEPM has high molecular chain stability and is difficult to be crosslinked, which causes problems such as low crosslinking efficiency and poor mechanical properties. The development of suitable cross-linking system is important for the performance improvement of FEPM [2].

Caged zwitterionic sesquicarbazone (POSS) is composed of a cage skeleton formed by alternating silicone-oxygen bonding, while the silicone-oxygen bonding gives POSS materials good thermal stability, and the cage skeleton gives POSS materials good mechanical properties [3]. The eight top corners of POSS materials are either reactive or inert groups [4]. POSS materials with inert top corners mainly act physically with the rubber matrix, while POSS materials with reactive top corners can form a crosslinked network with the rubber matrix to enhance the mechanical properties and thermal stability of rubber. POSS-based materials have been widely used as cross-linking agents in the preparation of polymers, however, their application in FEPM is relatively rare. Therefore, it is of practical significance to investigate the effect of POSS-based materials with different R groups as co-crosslinking agents on the properties of FEPM for the synthetic design of POSS-based materials and the selection of co-crosslinking agents for FEPM.

In this paper, the effects of different reactive functional groups and different chain lengths of the R groups of POSS materials on the cross-linking behavior of FEPM are analyzed. Then, the type and dosage of the main crosslinking agent were optimized by vulcanization characteristic test, mechanical property test and other characterization methods. The structures of the composites were characterized by IR spectroscopy, ^{13}C-NMR, ^{29}Si-NMR, and X-ray diffraction (XRD). Their mechanical and thermal properties were measured by tensile experiment, thermogravimetric analysis (TGA), and dynamic mechanical analysis (DMA).

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Poster Presentations

Optimization of Curing Conditions of Fluorosilicone Rubber

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Keywords: Fluorosilicone rubber, curing process, rheological and mechanical test.

The main purpose of this study is to investigate the effects of peroxide type, peroxide amount, and Type II co-agent TAIC on the curing and mechanical properties of fluoro vinyl methyl silicone (FVMQ). For this purpose, some compounds have been prepared. While the type of peroxide, and the amount of peroxide were changed in the first batch of compounds prepared, Type II TAIC was added to the second batch of compounds as a fixed amount of co-agent. Fluorosilicone elastomer compounds were prepared in a torque rheometer at 25°C at 50 rpm for 20 minutes. The rheological and mechanical properties of the compounds prepared in the presence and absence of TAIC were investigated. The prepared compounds were cured in a moving die rheometer at 160 °C, 170 °C, and 180 °C, and their rheological properties were examined. To determine the mechanical properties, samples in the form of plates and disks were prepared in a temperature-controlled press. Changes in mechanical properties such as tensile strength, elongation at break, hardness, and rebound were investigated in the presence of peroxide types, and co-agents using a universal tester, hardness tester, and rebound device. To examine the energy absorption capacity of the prepared elastomers, a cyclic compression test with 50% compression with 10 repetitions was applied with a universal test device

When the results of all these studies were evaluated, it was seen that the type of peroxide added to the compounds, the amount of peroxide, and the co-agent had an important role in the rheological and mechanical properties of silicone elastomers. It was concluded that elastomers with an elongation of 200-372% and tensile strength in the range of 5.0-9.4 MPa can be prepared in a controlled manner, depending on the type of peroxide, amount of peroxide and type of co-agent.

At the end of this study, the amount of peroxide, the type of peroxide, the use of co-agents, and the preparation conditions of fluorosilicone elastomers with a wide working range were determined.

Preparation of self-healing thermoplastic elastomers (TPEs) by reactive melt compounding

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Keywords: Thermoplastic elastomer (TPE); Self-healing; Smart materials.

Self-healing polymers and elastomers have been attracted great interests in recent years due to their superior properties such as improved mechanical properties, durability, and service life compared to conventional counterparts. “Self-healing” term as an inspired feature from biological systems, can be defined as the ability of materials to heal themselves autonomously or non-autonomously. When materials can heal themselves without any external stimuli, they are called autonomously self-healing materials. Non-autonomous self-healing materials can be defined as materials that self-heal with external stimuli such as heat, UV, electricity, mechanical effects, etc. [1]. It has been known that thermoplastic elastomers (TPEs) possess elastomeric properties like rubbers and easy processability and recyclability like thermoplastics. In recent years, self-healing rubber and TPEs development work have been extensively studied [2-5].

In this study, self-healing TPEs were prepared by reactive melt-compounding method in an internal mixer given in Figure 1 using poly(styrene-b-ethylene/butylene-b-styrene) (SEBS) and maleic anhydride grafted SEBS (SEBS-g-MAh) as TPE phase, paraffinic oil as plasticizer, 3-amino,1,2,4-triazole as cyclic amine compound and zinc nitrate as metal salt to form metal-ligand interactions. sample compositions and notations are listed in Table 1.

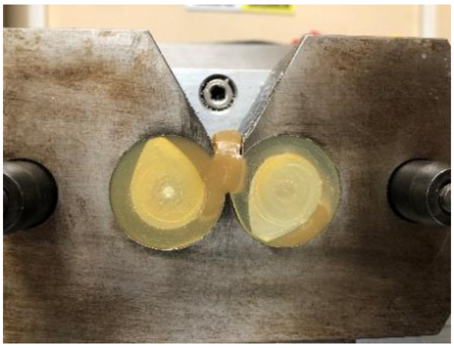

Fig. 1: The photograph of melt mixing device and a representative sample.

Reactive compounds were successfully prepared by the reaction of cyclic amine compound with maleic anhydride, and these functional elastomers formed metal-ligand interactions with zinc nitrate. Structural, morphological, physical, and thermally-triggered self-healing properties of reactive compounds were characterized with various analytical methods and tests such as FTIR, optical microscopy, DMA, tensile tests, and rheological measurements. Self-healing efficiencies of samples were determined as functions of healing temperature varied between 80-120 ºC and different healing times (4, 24 and 48 hours).

Table 1. Sample notations and compositions

Samples	% wt.				
	SEBS	Oil	SEBS-g-MAh	MAh:TA	$Zn(NO_3)_2$
GM20-T-Zn	40	40	20	1:1	TAx0.5
GM40-T-Zn	30	30	40	1:1	TAx0.5
GM60-T-Zn	20	20	60	1:1	TAx0.5
GM80-T-Zn	10	10	80	1:1	TAx0.5
GM100-T-Zn	-	-	100	1:1	TAx0.5
GM100	-	-	100	-	-

TA: 3-amino,1,2,4-triazole

It was found that the physical properties of TPEs strongly depend on the blend composition as expected and these functionalized TPEs showed intrinsic self-healing properties as seen in Figure 2.

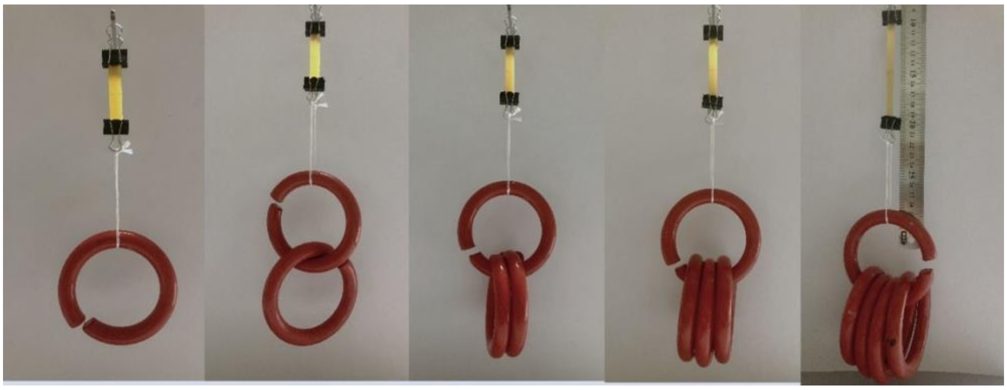

Fig. 2: Representative sample photograps healed at 120 °C for 24 h.

Acknowledgements

Authors would like to thank TÜBİTAK (The Scientific and Technological Research Council of Türkiye, Grant Number of 122M130 and BIDEB 2211-A Program) and İUC-BAP (The Scientific Research Projects Coordination Unit of Istanbul University-Cerrahpasa, Project number of FDK-2020-34522) for financial support to the study.

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Rheological assessment of synthesis of amine functional thermoplastic elastomers (TPE) prepared by reactive melt compounding

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Keywords: Thermoplastic elastomer (TPE); Reactive compounding; Rheology.

It is known that the rheological behavior of multi-component systems such as rubbers, polymer blends, compounds, and composites strongly depends on the chemical and/or physical interactions between components as well as environmental and operational conditions such as temperature, frequency, shear rate etc. Melt rheology tests can be successfully used to quantify dynamics of reactive compounding and blend systems [1-3].

In this study, amine functionalized TPE was prepared with reactive melt-compounding method in an internal mixer using maleic anhydride grafted SEBS (SEBS-g-MAh) as TPE phase and 3-amino,1,2,4-triazole (TA) as cyclic amine compound. Melt-compounding were performed at 165 °C with a screw speed of 75 rpm for 10 minutes. Structural, mechanical, and viscoelastic properties of functional TPE were characterized by various analytical methods and tests such as FTIR, DMA, and tensile test. Different rheological measurements in a rotational rheometry were used to quantify reaction between the functional groups.

The amine functionalization of TPE was successfully achieved with the reaction between amine and maleic anhydride groups as schematized in Figure 1. This reaction mechanism was previously suggested for the preparation of amine functionalized maleic anhydride grafted polypropylene (PP-g-MA) via reactive melt compounding at 195 °C for 5.5 minutes.

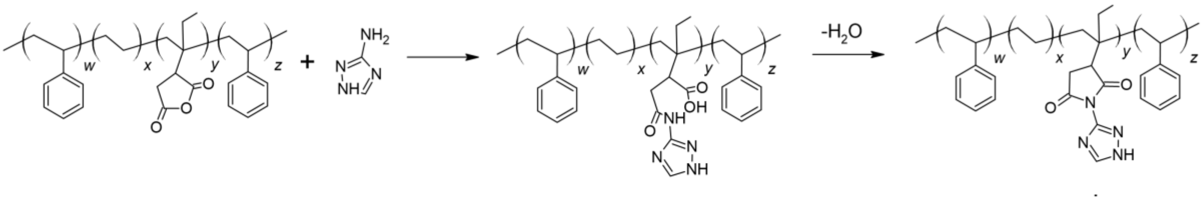

Figure 1. Functionalization reaction between maleic anhydride and amine groups.

Figure 2 compares the frequency dependence of storage modulus (G') and loss modulus (G") of SEBS-g-MAh and modified SEBS-g-MAh.

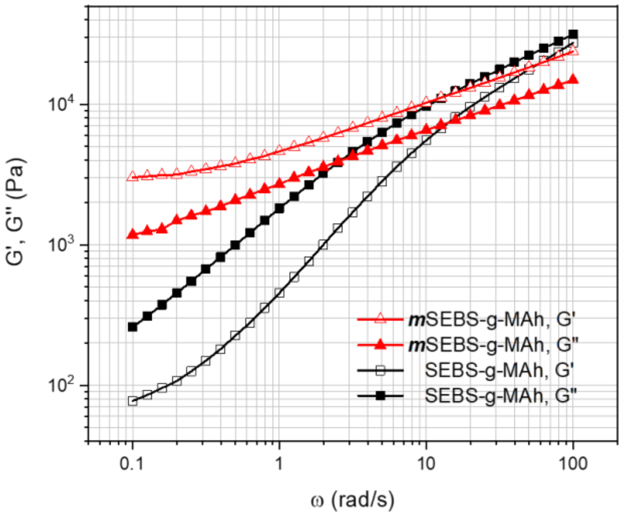

Figure 2. G’ and G” curves of samples as a function of angular frequency.

It was found that modification of SEBS-g-MAh with cyclic amine compound significantly changed the rheological behaviour of SEBS-g-MAh and enhanced its elastic properties due to the formation of dynamic interactions.

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Sustainable Antioxidant Use in EPDM Based Rubber Compounds in Cable Applications

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Keywords: Cable; peroxide vulcanization; EPDM rubber; henna.

Antioxidants are essential additives used to prevent the deterioration of rubber by inhibiting potential oxidation reactions [1]. Nowadays, due to the increasing environmental problems and the negative effects of chemicals on human health, the interest in natural materials is increasing in almost every field. Consequently, research is increasingly focused on identifying natural additives that can be utilized in rubber production. This study investigates the use of henna, a natural substance, as a potential alternative to traditional antioxidant additives in EPDM-based rubber compounds, which are vulcanized using peroxides. Due to its excellent electrical insulation properties, EPDM rubber is frequently used in cable applications [2]. Traditional sulfur vulcanization, as a method for cross-linking, tends to induce adverse effects on the cable's performance. These detrimental effects are effectively reduced by using peroxide vulcanization.

In this study, formulations were designed by gradually increasing the amount of henna in EPDM compounds vulcanized with peroxide, in order to compare them with the reference antioxidant. The reference antioxidant and henna were added into the formulations at concentrations of 1, 2, and 4 phr, respectively. A total of seven samples (D1, D2, D3, D4, D5, D6, D7) were prepared, including a control sample without any antioxidant. Additionally, to estimate the cable lifetime, the samples were subjected to aging at three different temperatures: 135˚C, 150˚C, and 160˚C, for varying durations. The aging temperatures and periods are detailed in the Table 1 below.

Table 1. Aging periods versus aging temperatures

Temperature	**Aging Period (days)**											
	3	5	7	10	12	14	16	18	21	24	26	28
135°C			X			X			X			X
150°C			X	X		X		X	X	X		X
160°C	X	X	X	X	X	X	X	X	X	X	X	X

A laboratory-type Banbury mixer and mill system were used sequentially to prepare the rubber compounds. The rheological properties of the rubber compounds were analyzed using a Mooney viscosity tester. The rheological properties were determined with a moving die rheometer (MDR), and the compounds were molded in a hydraulic hot press according to the optimal curing times. Test samples were cut from the vulcanized plates using standard knives and subjected to mechanical tests. Subsequently, the samples were aged in an air oven at three different temperatures.

Upon examining the test results, it was observed that both the rubber matrix composition and the addition of henna caused significant changes in the final product. These findings were systematically analyzed. When examining the cure torque increment (CE) of henna used as a natural antioxidant, it was observed that the cross-linking level decreases with the increase in the amount of antioxidants, a trend that holds true for both types of antioxidants. This relative decrease in the cross-linking level may be attributed to the increased antioxidant activity, which reduces the effectiveness of the accelerator during vulcanization. When examining the tensile strength values of the vulcanizates before aging, a decrease in tensile strength was observed for the compound with 2 phr of henna, while an increase was noted for the compound with 4 phr of henna. Additionally, an increase in tensile strength was observed with the addition of the reference antioxidant. After aging for 7 days at 135˚C, it was observed that the tensile strength of samples containing 2 phr antioxidants not only decreased less compared to the control sample without antioxidants but actually showed an increase in tensile strength. When samples aged at 150˚C for 7 days, the tensile strength of the sample containing the reference antioxidant decreased significantly (16%), whereas the sample containing 2 phr of the reference antioxidant exhibited the highest relative increase in tensile strength. Overall, the results indicate that henna improves resistance to aging by exhibiting antioxidant properties compared to the control sample that does not contain antioxidants. However, the change rates in compounds containing the reference antioxidant showed slightly better results compared to those with henna. In conclusion, henna can be used as an antioxidant, although it is not as effective as the reference antioxidant. Nonetheless, henna offers added value as a natural additive with a price advantage.

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Influence of various types and amounts of carbon black on the stiffness of rubber bushings

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Keywords: Carbon Black (CB), Mechanical Properties, Rubber Bushing, Stiffness.

Fillers play a critical role in enhancing the performance of rubber compounds. Among these, carbon black is indispensable due to its ability to improve mechanical properties and cost-effectiveness. The types of carbon black are typically determined by production methods (e.g., furnace black), and characteristics such as particle size, structure, and surface activity. Selecting the type of filler while developing the compound, product's requirements is of great importance.

In the automotive industry, rubber-metal parts are crucial for vehicle performance and safety. Rubber bushings, commonly used in vehicle suspension systems, perform essential functions such as damping vibrations, reducing road noise, and providing flexible connections between moving parts. Consequently, enhancing the mechanical properties of rubber bushings directly impacts vehicle performance and comfort.

This study aims to investigate the effects of different types and amounts of carbon black on the stiffness properties of rubber bushings. The rubber compounds will be prepared using different amounts of N550, N660, and N990 carbon black fillers, and rubber bushings will be produced from these compounds. Hardness tester, universal tensile test machine, heat buildup, rebound, and rubber process analyzer will be used to examine mechanical and dynamic properties of the compounds. On the other hand, the stiffness of the bushings will be evaluated using a servo-hydraulic testing system. The results will be correlated with the mechanical and dynamic test results at compound level. Thus, the correlation between filler type and product performance will be determined.

Effect of Phenyl and Silica Content on The Enhanced Damping Properties of Vinyl Dimethyl Terminated Methyl-Phenyl Polysiloxane (PVMQ) Elastomers

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Keywords: PVMQ, Elastomer, Silica, Damping

This study investigates the impact of phenyl and silica content on the mechanical and damping properties of Vinyl Dimethyl Terminated methyl-phenyl polysiloxane (PVMQ) elastomers. PVMQ elastomers, known for their flexibility, chemical resistance, and thermal stability, are widely used in industries such as aerospace, automotive, and electronics. Introducing phenyl groups can improve silicones' damping properties, as phenyl groups enhance energy dissipation. Additionally, incorporating silica into the silicone matrix further strengthens the material's mechanical properties and increases its damping capacity.

In this research, PVMQ elastomers with varying levels of phenyl and silica content were prepared to examine their cure characteristics, mechanical properties, and dynamic mechanical behavior. The findings indicate that an increase in silica content leads to a higher complex modulus, suggesting improved stiffness and resistance to compression. The study also reveals that dynamic stiffness changes with frequency, where the 8603SIL50 sample demonstrates the highest stiffness, particularly at higher frequencies. Furthermore, increasing phenyl and silica content raises the natural frequency of PVMQ elastomers, enhancing their performance as dampers at higher frequencies.

The dynamic mechanical analysis demonstrates that higher silica content increases tan delta values, indicating improved viscoelastic behavior. This enhancement allows the material to dissipate more energy and effectively dampen vibrations. The results suggest that by optimizing the phenyl and silica content in PVMQ elastomers, we can develop materials with superior vibration and noise reduction capabilities, paving the way for significant advancements in advanced engineering applications.

The Effect of Extrusion Process Parameters on Sponge Profile Cross- Section and Mechanical Properties

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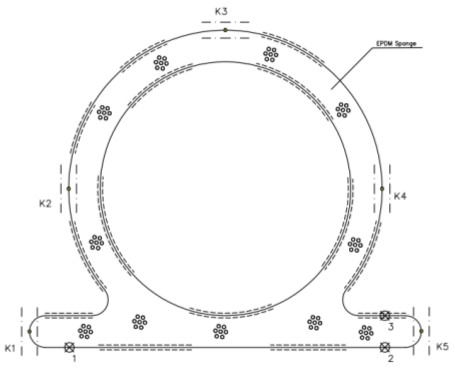
Keywords: EPDM rubber; extrusion; sponge profile; optimization

This study investigates the effects of various extrusion process parameters on the characteristics of a simple shape sponge profile. Utilizing a design of experiments (DOE) approach, the influence of extruder temperature, infrared (IR), ultra-high frequency (UHF), and high-temperature unit (HTU) settings on the blowing behavior of the sponge profiles was analyzed. The key performance metrics measured include density, cross-sectional area, compression load deflection (CLD), and compression set.

The experimental trials were conducted with different combinations of the process parameters. Samples were collected and tested, and the results were analyzed to determine the significant factors affecting the sponge profile properties. Pareto charts and regression models were employed to identify the main effects and interactions among the process parameters.

The findings indicate that HTU, UHF, and their interactions with IR and extruder temperature significantly impact the density and cross-sectional area of the sponge profiles.

This comprehensive analysis provides valuable insights into the optimization of extrusion process parameters to enhance the quality and performance of sponge profiles. The results highlight the importance of precise control over process conditions to achieve desired material properties.



Cross section of the trial die

Large amplitude oscillatory shear rheology of liquid silicone rubber: insights into filler structure and viscoelasticity

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Keywords: liquid silicone rubber; rheology; simulation; viscoelasticity.

One of the most employed methods to determine polymers' resistance to shear flow is applying rotational rheology under oscillatory shear, which is able to quantify complex viscosity η^* values. In the case of liquid silicone rubber (LSR), the linear viscoelastic conditions necessary to achieve meaningful η^* values are limited to small strain amplitudes (SAOS, or small amplitude oscillatory shear) [1] that are not compatible with the shear range experienced during injection moulding. However, departing to large amplitudes (LAOS) leads to a non-linear viscoelastic scenario that is complex to analyse [2], mainly concerning the calculation of η^*. Within this context, the present work introduces considerations concerning non-linear viscoelasticity of liquid silicone rubber and how these considerations impact the determination of η^*. By employing a strain-controlled rheometer (cone-and-plate geometry), LSR samples (32wt% filler, $M_w = 88673$ g.mol^{-1}) were analysed under linear (SAOS) and non-linear (LAOS) viscoelastic conditions and the deviation to linearity was assessed.

As shown in **Figure 1**, G' presented fairly constant values up to $\gamma = 0.2\%$, while G" remained constant until $\gamma = 0.6\%$. The range up to 0.2% can be then defined as the linear viscoelastic range for this sample, in accordance with Weißer et al. [1]. Within this range, G' > G", meaning that the sample behaves as an elastic solid gel. The solid gel-like behaviour can be justified by the high content of filler particles and the molecular weight above the critical molecular weight for entanglements formation (32 kg.mol^{-1} according to [3]). As the strain amplitude increases, the sample departs from mechanical equilibrium and G' and G" decrease, i.e., shear thinning occurs. Shear thinning is the consequence of two phenomena: chain orientation and microstructure alignment along the flow direction and breakage of the filler structure (Payne effect). The passage from G' > G" to G' < G" represents the transition between the solid gel-like and the liquid-like states of LSR, where it goes from low to high fluidity.

As a quantitative parameter to measure non-linearity, the 3rd harmonic's intensity $I_{3/1}$ in relation to the strain amplitude is also shown in **Figure 1** (right). Below $\gamma = 0.1\%$, $I_{3/1}$ varies with the instrument noise and is lower than 0.01. While the strain amplitude further increases, $I_{3/1}$ increases with γ^2 for sufficiently small amplitudes. $I_{3/1} \propto \gamma^2$ already occurs even when G' and G" seem to be constant, which means that phenomena ultimately leading to non-linearity already take place. The apparent two-step increase of $I_{3/1}$ may be related to the changes in the interactions among poly(siloxane) oligomers (entanglements, for example) and to the filler microstructure damage. From the $I_{3/1}$ values, it is reasonable to state that at $\gamma = 0.1\%$ the fundamental harmonic fully describes the stress response. At γ = 10%, however, $I_{3/1}$ reaches 0.1, which signifies that the 3rd harmonic is 10% of the fundamental harmonic, indicating non-linearity. At 10% strain, though, LSR's microstructure in terms of polymer-polymer, filler-filler, and polymer-filler interactions is closer to the one that is found during the injection moulding cycles.

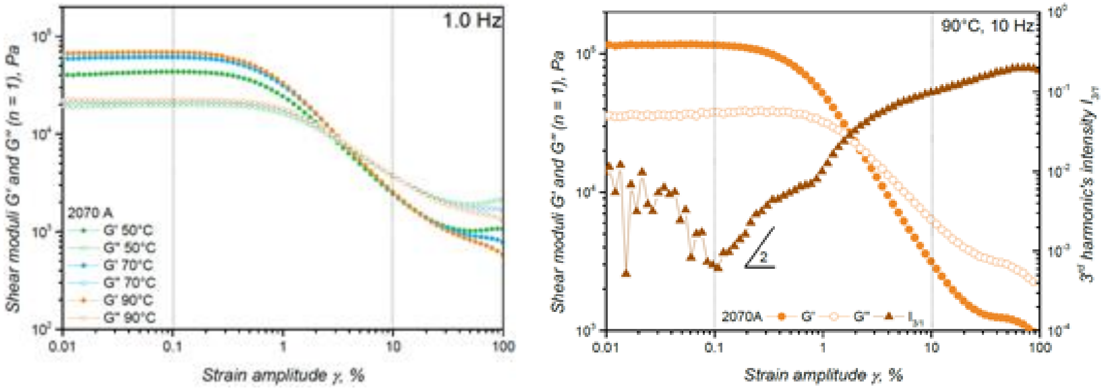

Figure 1. Variation of G' and G'' (left) and of the 3rd harmonic's intensity (right) with imposed strain amplitude

Thus, the variations of G', G", and η^* with the imposed frequency was studied at 10% amplitude and are shown in **Figure 2**. G' and G" increase with frequency due to the response of the polymer chains to the rapid applied strain associated to high frequencies. At the lowest frequency, the close-to-terminal slopes for G' and G" are obviously different and lower than respectively 2 and 1 for net PDMS as theorized by the Rouse model, since solid fillers are incorporated to the polymer matrix. The main difference between frequency sweeps at 0.1% and 10% is the sample's state during the decreasing frequency sweep. At 0.1%, the filler structure is intact, justifying G' > G", while at 10% the filler structure is damaged and G" overcomes G'. This is an important consideration when calculating complex viscosity, also shown in **Figure 2** (right). Complex viscosity values are lower for 10% amplitude due to the destruction of the filler structure; however, these values represent more faithfully LSR's condition during injection moulding. Therefore, the *modus operandi* for complex viscosity determination should be adjusted to account for these morphological changes, mainly when determining the resistance to shear flow for processing simulation purposes.

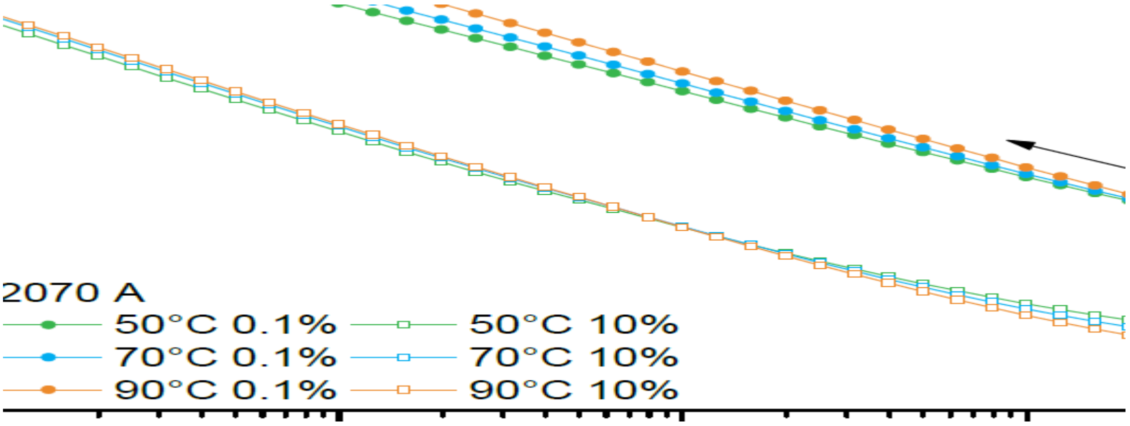

Figure 2. Variation of G' and G'' with strain frequency (left) and the calculated complex viscosity (right)

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Conductive nanocomposite of epoxidized natural rubber filled with carbonaceous fillers for strain sensing application

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Keywords: Conductive rubber nanocomposite; carbonaceous filler; graphene oxide; carbon nanotube.

Flexible strain sensors have been widely used for human motion monitoring. The key feature of this device is the changeability of electrical signal responsive to human motion. Although its stretchability and flexibility make natural rubber the assuming candidate for this application, intrinsically natural rubber is limited for this application because of its lack of electrical conductivity. The incorporation of conductive filler is highly required [1-3].

For this study we aim to develop natural rubber nanocomposites with capably electrical-conductive property by incorporating carbon nanotubes (CNT) and graphene oxide (GO). Previously, it was reported that for strain sensor application the epoxidized natural rubber is superior to unmodified one [4-5]. It demonstrated not only its inherently higher conductivity but also better CNT dispersion. Therefore, here the epoxidized natural rubber with 50% epoxidation (ENR 50) was used as a matrix. Graphene oxide was synthesized in-house from graphite by Hummer's method via oxidation. Nanocomposite was prepared by latex compounding method and followed by a sample casting method. Formular of latex compounding is given in Table 1. Firstly, the appropriate CNT quantity giving rubber nanocomposite the highest electrical conductivity was investigated. Then, once the appropriate CNT loading was revealed, the effect of CNT to GO ratios on the electrical conductivity and strain response performance of hybrid nanocomposite was determined.

The results showed that with increasing CNT loading from 1 to 6 phr, the electrical conductivity and tensile strength of ENR50 nanocomposite passed through the maximum value at the 5 phr of CNT. When GO was added, it was discovered that at the CNT:GO ratio of 5:1, the obtained hybrid nanocomposites showed higher tensile strength and electrical conductivity than the one filled with sole CNT. Obviously, with higher GO loading, both electrical and mechanical properties of hybrid nanocomposites were deteriorated.

Figure 1 compares the strain-sensing capability under the tension mode at 100% and 150% strain of ENR50/CNT5 and ENR50/CNT:GO at the ratio of 5:1. Clearly, the strain sensing of conductive hybrid nanocomposite showed more stable electrical resistance than that of ENR25/CNT5. The appropriate amount of GO seems to be the important part enhancing the performance of rubbery strain-sensor.

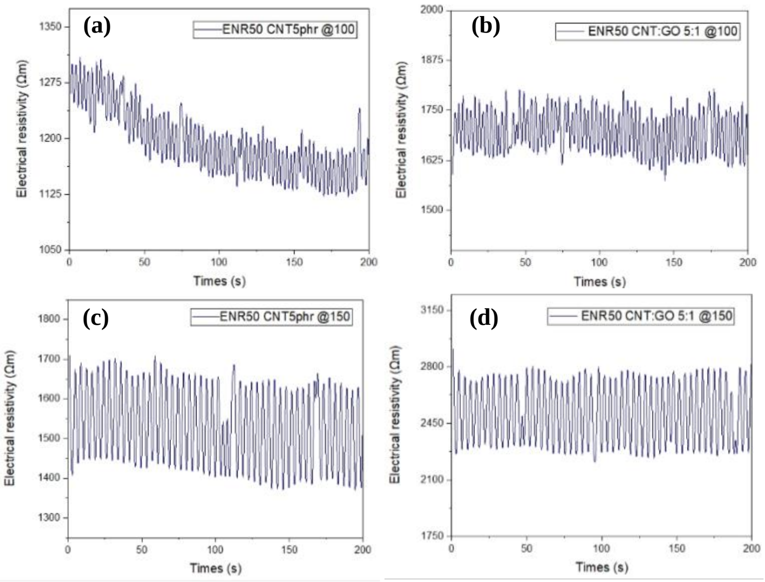

Figure 1. Piezoresistivity of (a), (c) ENR50/CNT5 and (b), (d) ENR50/CNT:GO at ratio of 5:1 at 100% and 150% strain

Table 1. Formular of latex compounding

Components	**Loading (phr)**
Epoxidized natural rubber[1] (ENR25, ENR50)	100
50% Zinc Diethyl Dithiocarbamate (ZDEC)	1.25
50% Wingstay L	1.00
50% Zinc oxide (ZnO)	3.00
50% Sulfur (S)	2.00
20% Potassium laurate (K-laurate)	1.00
10% Potassium hydroxide (K-OH)	0.25

[1] ENR is in latex form with DRC 40%

Acknowledgement

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Study on morphology and composition of a single tire-road wear particle (TRWP)

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Keywords: tire-road wear particle; single particle analysis; rubber composition; morphology.

Tire wear particles (TWPs) are generated by the friction between tire and road. TWPs commonly found in the environment are surrounded by various inorganic particles and are called tire-road wear particles (TRWPs) [1-3]. TRWPs are considered a broad definition of microplastics and act as a source of environmental pollution by moving into various environmental compartments [4,5]. They are heterogeneous in the physical and chemical properties, such as shape, diameter, density, and composition. Therefore, there is a need for characterizing TRWP in complex environmental samples. For accurate characterization of wear particles, analyzing individual particles is desirable. Pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) is suitable for the analysis of TRWP, which are predominantly composed of rubber, and can analyze even small amounts of samples [6-8]. In this study, TRWPs isolated from road dust samples collected from various locations (bus stop, taxi stand, and parking garage) were analyzed using Py-GC/MS. Before Py-GC/MS analysis, we analyzed their morphologies using a digital microscope. The characteristic pyrolysis products of NR, BR, and SBR, namely, dipentene, 4-vinylcyclohexene, and 4-phenylcyclohexene, respectively, were utilized to determine the rubber composition of individual TRWPs. The rubber composition of a single TRWP varied depending on the sampling site. Based on the observation that the tire treads of typical bus and passenger car are composed of NR/BR and SBR/BR, respectively, we discussed the sources of individual TRWP.

Acknowledgement

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Identification of Dynamic Mechanical Properties of Radiation Modified Silicone Elastomers by Dynamic Mechanical Yerzley Oscillograph

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Keywords: silicone; radiation; dynamic-mechanical properties.

One of the application areas for silicone elastomers is the production of vibration-damping materials. Noise and vibration are undesirable situation in many structures, such as rockets, spacecraft, automobiles, and white goods because they reduce the performance, stability, and lifetime of such structures. High-damping silicone elastomers used in space technology and nuclear technology are exposed to radiation. Thus, investigation of the effects of ionizing radiation on the damping capacity of silicone elastomers is important.

In our recent study, we investigated the impact of radiation on silicone elastomers' damping and energy dissipation properties in static conditions at low frequencies [1]. This study aims to determine the effect of radiation on the damping capacity of phenyl-vinyl-methyl-polysiloxane (PVMQ) and vinyl-methyl-polysiloxane (VMQ) elastomers at the natural frequency by using a Dynamic Mechanical Yerzley Oscillograph (DMYO-5). VMQ and PVMQ elastomers were cured in the presence of a Pt-catalyst and then irradiated up to 80 kGy. To examine the effect of absorbed dose on the dynamic mechanical properties of silicone elastomers at a natural frequency such as tan delta, Yerzley resilience, Yerzley hysteresis, dynamic compressibility, absorbed energy and energy density were calculated using DMYO.

As a result, these studies have proven that the dynamic mechanical properties of silicon elastomer, such as energy dissipation and damping at the natural frequency, can be changed in a controlled manner with ionizing radiation. It has also been observed that if VMQ or PVMQ is used in the preparation of silicon elastomer-based damping material, the effect of ionizing radiation on the dynamic mechanical properties is different.

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Investigation of the Effect of Waste Onyx Stone Powder on the Properties of Ethylene Propylene Diene Monomer (EPDM) Rubber

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Keywords: EPDM, waste onyx powder, Rheology, Mechanical properties.

Currently, efforts are being undertaken to recycle and repurpose cutting waste from the natural stone industry by producing new products and using them as additives in various sectors. This study aims to functionalize waste onyx powder obtained from the Cappadocia region by incorporating it into Ethylene Propylene Diene Monomer (EPDM) rubber, thereby contributing to the economy. Waste onyx powders were added in weight ratios of 10%, 20%, and 30%. The waste onyx powder was compounded with EPDM rubber using a 1.5-liter laboratory-scale mini Banbury mixer. The resulting compound was vulcanized in a press at 180°C for 20 minutes to produce test plates. The rheological and flow properties of the EPDM rubber with added waste onyx powder were examined using pre-press rheometry (MDR) and Mooney viscosity tests. To determine mechanical properties, tensile and compression tests were conducted; to determine physical properties, density and Shore A hardness tests were performed; and dispersion analysis was carried out to evaluate the distribution of additives in the EPDM rubber. The study concluded that the addition of waste onyx powder affects the rheological and mechanical properties of EPDM rubber. It was evaluated that waste onyx powder could be a potential alternative to the white fillers used in EPDM rubber production.

Effect of different vulcanization systems on physical and dynamic properties of EPDM rubbers

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Keywords: EPDM; vulcanisation systems; nitrosamine-free accelerators.

EPDM-based rubbers are widely used in industrial applications due to their high resistance to heat, ozone and weathering conditions. In recent years, it has been reported that some accelerators, which are extensively used in rubber formulations and consist of secondary amine groups, release harmful nitrosamine compounds via various thermal and/or chemical decomposition reactions [1,2]. Nitrosamines are also generated during the mixing, vulcanisation and storage of rubber articles. Several studies showed that nitrosamines can cause cancer in various animal species, therefore they have been considered to be potential carcinogens in humans. Therefore, one of the recent green trends in rubber science and technology is to replace these accelerators with alternative compounds classified as “nitrosamine-free” chemicals [3]. TMTD is very widely used as a primary and sulphur donor-standalone accelerator in traditional sulphur curing systems. Sheet et al. studied on the replacing of TMTD with Nitrosamine Free TBzTD in butyl rubber formulation and reported that TMTD can be replaced with TBzTD and ZAT type accelerators with a slight tweak in secondary accelerator type and level in the curing system [4].

In this study, different vulcanization systems were used in EPDM rubber formulations, as alternative compounds, classified as non-nitrosamine or safe category and tested. EPDM base rubber was prepared in a lab-scale (1.5 L) banbury operated at 110 °C for 5 minutes then the vulcazition agents were introduced in a two-roll mill operated at 60 °C for 2 minutes. Sample formulations and notations are given in Tables 1 and 2. Then samples were molded and vulcanized in a hot pres at 180 °C under the pressure of 200 bar.

Physical and mechanical properties of samples were characterized with measuring the rheological behavior (Alpha MDR 2000), density, hardness (ISO 48-4:2019), and compression set (ISO 815-1 Methot A) values, tensile (DIN 53504) and tearing (ISO 34-1) properties. Thermal and chemical agings were also applied to the samples and loss in physical properties was monitored depending on the type of vulcanization agents. Stress relaxation behaviors of samples were measured in a dynamic mechanical analyser (DMA) under an instantaneous deformation of 20% at 120 °C for 30 minutes.

Table 1. Compositions of EPDM base rubber

	EPDM (KEP 570)	Paraffinic oil	CB (Fef N550)	ZnO	Stearic acid	PEG4000
Base Rubber (phr)	100	70	112	3	1	1

Table 2. Compositional variation with different vulcanization agents

(phr)	CP1	CP2	CP3	CP4	CP5	CP6	CP7	Nitrosamine Class
S	0.75	0.75	0.75	0.75	0.75	0.75	0.75	S
CBS	0.70	0.70	0.70	0.70	0.70	0.70	0.70	S
MBT	2.0	2.0	2.0	2.0	2.0	2.0	2.0	F
ZDBC	1.0	1.0	1.0	1.0	-	-	-	G
TMTD	-	0.5	-	-	-	-	-	G
TBzTD	-	-	0.5	1.0	1.0	1.0	1.0	S
ZBEC	-	-	-	-	1.0	2.0	1.0	F
ZDTP	-	-	-	-	-	-	2.0	F

S: Safe, **G**: Generator, **F**: Free

It was found that the alternative accelerator compounds were not as active as the commonly used conventional compounds. Although the different accelerators exhibited similar physical properties before aging, loss in physical properties of such vulcanizates after different aging conditions was found to be higher than the conventional compounds. But, it has been concluded that higher physical properties and durability might be achieved by increasing the amount of compound in formulation.

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Baseline study on the influence of sulfuric acid on the aging behavior of elastomer sealing materials in PEM fuel cells

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Keywords: PEM fuel cell; accelerated aging; sealing material; degradation

The selection of suitable sealing materials in polymer electrolyte membrane (PEM) fuel cell stacks is a crucial step to guarantee a good performance over an extended lifetime (Fig. 1). These seals are in contact with a variety of media such as hydrogen, hot air, deionized (DI) water, and sulfuric and hydrofluoric acid. A superior chemical resistance, especially towards acids, is key to allow for a prolonged seal integrity. Liquid silicon rubber (LSR), ethylene propylene diene monomer (EPDM) rubber and fluoroelastomers (FKMs) are generally considered as suitable options in this regard.[1] Many studies have been conducted to evaluate their degradation behavior under fuel cell conditions. Typically, a mixture of sulfuric acid and hydrofluoric acid is chosen to mimic the actual conditions in a fuel cell (pH ~ 3) and accelerated aging is performed by increasing the concentration of these two components to pH levels below one. The temperatures in these studies match the typical PEM fuel cell operation conditions, or are further elevated to accelerate aging.[2-4] In this study, LSR, EPDM and FKM materials are evaluated in terms of their aging behavior. Aging solutions consisting of only sulfuric acid were applied and pH values were set to values significantly below the operation conditions. A fuel cell typical temperature of 80°C was chosen and aging times up to 168 h were selected. The increased acid concentrations allow for shortened aging times of one week. Furthermore, it provides a simplified, less toxic evaluation of the likely proton driven aging pathways and gives a better understanding of the role of sulfuric acid being the dominant acidic substance in the application. Rubber samples are submitted to hardness, tensile strength and compression set measurements before and after aging experiments. Volume and weight changes are recorded. Surface changes are evaluated by scanning electron microscope (SEM) analysis and the degree of degradation is investigated via spectroscopy methods analyzing the aged rubber as well as the material residues in solution.

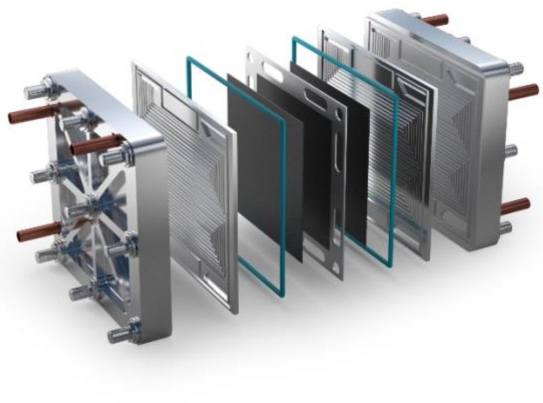

Figure 1. PEM fuel cell stack with applied elastomeric seal (blue).

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Homopolymer Based Magnetorheological Elastomer

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Keywords: Magnetorheological, Adaptive tuned, Epichlomer, Vibration isolation

I. INTRODUCTION

Magnetorheological elastomers (MREs) are a type of composite material, whose physical or mechanical properties can be altered upon the application of a magnetic field. MREs can be usually prepared by mixing micron-sized magnetic particles into rubberlike matrices. In the presence of a magnetic field, MREs exhibit an effect providing a field-dependent physical or mechanical property, for e.g. a controllable modulus, due to the sensitive response of the magnetic particles to the field. When the field is removed, MREs will reclaim their original property.

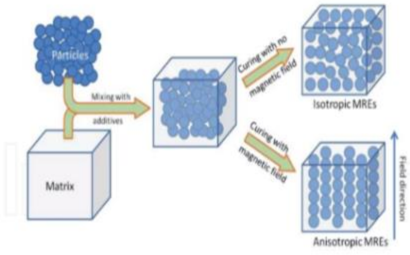
First research on MREs was reported by Rigbi and Jilken in 1983, although the discovery of the basic magnetorheological effect was done in 1940s for magnetic fluid. MREs are nothing but solid-state version to magnetorheological fluids (MRFs). They overcome major issues faced in MRFs, for example, the deposition of iron particles, sealing problems, and environmental contamination. Such advantages offer MREs great potential for designing smart devices to be used in various engineering fields, especially in fields that involve vibration reduction, isolation, and absorption.

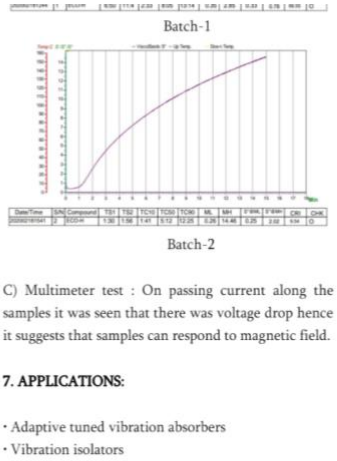
II. MATERIALS:

A) Magnetically polarisable particles Magnetic particles of higher permeability & higher saturation magnetization are highly desirable for obtaining stronger magnetic field-sensitive effect.Carbonyl iron (CI) powder is currently widely used as a magnetic particle for preparing MREs. Diameter of this kind of CI powder is in micrometers.The value of saturation magnetization can reach more than 600 kA/m and there is little remnant magnetization when magnetic field is removed. This results from the fact that the content of Fe element in CI powder is usually more than 97.5% in weight fraction.

B) Rubber Matrix: Elastomers containing polyepichlorohydrin, also known as ECO, CO, or GECO according to ASTM, offer an excellent balance of properties, combining certain desired dynamic properties of natural rubber (NR), with much of the fuel, oil, and chemical resistance of other specialty elastomers such as nitrile (NBR), polyacrylate (ACM), and neoprene (CR) rubbers. ECO-H provides properties such as Oil & Fuel resistance, Solvent resistance, Good gas impermeability, Heat &Weather resistance, Good mechanical & physical properties, Damping Properties.

C) Other regular ingredients: Besides the magnetic particles and the elastic matrices, additives are also key components for preparing MREs. Activator to activate the acceleration of curatives. Curative along with acid acceptor to cure the rubber. Plasticizers for the softening. More dosage of plasticizer improves CI effect. Reinforcing fillers to reinforce the rubber matrix. Other silane agent for good coupling of CI powder. Ester adipate is plasticizer. NDBC (Nickel-dibutyldithiocarbamate) works as antioxidant here. N-550 i.e. FEF Carbon black is reinforcing filler. Recipe: Ingredient Batch-1 (phr) Batch-2 (phr) ECO-H 100 100 NDBC 2 2 N-550 80 80 CI Powder 40 40 Ester Adipate 12 12 MgO(Acid acceptor) 5 5 VtMoEo(Silane) 2 2 NA-22(ETU) 1.5 1.5 S 0 0.5 CBS 0 0.5




Batch-1

Batch-2

C) Multimeter test : On passing current along the samples it was seen that there was voltage drop hence it suggests that samples can respond to magnetic field.

7. APPLICATIONS:

- Adaptive tuned vibration absorbers
- Vibration isolators

II. APPLICATIONS:

Adaptive tuned vibration absorbers, Vibration isolators, Variable stiffness bush, Adaptive tuned dampers, Magneto-sensitive strain sensors, Actuators, MEMS Magnetometer

III. ACKNOWLEDGEMENT:

We sincerely thank Prof. Rupande Desai (Head of Department) and Rubber technology department of L.D. College of Engineering for their immense support to accomplish this research work.

VIII. REFERENCES

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Enhancing Rubber Sustainability: The Role of Lignin in Rubber Compounds

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Keywords: renewable sources; rubber-lignin composites; sustainable materials; rubber reinforcement.

The use of naturally sourced components in rubber compounds is gaining importance due to increasing environmental concerns and the demand for sustainable materials. Lignin, a biopolymer derived from renewable sources, presents a promising alternative to traditional petrochemical-based additives in rubber compounds. This biopolymer not only enhances the material properties but also contributes to environmental sustainability by improving antioxidative stability, extending service life, and reducing the emission of harmful chemicals and particles. However, the inherent rigidity and polarity of lignin require the use of plasticizers to improve its compatibility and dispersion within the non-polar rubber matrix. [1], [2], [3], [4].

This study investigates the effects of lignin, specifically calcium lignosulfonate (*CaL*; Borregaard Deutschland GmbH, Germany) and kraft lignin (*kL*; UPM Biochemicals GmbH, Finland), on rubber properties. The research emphasizes optimizing processing methods to enhance lignin's compatibility with rubber, thereby maximizing its potential as a reinforcing and antioxidative additive. Utilizing plasticizers is one of the most cost-effective and straightforward strategies to improve polymer processability. The effect of a plasticizer largely depends on its chemical structure and molecular weight, as well as the nature of the targeted polymer. For this reason, glycerol and sorbitol were used for the plasticization of lignin. Improved adhesion and homogeneity between the rubber and the biopolymer at their interface were expected to enhance the mechanical properties of the final materials. This expectation proved correct, as depicted in Figures 1 and 2. Significant differences can be seen in the mechanical properties when using *CaL* and *kL*. Higher tensile strength was achieved using *kL* without a plasticizer, which can be attributed to the fact that *kL* has a broader molar mass distribution, allowing it to essentially plasticize itself. Different plasticizers evidently result in varying mechanical properties, but it was concluded that 10-15 phr of plasticizer is the optimal amount for achieving enhanced flexibility of lignin parts and better interaction with the rubber matrix. The downside of using polar plasticizers in a polar matrix (such as *NBR*) is that they can migrate into the matrix, thus disrupting its characteristics, which can manifest as an increase in elongation at break (Fig.2).

Notably, glycerol and sorbitol are not only effective plasticizers but also environmentally friendly options. As biobased and biodegradable compounds, they align with the growing demand for sustainable and eco-friendly materials in the rubber industry. Their use contributes to reducing the overall environmental impact of rubber production, further enhancing the appeal of lignin-based composites. To further enhance the performance and stability of such composites, ongoing research could explore alternative plasticizers or compatibilizers that mitigate migration issues. Additionally, investigating the long-term effects of plasticizer migration on the durability and performance of the rubber-lignin composites will be essential to fully harness their potential for industrial applications.

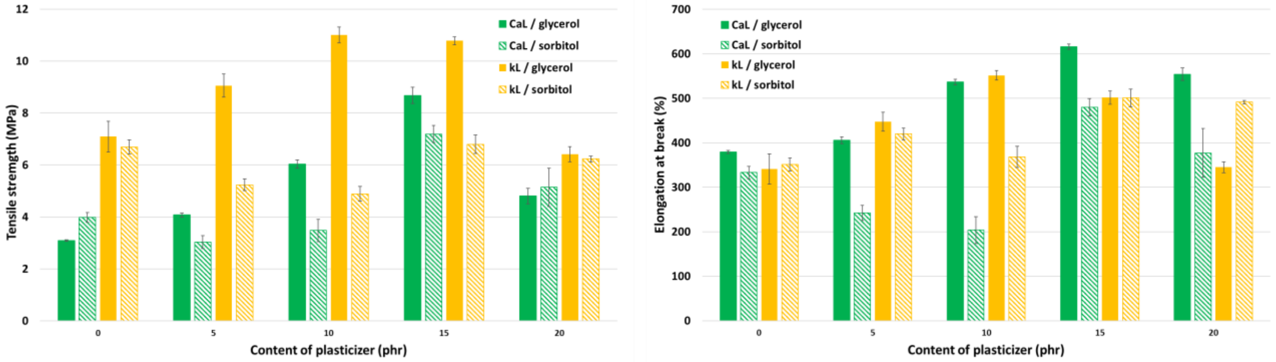

Figure 1. Dependence of tensile strength and elongation at break on the plasticizer concentration in ***nitrile rubber*** blends containing both calcium lignosulfonate (CaL) and kraft lignin (kL)

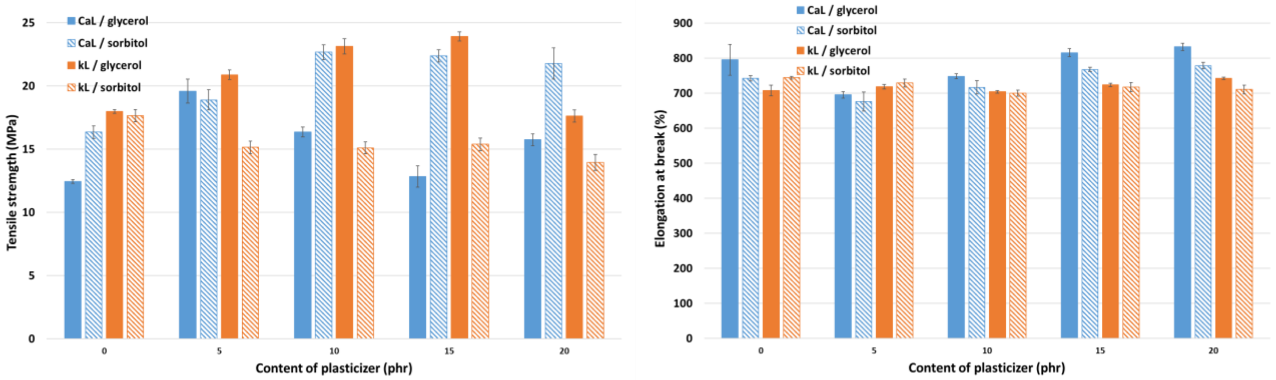

Figure 2. Dependence of tensile strength and elongation at break on the plasticizer concentration in ***natural rubber*** blends containing both calcium lignosulfonate (CaL) and kraft lignin (kL)

Acknowledgement

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Effect of vinyl silane trated aluminium hydroxide and huntite on silicone rubber's flame retardancy

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Keywords: Silicone, Flame Retardancy, Aluminium hydroxide, Huntite.

Silicon is known as the second most abundant element on earth's crust with a percentage of 27,7% [1]. This versatile element is used in a wide variety of industries, such as agriculture or gasket manufacturing. Its polymeric structure is composed of silicon-oxygen bonds [2]. The inorganic molecular structure gives silicone rubber superior properties in comparison with organic rubbers. Properties like good heat stability, flexibility, resistance to ozone and UV stem from Si-O bond. Si-O bond energy is about 106 kcal/mole which makes it very stable and Si-O-Si bond angle is 143° which makes it significantly more elastical.

Vinyl methyl silicone (VMQ) is a commonly used synthetic silicone rubber since it has resistance to chemicals, high-temperature resistance and biocompatibility. The methyl side group in the structure imparts elasticity to the polymer, while the vinyl side group provides resistance to permanent deformation and enhances temperature resistance. Although it does not melt when it is exposed to flame, it can burn and conduct the flame [3]. Flame retardant additives, mostly mineral salts, are used to improve VMQ flame retardancy [4].

In this study, the effect of vinyl silane treated ATH (Aluminium hydroxide) and huntite flame retardant additives was tested with vertical burning UL94 and limting oxygen index (loi) test methods. Eight different recipes as shown in Table 1 were prepared in the two-roll mill mixing system. Identical types of vinyl methyl silicones (VMQ) and equivalent quantities of Bis(2,4-dichlorobenzoyl) peroxide catalysts (DCLBP) were utilized, varying only the amounts of aluminium hydroxide (ATH) mixed. In four of these recipes, 10 phr of amount huntite was added as a blend with ATH. Since huntite is known to deteriorate the mechanical properties of silicone, it was not added to the recipe at a higher amount.

Table 1 Sample compositions

Sample ID	VMQ	ATH (phr)	Huntite (phr)	DCLBP (phr)
S	100	0	0	1,5
S-ATH20	100	20	0	1,5
S-ATH30	100	30	0	1,5
S-ATH40	100	40	0	1,5
S-H	100	0	10	1,5
S-ATH20-H	100	20	10	1,5
S-ATH30-H	100	30	10	1,5
S-ATH40-H	100	40	10	1,5

As shown in the table 2, with the content of ATH increased, the LOI of samples also increased, which was 38,2% when 40 phr ATH was added. It was concluded that S-ATH40 recipe containing flame retardant has an UL94 V0 rating. On the other hand, when huntite is added to the recipes, LOI values increase further. As a result, blends of ATH and huntite improve flame retardancy properties.

Table 2 UL-94 and LOI test results of the samples

NO	ID	UL-94 CLASS	LOI	NO	ID	UL-94 CLASS	LOI
1	**S**	**V1**	**29,5**	**5**	**S-H**	**V1**	**31,9**
2	**S-ATH20**	**V1**	**31,2**	**6**	**S-ATH20-H**	**V1**	**33,5**
3	**S-ATH30**	**V1**	**35**	**7**	**S-ATH30-H**	**V0**	**40,402**
4	**S-ATH40**	**V0**	**38,2**	**8**	**S-ATH40-H**	**V0**	**40,408**

Although it is known that the mechanical properties of silicon deteriorate as huntite is added, it has been determined that adding only 10% does not deteriorate the mechanical properties much. In addition to all these tests, thermogravimetric analyzes are conducted to be able to observe decomposition temperature.

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Preparation And Characterization of Advanced Technology High Damping Earthquake Isolator Rubber Composites

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Keywords: HDRB (High Damping Rubber Bearing), Isolator, Rubber Bearing, Seismic Isolator.

Seismic base isolation is a system positioned on the foundation and under the building, separating the structure from the movement of the foundations during the construction exposure to an earth-quake, damping the force transferred from the foundations to the structure, and absorbing the seis-mic load by breaking the carbon bonds of rubber. Therefore, it protects installations in general from earthquake damage. In other words, the function of the isolator is to increase the period of the struc-ture, dissipate the earthquake energy, and give the structure appropriate horizontal flexibility to be able to resist earthquakes.[1]

The high damping rubber used in HDR is based on rubber with some enhancement materials (carbon black, high viscosity enhancing resin et al.). The enhancement materials improve the energy dissipation capacity; meanwhile, ensure the elastic recovery ability of the rubber, resulting in HDR having a higher damping ratio than LNR. Besides, HDR has greater pre-yield stiffness than LRB, which is more favorable to the wind resistance of the structure. Moreover, due to no lead in HDR, it is well-fitted to places with special requirements for ecological protection, such as oceans and lakes.[2]

It is necessary to develop high performance damping rubber to meet the urgent demand for high quality damping materials under the interactive stress of earthquakes and vehicle traffic. Natural rubber (NR) has excellent resilience and good processing properties. It is widely used in the manufacture of damped rubber products.[3] Furthermore, mixing two or more types of rubber is a useful and economical strategy for preparing materials and products with superior properties which would be probably hard-achieved in single-component rubber.[4]

TABLE 1. SAMPLE COMPOSITIONS	**E1**	**E2**	**E3**	**E4**	**E5**
NR	80	80	80	80	80
NBR		**20**			**20**
KBR			20		
ENR				**20**	**20**
Carbon Black	90	90	90	90	90
Stearic Acid	**2**	**2**	**2**	**2**	**2**
Antioxidant	7	7	7	7	7
Hydro Carbon Resin	**20**	**20**	**20**	**20**	**20**
Resin	**5**	**5**	**5**	**2**	**2**
Accelerator	3,1	3,1	3,1	3,1	3,1

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A Novel Approach to EPDM Formulation Optimization: Integrating Nonlinear Regression and Stochastic Optimization Methods

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Keywords: EPDM Formulation Optimization; Nonlinear Regression; Mechanical and Rheological Testing; Stability Study.

This study presents an innovative approach to the modeling-design-optimization process for the formulation optimization of Ethylene Propylene Diene Monomer (EPDM) compounds (table 1.). A series of EPDM formulations were prepared, with their input variables meticulously recorded. The study investigates the effects of these input variables on various output properties, including tensile strength, elongation, rebound resilience, and compression set. A comprehensive series of mechanical and rheological tests were conducted to gather the necessary data.

The mathematical modeling of the process was achieved using a multiple nonlinear neuroregression approach. A stability study was integrated into the modeling phase to assess the robustness and reliability of the output parameters—an innovative criterion that has not been previously employed in similar modeling studies [1].

Furthermore, this study involves the optimization of manufacturing process parameters through a modified version of various stochastic and derivative-free optimization methods. The methods utilized include Differential Evolution (MDE) and Simulated Annealing (MSA). These optimization techniques were applied simultaneously to achieve an optimal design framework.

Table 1. An example of sample compositions

Components [phr]	**Sample notations**				
	N1	**N2**	**N3**	**N4**	**N5**
EPDM1 %	3,12				
EPDM2 %		0,31	16,22		1,05
EPDM3 %	28,30	0,81	1,09		0,27
EPDM4 %		22,24	5,16	24,29	22,20
CB1 %	25,53	1,28	36,85	43,84	37,06
CB2 %	1,64	33,91		0,59	4,26
Oil %	11,92	22,79	13,55	16,97	16,22
Other%	29,49	18,66	27,13	14,31	18,93

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Effect of Chain Mobility in the Rubber Formula on the Tg and Arrhenius Activation Energy

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Keywords: dynamic mechanical analyser; rubber; crosslinking density; Tg.

The viscoelastic properties of the polymers are a function of the type of crosslinking type and density of the material when dealing with the elastomeric substances. Glass transition temperature (Tg) is an indication of this network structure and can be obtained under dynamic conditions via dynamic mechanical analyzer (DMA).

The dynamic mechanical analyzer used was TA DMA 850 equipped with liquid N_2 cooling system with patented frictionless air bearing configuration and high-speed electronics and data acquisition. Precision for the modulus is ±1% thanks to its non-contact motor design while the tan delta sensitivity is 0.0001 with a resolution of 0.00001. The temperature is recorded by a thermocouple placed adjacent to the sample surface.

For the tests, dual/single cantilever was used considering the sample types and geometries where the sample was subjected to temperature ramp where liquid nitrogen was used as the furnace coolant, allowing for temperature scans from -50 °C up to 150 °C. Frequencies in the range of 0.5-50 Hz were used for the determination of activation energies in case of the glass transition relaxation to occur based on the sample formula and test conditions. The program was set within the temperature range at a heating rate of 4 °C/min, oscillatory strain of 0.1% at a constant amplitude. Materials tested were HNBR and SBR / NBR mixtures. Mixing of all the ingredients was carried out in a production scale Banbury mixer and brought down to the desired thickness of ca. 2 mm in a lab-scale counter-rotating open kneading roller system. Consecutively, the uncured rubber samples were vulcanized based on predetermined cure conditions in between the pressure and temperature controlled heated platens at 10X10 cm dimensions. Following curing the samples were allowed to set at least for 24-hrs for the vulcanization reaction to finalize at the desired level and then cut to required dimensions for DMA investigation.

Figure 1 demonstrates the DMA curves at 1Hz for sulphur-cured two rubber formulations; one of a Tg of -17.66 °C while the other with Tg observed at -13.96 °C. This difference can be ascribed to presence of higher propensity of H-linkages in the latter requiring higher energy to pass the threshold for the chain movement. The second formula with ca. 4 °C lower Tg contained NBR and SBR segments at a ratio 24. On the other hand, this variation in the chemical structure of the rubbers was also reflected in the magnitude of the storage modulus values as well where the HNBR formula resulted in slightly lower storage modulus over the temperature range studied due to decreased elasticity emanating from the hydrogenation of the NBR chains.

Furthermore, frequency dependence of the Tg is given in Figure 2 below in Arrhenius plot. From the plot, activation energy as a function of temperature and frequency was obtained for each formula and the calculated apparent activation energies were observed as 111.03 and 104.36 KJ /mole for Sample A and B, respectively.

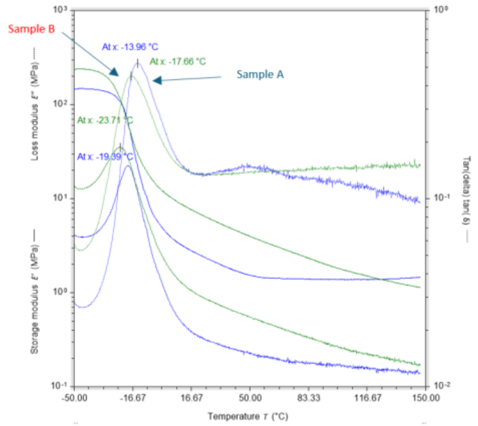

Figure 1. Storage and loss modulus with tan delta curves recorded at 1 Hz on Sample A and Sample B

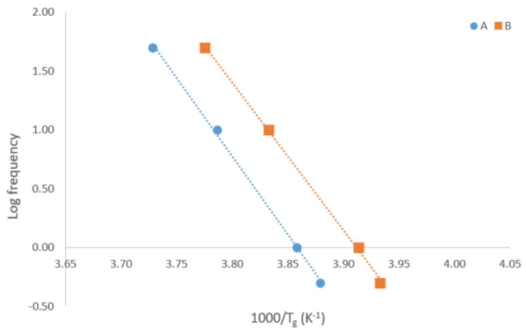

Figure 2. Log frequency vs inverse tan δ for the rubber samples

The energy requirement for the hydrogenated formula was found to be approximately 7 °C higher than the SBR/NBR formula as expected due to increased chain immobility not only from the vulcanization process but also the hydrogen linkages present in the former. These results suggest that while designing the hydraulic hose structure for intended applications, particular attention should be placed on the rubber material selection as well.

Acknowledgement

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Investigation of Torsional Behavior of No-Backlash Flexible Couplings

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Keywords: coupling, power transmission, backlash-free, torsional analysis.

Couplings are machine elements used in power transmission. With changing needs, the performance requirements of couplings have also increased.[1] Additional performance requirements such as the ability to transfer the transmitted power without backlash, to tolerate misalignment to a certain extent and to dampen the vibration caused by the power generator have emerged. In order to meet these requirements, elastomer-based materials and metal materials are used together to meet these requirements. [2] Within the scope of the study, the behavior of different couplings that can provide these properties against the torsional force generated during power transmission is investigated. The mechanical behavior of the couplings selected within the scope of the study was analyzed by applying the torsional torques that the couplings can stay within the gap-free limits on the modeled couplings in the analysis (Ansys) environment. The stress points on the coupling in response to the torsional torque and the effect of the geometries of the couplings with different geometric structures on the stresses were analyzed. By evaluating these results, a model was created in the analysis environment for the ideal coupling formation based on material preferences and geometries. Using this study, the ideal coupling components were determined within the selected couplings in terms of flexibility and backlash free in transmission.

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Recyclable, and Crosstalk-free Thermoplastic Polyurethane-Carbon Materials Based Flexible Electronics

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Keywords: Flexible electronics; Strain sensor; Temperature sensor; Recycling.

Development of sensors that are highly flexible and highly sensitive, which can precisely detect external strains such as tensile strain, pressure, bending strain, humidity, or temperature in real-time, without any crosstalk from undesired external stimuli has become particularly important because of its applications in human health monitoring, soft robotics, and human-machine interactions.[1] In the current market scenario, non-flexible sensors made of metals or semiconductors are available. The inability of these sensors to conform to complex structures due to their rigid form factor limits their applicability. Furthermore, the management of electronic waste generated by these sensors is also critical. Last two decades, humankind has witnessed a meteoric rise in technological advancements. Coupled with advancements in quality of life and human health sectors, technological advancements also came with an allegorical detrimental effect of a sea of waste electrical and electronics equipment (WEEE), often known as e-waste.[2] Hence, in order to change the dire scenario, we will face in the future, it is imperative that sustainable technologies and tools be developed.

To address this combined, limitation of crosstalk of responses, rigid form factor, and admonition of waste generation associated with sensors, there is an impetus to develop electronic sensors/electronics which are flexible, crosstalk-free, and recyclable in nature. Hence here, we report our efforts to create a flexible, recyclable sensor capable of providing precise measurements of strain, pressure, and temperature without any crosstalk (**Figure 1**). The developed strain sensor was used to track a wide range of human motions, whereas, in another application, the developed sensor was used to detect temperature variation and also as an e-heater. Finally, recycling resulted in a small decrease in sensitivity without significantly impacting detecting capacities as well as thermoelectric properties. These results provide a potential new path towards creating flexible sensors as well as electronics with reduced environmental impact.

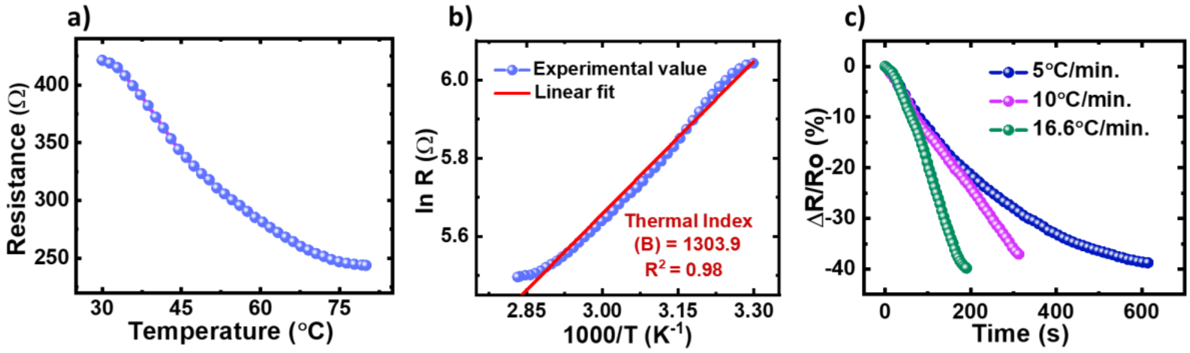

Figure 1. Characterizations of developed temperature sensor sensing properties – a) Change in resistance with temperature. b) Determination of thermal index. c) Relative resistance changes with varying heating rates.

Acknowledgment

Thanks to the Indian Institute of Technology Kharagpur for funding this study.

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Effect of modified palm oil on the properties of silica-reinforced SBR/BR blends

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Keywords: SBR/BR blend, Silica, Processing oil, Vegetable oil.

To enahnce the performances of styrene butadiene rubber (SBR)/ butadiene rubber (BR) blends for tire tread application such as low rolling resistance and good wet traction, silica as a reinforcing filler is required in rubber formulation [1]. The amounts of silica incorporated into the blends is over 20% [2]. Silica-filled rubber compounds with high filler loading shows high viscosity. So, rubber process oil is an important ingredient to reduce the viscosity of rubber compounds and promote filler dispersion and distribution within rubber matrix. Distillate aromatic extract (DAE)-based rubber process oil is most used in SBR/BR blends due to the good compatibility between oil and rubber molecule [3]. However, DAE oil has been banned due to the contamination of polycyclic aromatic hydrocarbons (PAHs) in which some of them were classified as a carcinogen [4-6]. Therefore, to promote non-toxic and green rubber compounds, bio-oil was chosen as an alternative to rubber process oil for silica-reinforced SBR/BR blends in this study. Two types of palm oil, i.e., unmodified palm oil (UPO) and modified palm oil (MPO), were used by comparison with DAE oil. The MPO was prepared by the reaction between silane coupling agent and palm oil. Results revealed that the use of MPO in the blends promoted the vulcanization reaction, i.e., short scorch time and cure time, and high cure rate index, when compared to the blends with DAE and UPO. Tensile properties, i.e., tensile strength and elongation at break, were improved by the addition of MPO. Furthermore, tire performances of silica-reinforced SBR/BR blends with different types of rubber process oils were investigated. It was found that the use of palm oil, i.e., UPO and MPO, showed lower tan δ at 60°C than the use of DAE, which is referred to the low rolling resistance of the blends containing UPO and MPO. So, the replacement of DAE in the silica-reinforced SBR/BR blends by MPO is possible for tire tread application.

Acknowledgement

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Using Devulcanized Rubber in EPDM/PP blends

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Keywords: Thermoplastic Vulcanizates; polypropylene; EPDM.

Thermoplastic vulcanizates (TPVs) are a special class of thermoplastic elastomers produced by dynamic vulcanization of an elastomer with a thermoplastic, i.e. by selective cross-linking of the elastomer phase during mixing with the thermoplastic in the molten state. In this process, the elastomer phase is cured by crosslinking agents and the resulting dynamic vulcanizate consists of crosslinked rubber particles dispersed in a continuous thermoplastic matrix phase. In TPVs, the increase in viscosity of the rubber promotes phase transformation and provides a hetero-phasic morphology. The dispersed rubber particles increase the elasticity of the TPV while maintaining the melt processability of the thermoplastic phase. The major advantage of these dynamically cured compounds is that their morphology is stabilized and does not change with subsequent melting processes. As a result, TPVs exhibit more elastomeric properties compared to simple non-crosslinked blends and offer superior performance such as lower compression set, lower stiffness, fatigue resistance, better elastic recovery, high mechanical properties, high melt strength, and increased resistance to heat and chemicals [1-2].

Although there are various types of TPV based on rubber and polymer differences, the most commercially popular are usually PP/EPDM-based. EPDM rubber gives TPVs excellent stability against heat, oxygen, and ozone due to its saturated main chain backbone. TPVs are produced using different cross-linking agents during the dynamic vulcanization of EPDM. Polypropylene (PP) has advantages such as low cost, chemical resistance, and thermal stability, but poor toughness and low-temperature resistance limit its applications. To overcome these problems, melt-blending with EPDM via dynamic vulcanization is being widely investigated. The good compatibility of EPDM with PP gives TPVs excellent flexibility, mechanical strength, and stable performance, which has made PP/EPDM TPVs one of the most widely used commercial TPVs [3].

Devulcanization is a method that has been used in recent years to evaluate waste rubber. As expected, the process of breaking the sulfur-carbon and sulfur-sulfur bonds formed by vulcanization is called devulcanization. When subjected to various influences (ultrasonic, microwave, chemical, mechanical, and thermomechanical), the sulfur-sulfur and carbon-sulfur bonds in the rubber matrix are affected and broken more than the carbon-carbon bonds. The energies required to break the sulphur-sulphur and carbon-sulphur bonds are 227 and 273 kJ/mol respectively, and the energy required to break the carbon-carbon bonds is 348 kJ/mol. The choice of devulcanisation method is important because of these very similar energy values. With the appropriate devulcanisation method, devulcanized rubber that has a high rate of broken sulfur-sulfur and carbon-sulfur bonds, but whose carbon-carbon bonds are retained, can re-form sulfur-carbon and sulfur-sulfur bonds with or without mixing with virgin rubber, i.e. it can be vulcanized [4-6].

A green and circular economy is one of the objectives of the Green Deal Action Plan published by Our country in 2021. The circular economy requires the adoption of an economic approach while recycling materials maintain the value of the product. On the other hand, the amount of waste should be kept to a minimum.

In this study, EPDM/PP blends were prepared by adding EPDM-based devulcanized rubber with different curing agents (phenolic resin and peroxide) in a twin-screw extruder. These samples were tested according to the DBL 5562.17 standard used in the automotive industry. It was found that EPDM-based devulcanised rubber can be blended with EPDM/PP and is suitable for use in plastic injection molds. When the mechanical test results were examined, a slight increase in the hardness value and a decrease in the tensile strength and elongation at break values were observed with the use of EPDM-based devulcanized rubber in the EPDM/PP blend. As a result of this initial evaluation, it was concluded that the devulcanized rubber behaves as a filler in the EPDM/PP blends.

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Stretchable Thermal Conductive Composites with Modified-Natural Rubber for Thermal Management in Flexible Device

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Keywords: modified natural rubber, thermal conductive composites, shape adaptability.

Thanks to outstanding elastic properties originating from the flexible nature of the alkyl chain, natural rubber (NR) is an indispensable biomass material in various industries. However, it has low thermal conductivity due to phonon scattering caused by its flexible chain structure, which restricts its use in the thermal management field.

In this work, to develop a stretchable thermal conducting material utilizing the inherent elastic properties of NR, a modified-NR (m-NR) was newly designed and synthesized by introducing side chain thermal conducting monomer (TCM) to NR (Scheme 1).

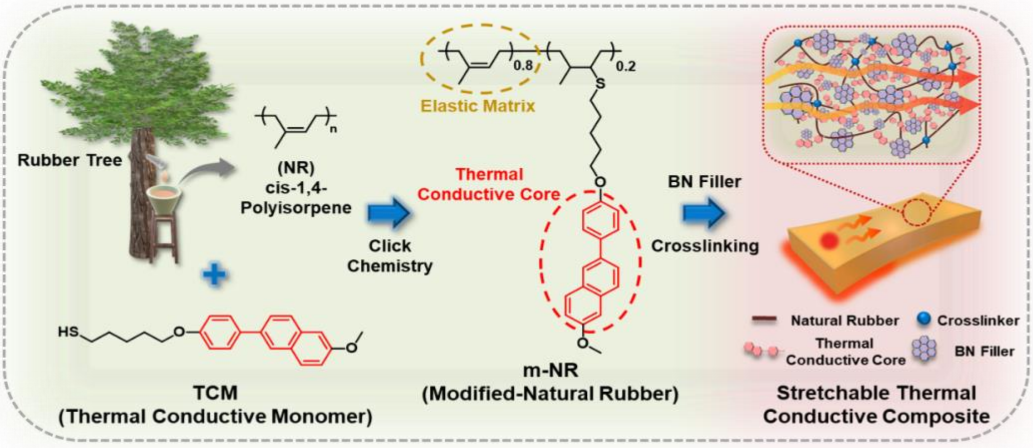

Figure 1. Schematic illustrations of the fabrication process for stretchable thermal conductive composite .

Owing to phonon transfer assistance of TCM, the m-NR film exhibited around 120% higher thermal conductivity (0.38 W/m·K) compared to the NR film (0.17 W/m·K). Also, when the same hexagonal boron nitride (h-BN) content was incorporated, m-NR composites showed higher enhancement in thermal conductivity, and the m-NR composite film fabricated with h-BN of 15 wt% show the thermal conductivity of 0.87 W/m·K. Due to the inherent flexible mechanical properties of NR, the m-NR film exhibited 160% stretchability, and the m-NR composite film fabricated with h-BN of 15 wt% exhibited 140% stretchability. Furthermore, the m-NR composite film showed the ability to easily transform into various shapes. With the enhanced thermal conductivity and the flexible mechanical properties, it is demonstrated that the NRSCP composite can be utilized as a thermal management material for flexible and wearable devices in upcoming industries.

Acknowledgement

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Secret Coating Consisting of Photoisomerizable Side-Chain Cyanostilbene and Self-Crosslinkable Backbone Polysiloxanes

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Keywords: Self-crosslink, Polysiloxane, Optical coating, Photoisomerization**.**

Stimuli-induced fluorescence and color-tunable organic materials with great performance and processability are essential to the development of advanced optical coatings. Among them, photoisomerizable dyes are garnering considerable interest due to their advantages, such as remote switching and photopatterning. However, the photoisomerization process involves a significant volume change. As a result, photoisomerization is hindered in the solid state or at room temperature. To enhance their practicality, it is crucial to broaden the applicability of photoisomerizable dyes to encompass all circumstances, including polymer network systems. To develop secret paints, photoisomerizable side-chain mesogen polysiloxane (SPS) consisting of self-crosslinkerable backbones and the AIE side chains was synthesized. Based on the phase behaviors, it was realized that SPS has a low-ordered smectic mesophase over a wide temperature range of its flexible backbone.

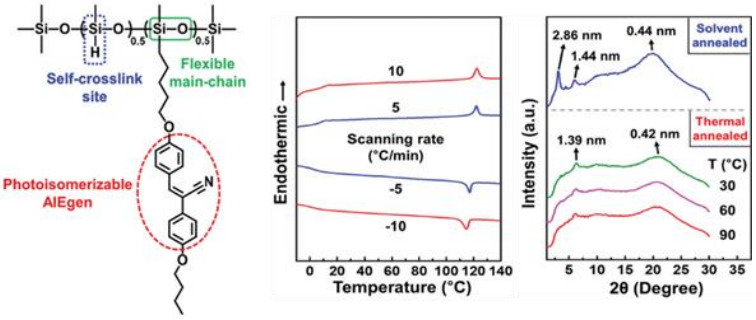

Figure 1. Chemical structure and thermal analysis of SPS

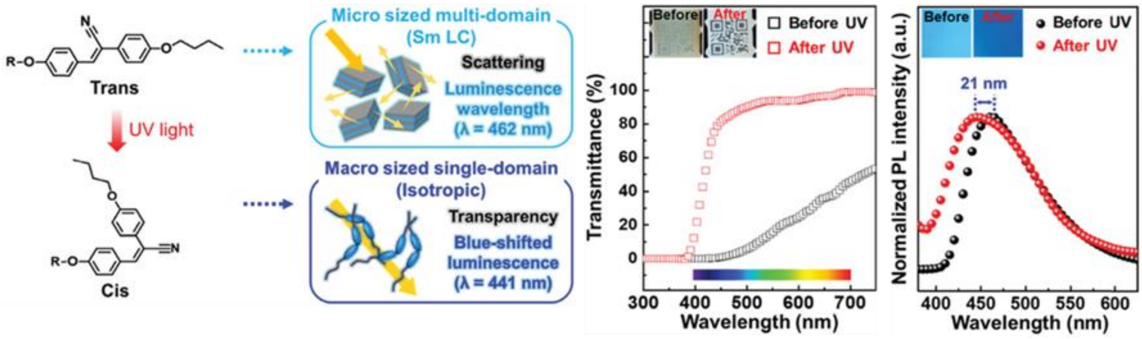

Figure 2. Optical changes upon photoisomerization of SPS.

The photoisomerization of the cyanostilbene moiety at the molecular level has been effectively transferred and amplified to induce a phase transition in SPS, leading to obvious changes in the macroscopic optical properties of the resulting thin film.

The self-crosslinking reaction involving Si–H groups within the SPS polymer backbone imparts exceptional elasticity and both thermal and chemical stability to the self-crosslinked SPS thin film. Consequently, this film demonstrates resilience against stretching and bending deformations even under challenging conditions.

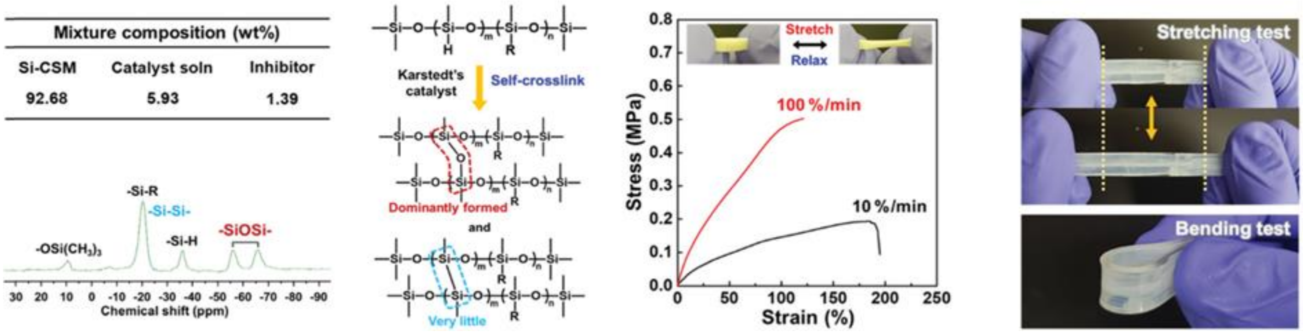

Figure 3. Self-crosslinkable SPS and its mechanical properties.

Furthermore, through a spontaneous self-crosslinking reaction following the application of SPS polymer and ultraviolet (UV) light irradiation through a photomask, polarization-dependent and photopatternable secret coatings have been successfully fabricated. The flexible optical Si–CSM paint, thus developed, holds promising applications in next-generation optical coatings.

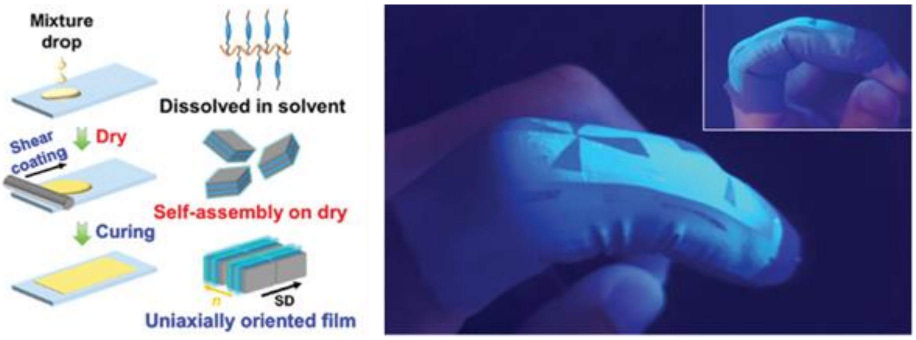

Figure 4. Demonstration of the advanced flexible optical coatings using the SPS.

Acknowledgement

This work was supported by Mid-Career Researcher Program (2021R1A2C2009423), and BK21 FOUR.

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Green tyre retreading: Improving sustainability and efficiency in TBR systems

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Keywords: S-SBR; low rolling resistance; highly dispersible silica (HDS); retreading.

The aim of this study is to develop a compound that will provide fuel efficiency, low rolling resistance, and low carbon emission in TBR (Truck, Bus, and Radial) tyre retreading. Today, many studies are carried out with the goal of sustainability, which has become a necessity of our time. Tyre manufacturers in major industries have long been using tyres that reduce carbon emission and save energy for an environmentally friendly and sustainable society.

On average, 20 kg of compound is required for retreading a truck tyre casing. In contrast, producing a new tyre from scratch requires nearly 70 kg of compound, making retreading provide a material saving of 70%. In this way, the retreading process also consumes 56% less crude oil than manufacturing a new tyre. One of the significant material savings obtained by opting for retreading is the re-use of steel used to construct the tyre's casing. Tyre retreading is thus more sustainable and environmentally friendly compared to new tyre production.

Rekor Kauçuk aims to be sustainable with the steps it takes in areas such as energy efficiency, waste reduction and adoption of circular production principles. In line with this goal, A new tyre retreading compound with minimized carbon black content has been developed "with the named **Green Tyre** retreading compound" for the production of retreading for use in trucks, buses and light commercial vehicles.

Low rolling resistance and low fuel consumption performance in vehicles, which are in the magic triangle of the tyre industry, stand out in environmentally friendly tyres. The new tyre retreading compound developed in this study carried out with an environmentally friendly approach aims to participate in the sector with its low fuel consumption performance.

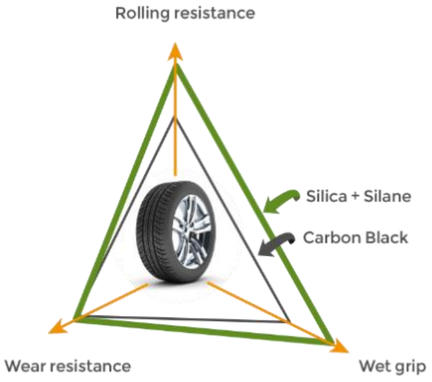


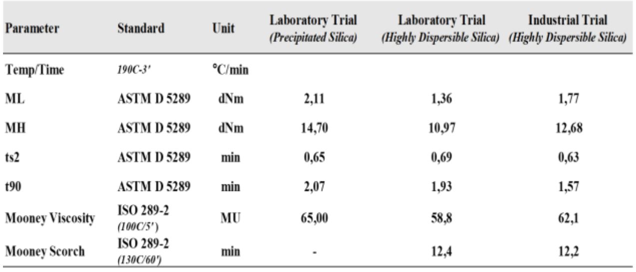
Figure 1. Tyre Magic Triangle

Trial studies to reduce carbon emission have started on a tangential rotor laboratory mixer with a volume of 4 liters. The studies aimed to minimize the amount of carbon black, which constitutes 33% of the current recipe, which was the starting point. With the use of high-rate inert filler, the carbon black rate in the recipe was reduced to 3.5%. Trial studies started with the use of precipitated silica and trials continued with HDS silica.

Table 1. Formulation of green tire retread compound

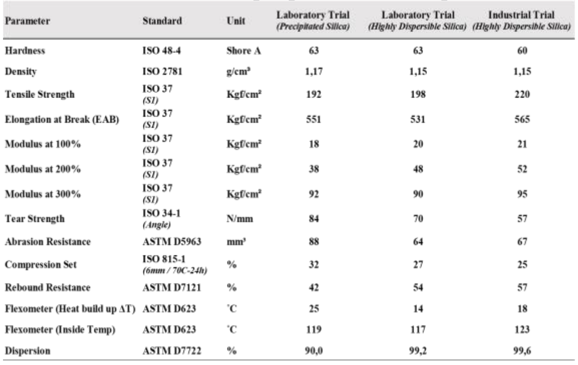
Polymer	**NR - SSBR (%5 oil content) - BR**
Filler	**CB** **HDS**
Silane coupling agent	**TESPT**
Curing system	**Sulphur** **CBS** **DPG**

Table 2. Rheological and viscosity results of compound



Parameter	Standard	Unit	Laboratory Trial *(Precipitated Silica)*	Laboratory Trial *(Highly Dispersible Silica)*	Industrial Trial *(Highly Dispersible Silica)*
Temp/Time	*190C-3'*	°C/min			
ML	ASTM D 5289	dNm	2,11	1,36	1,77
MH	ASTM D 5289	dNm	14,70	10,97	12,68
ts2	ASTM D 5289	min	0,65	0,69	0,63
t90	ASTM D 5289	min	2,07	1,93	1,57
Mooney Viscosity	ISO 289-2 *(100C/5')*	MU	65,00	58,8	62,1
Mooney Scorch	ISO 289-2 *(130C/60')*	min	-	12,4	12,2

Table 3. Mechanical properties of compounds



Parameter	Standard	Unit	Laboratory Trial *(Precipitated Silica)*	Laboratory Trial *(Highly Dispersible Silica)*	Industrial Trial *(Highly Dispersible Silica)*
Hardness	ISO 48-4	Shore A	63	63	60
Density	ISO 2781	g/cm^3	1,17	1,15	1,15
Tensile Strength	ISO 37 *(S1)*	Kgf/cm^2	192	198	220
Elongation at Break (EAB)	ISO 37 *(S1)*	Kgf/cm^2	551	531	565
Modulus at 100%	ISO 37 *(S1)*	Kgf/cm^2	18	20	21
Modulus at 200%	ISO 37 *(S1)*	Kgf/cm^2	38	48	52
Modulus at 300%	ISO 37 *(S1)*	Kgf/cm^2	92	90	95
Tear Strength	ISO 34-1 *(Angle)*	N/mm	84	70	57
Abrasion Resistance	ASTM D5963	mm^3	88	64	67
Compression Set	ISO 815-1 *(6mm / 70C-24h)*	%	32	27	25
Rebound Resistance	ASTM D7121	%	42	54	57
Flexometer (Heat build up ΔT)	ASTM D623	˚C	25	14	18
Flexometer (Inside Temp)	ASTM D623	˚C	119	117	123
Dispersion	ASTM D7722	%	90,0	99,2	99,6

When the field performance results were examined, it was seen that the green tyre retreading provided approximately 4% fuel savings compared to the existing tyre retreading. At the same time, the product developed with this project also reduces the carbon footprint.

The first phase of this study to reduce carbon emission has been completed well. Both laboratory-industrial compound trials and field performance result of the green tyre retreading appear to be positive. In the second phase of the study, alternative bio-based raw materials to the raw materials used in the recipe will be studied. First of all, studies wiill be carried out using bio-based silica instead of HDS. The use of recycled carbon black is also a second priority. It is aimed to turn the recipe green to a large extent by using bio-based types of raw materials such as zinc oxide and DPG in the recipe.

Acknowledgement

Thanks to the Rekor Kauçuk A.Ş. for providing financial and spiritual support for this research.

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Azobenzene-Based Liquid Crystal Polymer Networks with a Photothermal Effect for Shape Memory and Self-Healing Properties

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Keywords: azobenzene, photothermal effect, shape memory, self-healing.

For the development of liquid crystal polymer (LCP) materials with photothermal effects, an azobenzene-based monomer (AzM) was newly synthesized as a building block for LCP networks. Depending on the molecular structure and UV absorption capacity of azobenzene molecules, the photothermal effect can induce stimuli-responsive properties in the azobenzene-based LCPs. As shown in Figure 1, the formation of AzM-based polymer networks was optimized by adjusting the ratio of AzM, RM257, and thiol-based molecules. The thermal, mechanical, and structural characteristics of the LCPs were investigated through various experimental analyses.

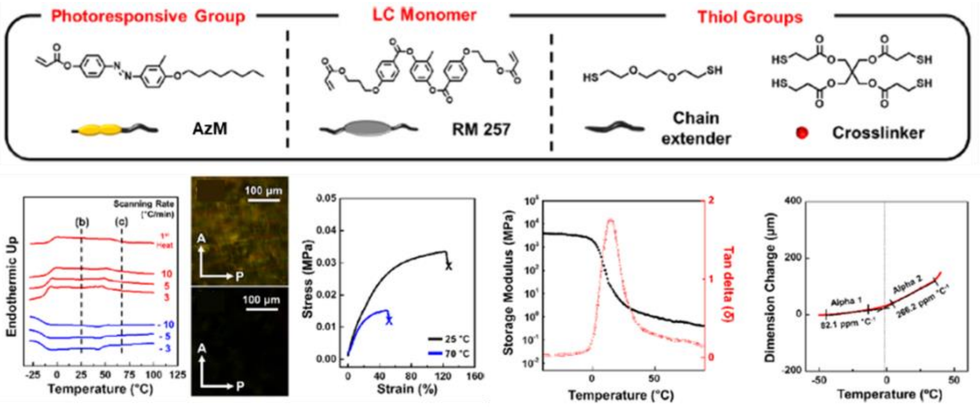

Figure 1. Molecular structures of AzM-based LCP and its thermal and mechanical behaviors.

Due to its low T_g below room temperature, the AzM-based LCP can be classified as an elastomer that could have shape memory behaviors. Various results on the photothermal effect demonstrate the significant influence of azobenzene moieties in the shape memory process of the LCPs (Figure 2).

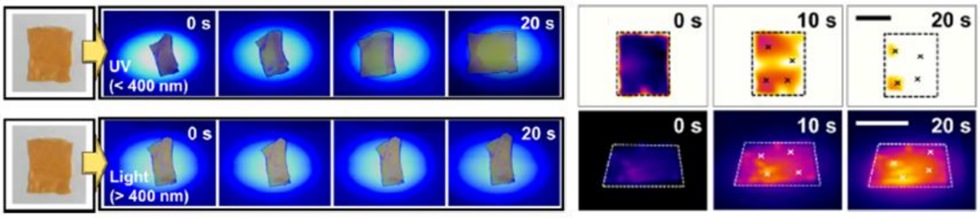

Figure 2. Shape memory process and photothermal effect of the AzM-based LCPs.

Furthermore, the disulfide bonds present in the LCPs can impart a self-healing characteristic. This attribute arises from the exchange of disulfide bonds activated by heat and the photothermal effect generated by AzM under UV irradiation, respectively. Strain-stress curves reveal that AzM-based LCPs exhibit superior self-healing properties under heat compared to UV-irradiation, attribute to the interference of partial azobenzene molecules during UV irradiation (Figure 3).

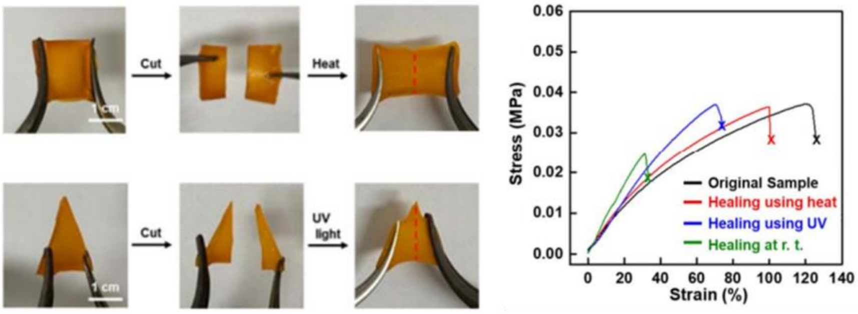

Figure 3. Self-healing process and strain-stress curves of the AzM-based LCPs under heat or UV irradiation.

Based on the results from shape memory and self-healing experiments, the AzM-based LCP shows potential for applications in stimuli-responsive soft materials.

Acknowledgement

This work was supported by Mid-Career Researcher Program (2021R1A2C2009423) and BK21 FOUR Program.

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Rubber composites based on ferrites and carbon fillers with EMI absorption shielding performance

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Keywords: Rubber; ferrites; carbon-based fillers; EMI shielding

Polymer composites used as efficient electromagnetic interference (EMI) shields have been much more preferred in practical applications over traditional metal based solid plates due to their advantages such as flexibility, lightweight, stability, corrosion resistance, ease processing, or low cost. They can be easily shaped, processed, diffracted, or coiled without the loss of their electromagnetic characteristics. As polymers are typical electrical insulators, EMI shielding properties to the polymer composites can be imparted by incorporation of different fillers. These fillers include metallic powders, metal oxides, ferrites, MXenes, or various carbon-based fillers (as carbon black, graphite, graphene, graphene oxide, carbon fibers, carbon nanotubes, etc.). The application of filler can not only modify electromagnetic characteristics of composite shields, but also influences process-ability, physical-mechanical properties, dynamic and elastic characteristics, viscosity, or thermo-oxidative stability. Polymer composites as efficient EMI shields have already been used in practical applications in the sphere of automobiles, aerospace, aircraft, power electronics, and communication systems.

In this work, magnetic soft ferrites, namely manganese-zinc ferrite, nickel-zinc ferrite, and the combinations of both fillers were used for fabrication of composites based on acrylonitrile-butadiene rubber. The overall content of the ferrites, or ferrites combinations was kept on 200 phr, only the mutual ratio of both fillers was uniformly changed. In addition to ferrites, carbon black or carbon fibers were added into rubber formulations in constant loading – 25 phr. The main goal was to investigate the influence of ferrites and carbon-based fillers on absorption shielding efficiency and physical-mechanical properties of composites. It was revealed that incorporation of ferrites into rubber matrix leads to fabrication of composites that can shield electromagnetic radiation. The higher was the amount of nickel-zinc ferrite in fillers combinations, the higher was the shielding performance of composites. The results showed that nickel-zinc ferrite demonstrated better shielding potential. Higher electrical conductivity of composites based on ferrites and carbon black resulted in their lower EMI absorption shielding performance when compared to their equivalents based on ferrites and carbon fibers. The biggest preference of rubber composites based on ferrites and carbon fillers is their ability to shield electromagnetic radiation by absorption mechanisms.

Acknowledgement

This work was supported by the Science Grant Agency VEGA under the contract No. 1/0056/24.

Electromagnetic interference shielding performance of rubber-based composites using soft magnetic ferrites as absorbers

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Keywords: Electromagnetic absorption; rubber composites; ferrites; hybrid fillers.

Electromagnetic interference (EMI) is a type of modern-day pollution that has become a major concern, especially with the rapid development of communication technology. Due to the higher number of electronic devices existing close to each other, there is a higher chance for the electronic components to be susceptible to unwanted electromagnetic emissions. The effects of these unwanted emissions can be noises interfering with signal transmissions to total data loss and device failure. It is thus important to introduce a shielding mechanism that can limit unwanted emissions toward susceptible devices as well as limit any potential interference that may originate from the device itself. Depending on the desired practical application, there is a very wide variety of shielding materials that can be utilized. For example, hexagonal ferrites have long been known to possess salient properties such as good chemical stability, large crystal anisotropy, and big values of permeability, enabling them to exhibit good electromagnetic wave-absorbing properties. Carbon-based shielding materials have seen widespread adoption in various fields of application due to their lightweight and are known to show good electrical properties. Among the allotropes of carbon, MWCNT has shown promising EMI shielding capabilities through synergistic effects when paired with other types of shielding materials.

Rubber magnetic composites tested in this work were prepared by incorporation of magnetic soft manganese-zinc ferrite with the combination of carbon-based fillers into a rubber matrix based on acrylonitrile butadiene rubber. The aim was to evaluate the influence of manganese-zinc ferrite with the combination of carbon-based fillers on physical-mechanical and magnetic properties. The results of experiments revealed that all composites containing 200 phr or more exhibited sufficient absorption shielding ability, as they provided return loss at the level of -10 dB in the tested frequency range. It has been reported that shielding materials having return loss at -10 dB can provide a total absorption of 95% of the incident electromagnetic radiation. Additionally, the incorporation of carbon-based fillers in composites leads to the absorption maxima and absorption shielding efficiency shift to lower frequencies. In general, the incorporation of carbon-based fillers improved the physical-mechanical properties of the prepared composites.

Acknowledgement

This work was supported by the Science Grant Agency VEGA under the contract No. 1/0056/24 and by the Grant scheme to support excellent teams of young researchers under the conditions of STU in Bratislava No. 1389.

Experimental contact mechanics analysis of a rubber sample under complex loading representative of a rolling tire

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Keywords: Wear; Contact and adhesion; Modelling in tribology; Rubber elastomers.

Under increasing shear, the contact between a rough elastomer and a rigid surface, for example in the case of contact between a tire and a road surface, may undergo significant changes in terms of morphology of the micro-contacts due to the presence of wear [1]. In such contacts, it is also possible to observe strong variation of the local pressure during shearing that may be related to the wear patterns that are frequently observed in literature [2]. Such morphological and loading changes are indeed expected to affect all macroscopic responses of the interface. In particular the transition to full sliding may differ significantly from the classical behavior described by Cattaneo and Mindlin [3].

In this study, our aim is to analyze the contact stress/strain state during shearing of a sphere made of model elastomers representative for tire tread materials prepared by using different types of silica. These analyses are performed by measuring not only the classical evolution of macroscopic normal and tangential forces but also that of the true contact area and interfacial stress/strain fields. The experimental tests consist in using a complex loading representative of the behavior of a tire during rolling. To do so, we perform a normal loading/unloading cycle during a continuous shearing motion in a new generation opto-mechanical device recently developed in our laboratory [4]. The latter enables rich contact loading through five simultaneous and independent degrees of freedom with simultaneous high-resolution monitoring of all three forces and three moments at the contact interface. It also enables high-resolution in-situ visualization of the contact area, giving access to in-operando, measurements in the real contact area of the stress/strain fields through advanced image analysis techniques [5]. This experimental procedure makes it possible to study the effect of several characteristic parameters, such as the "landing" speed, the maximal normal force and the sliding speed. Prior to using complex worn charged rubber, we performed preliminary tests on unworn spheres of uncharged elastomer (PDMS) seeded with markers to monitor the evolution of contact area and interfacial displacement field via image analysis. Subsequent tests on tire-type rubber enabled us to extend our understanding to more realistic rubber materials.

Future experiments will allow the investigation of worn samples which should help in understanding the link between local contact conditions and wear patterns.

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A new approach for waste rubber recycling "Hydrothermal Devulcanization"

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Keywords: devulcanization; rubber; hydrothermal; recycling

Studies on the devulcanization of waste elastomers generally focus on thermal, mechanical, chemical, or a combination of these. The main problem in this area is seen to be the confusion of the terms "Devulcanization" and "Reclaimed". However, technical details are more important than anything else in the recycling of elastomeric waste. Achieving the right recycled product requires having the right technique. According to ASTM D 6814, "devulcanization" is the destruction of chemical cross-links in cured rubber. On the other hand, ASTM D 1566 defines the term "reclaimed rubber" as vulcanized rubber treated by a combination of heat, chemical agents, and intense kneading to give a material with essentially its pre-vulcanized plasticity, which is useful as a rubber compounding material.1-3]

The presented poster describes the use of Hydrothermal Technology on waste elastomers to create an alternative devulcanization process. The method basically allows the use of temperature and pressure, together with catalyst systems when necessary, to create a reactive environment within water. The method has a national patent with the registration number "2021/017115 and the name "A METHOD FOR DEVULCANIZING WASTE RUBBER IN A HYDROTHERMAL ENVIRONMENT". In this solution, all known applications of the method are defined as an alternative thermochemical technology for the conversion of biomass. However, clear information is lacking regarding its use for elastomeric structures. The fact that the method is compatible with similar processes and circular economy has attracted the attention of leading polymer companies in the field (especially for plastic waste) in recent years. [2] In the preliminary devulcanization tests conducted SBR-Table 1 (tire tread - Crosslink Density 48,03 (mol/cm^3)) and EPDM Table 2 (profile parts- Crosslink Density 43,44 (mol/cm^3)) based on waste rubber parts, the following results were obtained.

Figure 1. Hydrothermal Reactor – PARR

Table 1. Test results for SBR based waste

Analysis	Measurement	Test Metod
Crosslink Density (mol/cm³)	10,11	ASTM D- 6814-02
Devulcanization	%78,95	ASTM D- 6814-02
Sol Fraction	%26,2	ASTM D- 6814-02

Table 2. Test results for EPDM based waste

Analysis	Measurement	Test Metod
Crosslink Density (mol/cm³)	7,45	ASTM D- 6814-02
Devulcanization	% 82,85	ASTM D- 6814-02
Sol Fraction	%30,2	ASTM D- 6814-02

This Poster, The Scientific and Technological Research Council of Turkey (TÜBİTAK) 1507 program has been deemed appropriate to support the following studies within the development.

- Increasing the devulcanization rate using bimetallic catalysts without damaging the C-C polymer chain,
- Bringing process parameters to industrially applicable levels,
- Developing rubber compound formulations for the devulcanizates to be obtained,

Acknowledgment

The method is of the outputs of a project that received a grant under TÜBİTAK 1512. Preliminary studies were carried out with the support of this grant. We would like to thank Prof. Dr. Ali SINAĞ for informing us about the hydrothermal reactor service procurement and hydrothermal methods, and Uludağ University Technology Transfer Office for supporting us in the patenting of the method.

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Multi-Stimuli Responsive Smart Skins Based on Ionic Azobenzene Reactive Mesogens Capable of Controlling Ionic Conductivity and Shape Actuation

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Keywords: azobenzene; ionic conductivity; actuators; artificial skin; artificial muscle.

In this research, an ionic asymmetric azobenzene monomer (i-AAM) is newly synthesized to develop smart skins with switchable ionic conductivity.[1] The liquid crystal elastomer (LCE) with i-AAM is fabricated and analyzed for its multi-stimuli responsive actuating property and ionic sensing property. The unique design and selective uniaxial orientation of i-AAM LCE enable it to serve as both multi-stimuli responsive actuators and ionic skins depending on the polymerization process.

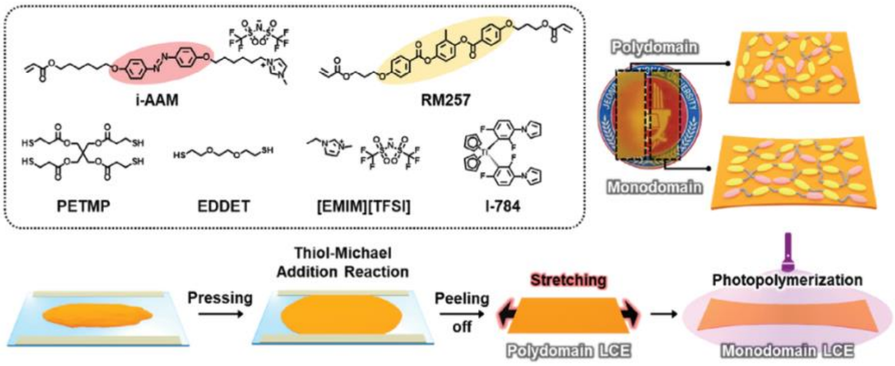

Figure 1. Composition of the mixture and fabrication process of i-AAM LCE

The monodomain i-AAM LCE exhibits contraction above its nematic to isotropic phase transition temperature (T_{NI}) and bending under UV light irradiation reversibly, providing versatile actuation capabilities. These responses allow the elastomer to adapt to various stimuli, making it suitable for applications requiring dynamic and precise control.

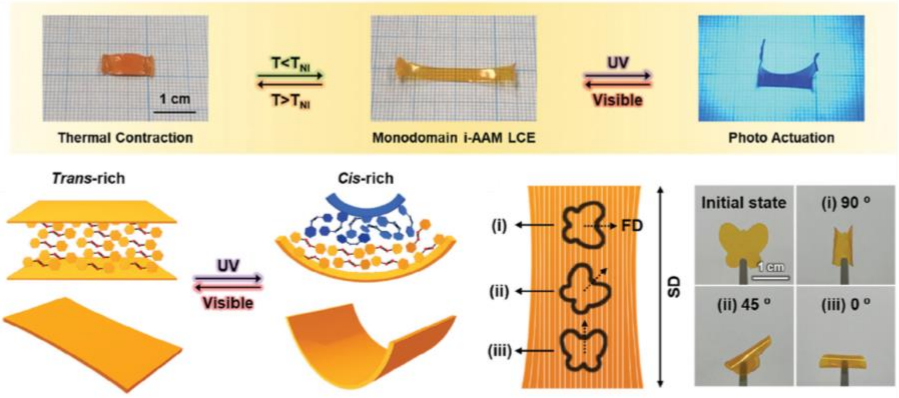

Figure 2. Multi-stimuli responsive actuation property of monodomain i-AAM LCE.

In contrast, the randomly oriented polydomain LCE demonstrates ionic conductivity switching properties when exposed to heat, light, and external stresses. This characteristic offers potential for smart sensing and adaptive control in diverse environments.

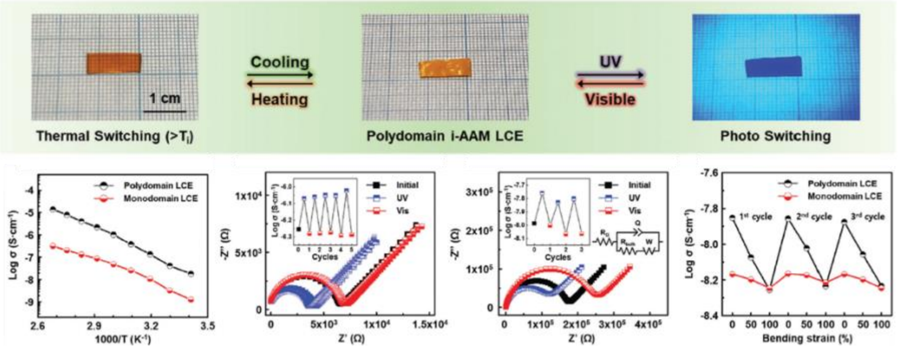

Figure 3. Multi-stimuli responsive ionic conductivity switching property of polydomain i-AAM LCE.

By complexing the different functions of actuating and sensing in each domain state, a soft gripper was designed and fabricated, capable of implementing two functions within one system. The soft gripper can deform and detect the degree of deformation in response to multiple stimuli, showcasing the potential of this material for soft robotics.

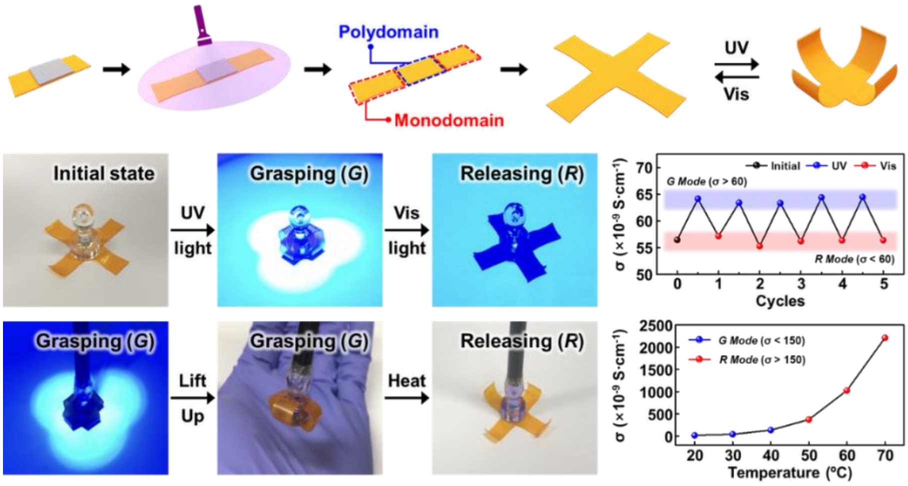

Figure 4. Fabrication process of dual-domain soft gripper and its actuating and ionic sensing property.

Acknowledgement

This work was supported by the BK21 FOUR program and Mid-Career Researcher Program (2021R1A2C2009423).

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Properties of cured products by crosslinking of 1,2-Polybutadiene

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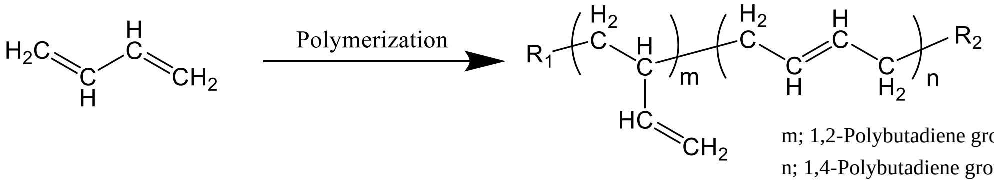
Keywords: Polybutadiene; EPDM; CSM.

Introduction

The distinguishing features of Nippon Soda's liquid polybutadiene “NIPPON SODA PB” are: (1) It includes at least 85% branched 1,2-vinyl groups (Fig. 1, m) in its molecular chain, and (2) It has substituents at both terminals of the molecule. These structural features are attributable to unique living anionic polymerization, and NIPPON SODA PB has been used in various industrial applications since 1970, when it was first manufactured and sold.

Polybutadiene has two regioisomers that depend on the polymerization position. There are a number of liquid polybutadienes on the market, but most of products contain a large quantity of 1,4-vinyl groups (Fig. 1, n), so we make a clear distinction between them and our “NIPPON SODA PB”. In addition, we have developed 1,2-epoxylated polybutadiene (1,2-epoxylated PB) which is based on 1,2-polybutadiene (1,2-PB).

By adding NIPPON SODA PB to rubber or resin and carrying out a crosslinking reaction of 1,2-vinyl groups, 3-dimensional network structure is formed in these materials. This makes the effect of improving elasticity and strength, as well as oil/water resistance. In addition, 1,2-epoxylated PB reacts with chlorine in chlorine rubbers, which also contributes to various performance improvements.



m; 1,2-Polybutadiene group (including 1,2-Vinyl)
n; 1,4-Polybutadiene group (including internal olefin)

Figure 1. Structure of Polybutadiene [Poly(1-butene-*co*-2-butene)]

EPDM(Ethylene Propylene Diene Terpolymer) modification

Table 1 shows an example of EPDM rubber formulation using 1,2-PB. Properties of EPDM with Polybutadiene are in Table 2, and it shows that there was a certain correlation between the amount of 1,2-PB and the extent of crosslinking (hardening). Next, we confirmed the relationship between the 1,2-vinyl content in polybutadiene and outcomes of the crosslinking reaction (Table 2). As the 1,2-vinyl content is increased, the mechanical strength and oil resistance are improved. This is due to the increase in crosslinking density. The compression set is also correlated with the 1,2-vinyl content, and the need for adding an appropriate amount was not observed. Therefore, high 1,2-viniyl content of polybutadiene is demanded by EPDM formulations.

Table 1. Example of EPDM modified with 1,2-PB

Material name	**phr**
EPDM 1)	100
1,2-Polybutadiene	0, 10
Zinc oxide	5
Stearic acid	1
Calcined clay	120
Carbon black	5
Paraffinic oil	6
Paraffin wax	5
Dicumyl peroxide (DCP)	7
Dibenzoylquinone dioxime	1.5

1) Ethylene content: 42%,
ENB content: 0.7%, ML1+4 (125°C): 27

Table 2. Properties of EPDM with Polybutadiene

Polybutadiene 1)	phr	Mechanical properties		Oil resistance 2)		Compression set 3)
		Shore hardness	Tensile strength at break [MPa]	Standard oil IRM901		23°C [%]
				Δm [%]	ΔV [%]	
Not added	0	A69	6.69	46	72	17
m/n = 22/78: M_n=2,500	10	A67	7.08	46	70	17
m/n = 48/52: M_n=2,100	10	A69	6.98	44	66	14
m/n = 66/34: M_n=2,500	10	A70	7.24	41	63	13
m/n = 92/8: M_n=3,200	10	A71	7.42	38	58	12

1) m: 1,2-vinyl, n: 1,4-vinyl, 2) Temperature: 70°C±2°C, 72hours, 3) Compression ratio: 25%, 72hours

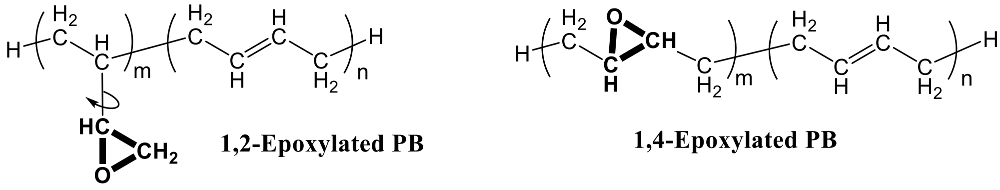
CSM (Chlorosulfonated Polyethylene) modification

1,2-epoxylated PB includes two functional groups: epoxy groups and 1,2-vinyl groups. This polybutadiene can undergo a cross-linking reaction of 1,2-vinyl groups and a ring-opening reaction of the epoxy groups. Reactivities of 1,2-epoxylated PB are different from 1,4-epoxylated PB because of the stereo chemistry of the epoxy group. Physical properties such as Mooney viscosity, hardness, tensile strength, tear strength and compression set could be improved by using 1,2-epoxylated PB for CSM rubber, owing to the crosslinking reaction of the 1,2-vinyl groups. In addition, CSM rubber using 1,2-epoxylated PB showed equivalent or superior acid resistance compared to existing acid acceptors or 1,4-epoxylated PB.

Table 3. Example of CSM modified with 1,2-Epoxylated PB

Material name	phr
CSM 1)	100
1,2-Epoxylated PB	10, 15, 20
Sorbitan stearate	3
FEF Carbon black	30
DOZ	10
Dicumyl peroxide	3
TAIC (Triallyl isocyanurate)	4
Total	165

1) TOSO-CSM TS-530



1,2-Epoxylated PB **1,4-Epoxylated PB**

Figure 2. Structural Difference of 1,2-Epoxylated PB and 1,4-Epoxylated PB

Table 4. Volume expansion properties of CRM with 1,2-Epoxylated PB

Solvent	Condition	Unit	MgO	PbO	1,2-Epoxylated PB		
			15 phr	15 phr	10 phr	15 phr	20 phr
20 wt% HCl	80℃ × 7 days	%	174	1	0	3	5
10 wt% HNO_3	80℃ × 7 days	%	181	18	5	2	0

Conclusion

In this presentation, we'll describe the contribution of the 1,2-PB for EPDM and CSM rubbers based on cross linking reaction. It is expected that the findings will be useful for rubber formulation and design.

Effect of molecular architecture of poly(epichlorohydrin-co-ethylene oxide-co-allyl glycidyl ether) (GECO) on the ozone resistance of its elastomers

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Keywords: Ozone resistance; epichlorohydrin; GECO; structural parameters.

Use of polymers containing epichlorohydrin (ECH) monomers has gained importance in the rubber industry in recent years [1,2]. ECH monomer has a chloromethyl group, which allows curing and provides resistance to gas permeability and fuels [2,3]. Terpolymers produced from ECH, ethylene oxide (EO), and ally glycidyl ether (AGE) monomers, namely poly(epichlorohydrin-co-ethylene oxide-co-allyl glycidyl ether) or GECO have been produced and used for various applications in the elastomer industry. The AGE monomer in the GECO terpolymer contains a side group with a double bond, which allows for the use of additional vulcanization systems. GECO can be produced with differing ratios of monomers and molecular weights, which affect its mechanical and chemical properties. Besides gas and fuel resistance, GECO-based elastomers also have good electrostatic dissipation and vibration-damping properties [4-6]. These properties make them suitable for many applications, such as the production of hoses, gaskets, and vibration mounts. The structure of the GECO polymer is shown in Figure 1.

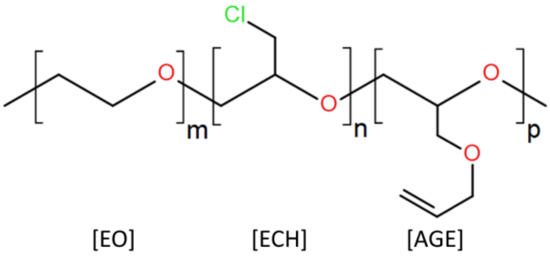

Figure 1. GECO polymer structure.

Ozone resistance is an important property of polymers that affects their lifetime. Atmospheric ozone can degrade rubbers by reacting with the polymer chains and cause scission, which leads to cracks on the elastomer surface and diminishes their strength [7]. ECH polymers are advertised to have good ozone resistance compared to alternative elastomers [2,3]. In one study, Chunjiang et al. [8] found that an ECH homopolymer called ECO has much better ozone resistance compared to NBR, supporting this claim. However, we did not find detailed information on the effect of the monomer architecture of GECO terpolymers on the ozone resistance of elastomers based on these polymers. Therefore, in this study, four grades of GECO polymers with differing monomer ratios and Mw values produced by the Zeon Company were used to prepare elastomers, and their ozone resistance was studied. Some structural properties of the used GECO polymers are given in Table 1.

Table 1. Monomer composition of GECO polymers and their weight average molecular mass.

GECO type	ECH [wt%]	EO [wt%]	AGE [wt%]	Mw (g/mol)
T3108	49.7	43.1	7.2	652.835
T3000LL	64.3	30.7	5.0	763.050
T3100	74.2	14.8	11.0	2.043.920
T3102	75.8	20.5	3.7	2.154.850

Table 2 gives the compound formulations of prepared GECO elastomers. Six test samples were prepared for each elastomer and placed in the ozone test device to test ozone resistance. The ozone concentration is 200pphm, the test temperature is 40°C, the relative humidity is 50%, and the extension ratio is 20%.

Two samples were taken out of the ozone test chamber after 24, 48, and 78 hours of exposure. The surfaces of samples were investigated for each time period for signs of degradation and cracks and mechanical physicomechanical properties were determined

Table 2. Recipes of prepared compounds.

Compound	phr
GECO (T3108, T3102, T3100, T3000LL)	100
TESPT-Silica	20
Naphthenic Oil	5
2,2,4-trimethyl-1,2-dihydroquinoline (TDQ)	1
N-(1,3-Dimethylbutyl)-N'phenyl-*p*-phenylenediamine (6PPD)	1
MgO	3
Stearic Acid	1
Diphenyl Guanidine (DPG)	0.5
2,4,6-Trimercapto-*s*-triazine (TMT)	0.8

The results indicate that the molecular architecture of GECO rubber controls the curing, mechanical, and also ozone resistance of elastomers, and ECH content is one of the important factors that affects the ozone resistance of elastomers.

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Exploring hybrid cure system in EPDM rubber to achieve optimum performance properties

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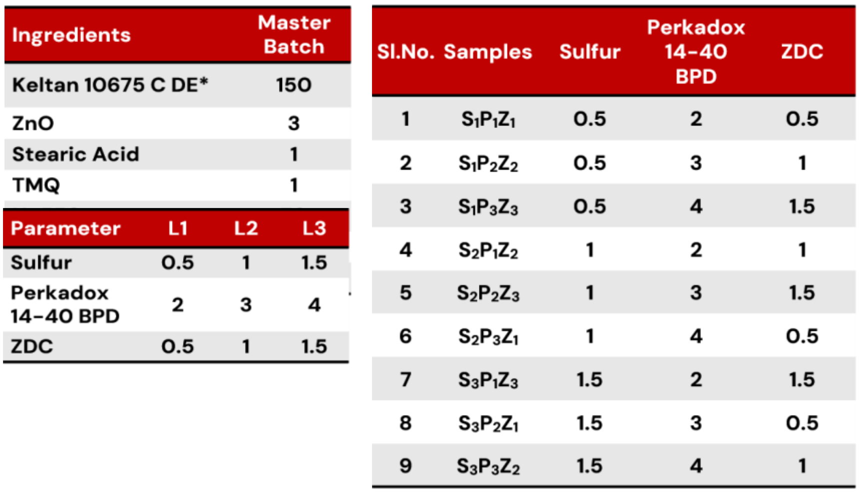
Keywords: Crosslinking, EPDM, Hybrid Curing, TSSR.

ABSTRACT: In polymer science, the invention of crosslinking led to a paradigm change. Despite ongoing research, cross-linking science and technology has a great deal of untapped potential. This work explores how the different crosslinking systems, such as sulfur-based, peroxide-based, and their hybrid systems, would reflect changes in the physio-mechanical and performance properties of ethylene-propylene-diene monomer (EPDM) rubber with various molecular configurations. This kind of analysis illuminates the characteristics of the cross-linking network established by each cross-linking technology. Since solid viscoelastic elastomers contain a large number of components, it is nearly impossible to deduce the structural properties of the crosslinking network directly. If all components other than crosslinking ingredients remained unchanged, stress relaxation behavior correlated directly with the crosslink network in the samples. In this work, temperature scanning stress relaxation (TSSR), a relatively new technique capable of creating the whole spectrum of stress relaxation, was effectively explored.

The information obtained from various analytical measurements and TSSR about the crosslink structure present in samples cured with different cure packages explains the performance properties (related to automotive application) of EPDM composites under this study. The findings suggest that sulfur and carbon crosslinks coexist in hybrid systems regardless of the molecular structure of the elastomer, and their synergistic impact is evident in their performance properties. Furthermore, it is clear from the results that the molecular structure of the EPDM has an impact on the final properties, such as tensile strength, compression strength, and thermal properties of the samples. In addition, the recipe used in the hybrid cure system is further optimized in this work using statistical tools to leverage the synergistic impact on performance properties.

Table 1: Formulations used for optimization of hybrid cure system

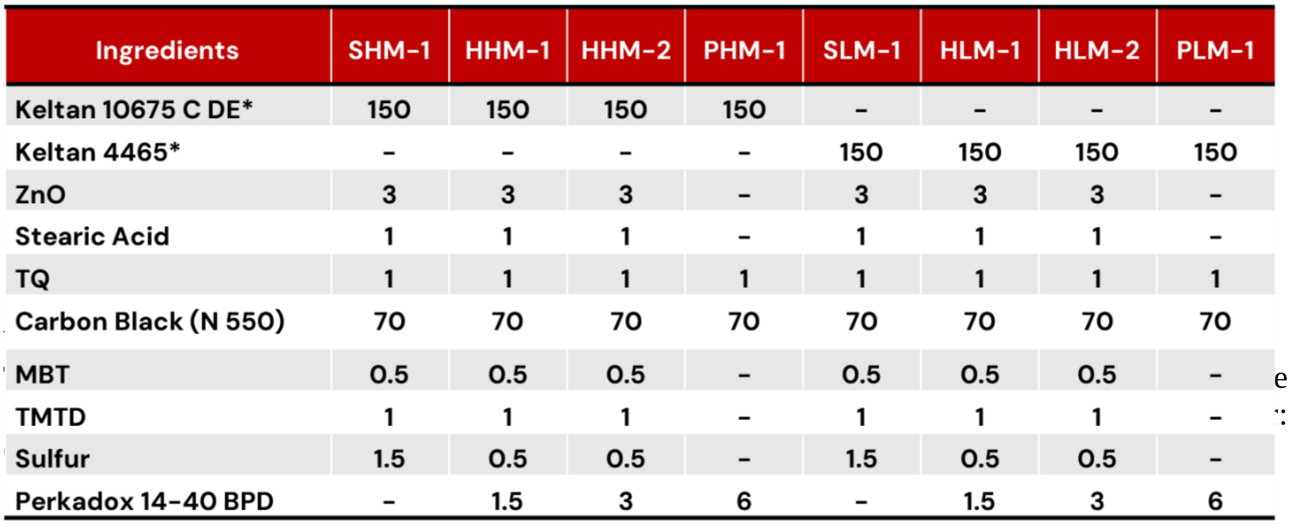


Ingredients	Master Batch
Keltan 10675 C DE*	150
ZnO	3
Stearic Acid	1
TMQ	1

Parameter	L1	L2	L3
Sulfur	0.5	1	1.5
Perkadox 14-40 BPD	2	3	4
ZDC	0.5	1	1.5

Sl.No.	Samples	Sulfur	Perkadox 14-40 BPD	ZDC
1	$S_1P_1Z_1$	0.5	2	0.5
2	$S_1P_2Z_2$	0.5	3	1
3	$S_1P_3Z_3$	0.5	4	1.5
4	$S_2P_1Z_2$	1	2	1
5	$S_2P_2Z_3$	1	3	1.5
6	$S_2P_3Z_1$	1	4	0.5
7	$S_3P_1Z_3$	1.5	2	1.5
8	$S_3P_2Z_1$	1.5	3	0.5
9	$S_3P_3Z_2$	1.5	4	1

Table 2: Formulations used to deduce correlations between molecular and crosslink structure in terms of performance properties



Ingredients	SHM-1	HHM-1	HHM-2	PHM-1	SLM-1	HLM-1	HLM-2	PLM-1
Keltan 10675 C DE*	150	150	150	150	-	-	-	-
Keltan 4465*	-	-	-	-	150	150	150	150
ZnO	3	3	3	-	3	3	3	-
Stearic Acid	1	1	1	-	1	1	1	-
TQ	1	1	1	1	1	1	1	1
Carbon Black (N 550)	70	70	70	70	70	70	70	70
MBT	0.5	0.5	0.5	-	0.5	0.5	0.5	-
TMTD	1	1	1	-	1	1	1	-
Sulfur	1.5	0.5	0.5	-	1.5	0.5	0.5	-
Perkadox 14-40 BPD	-	1.5	3	6	-	1.5	3	6

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Carbon dots from cup lump via hydrothermal process for fluorescent ink

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Keywords: Carbon dots; Cup lump; Fluorescent ink.

In this research, carbon dots were synthesized from the reaction between cup lump and ammonium persulfate through a hydrothermal process at 200°C. The effect of reaction times (16, 18, 20, and 24 h) on carbon dot formation was investigated in order to find the optimal condition. The functional groups of the carbon dots were studied by fourier transform infrared spectroscopy. The binding energy of the carbon dots was measured by X-ray photoelectron spectroscopy. Transmission electron microscope was used to analyze the morphology of the carbon dots. Optical properties were then investigated by using UV–vis and fluorescence spectrophotometers. The obtained results showed that the reaction time of 18 h was the most appropriate for synthesizing carbon dots from cup lump, considering the maximum fluoresnence intensity. The concentration of carbon dots was approximately 0.621 mg/ml, and the particle size of the carbon dots was about 6.3 nm. Finally, the carbon dots obtained from this research can be applied for fluorescent ink in anti-counterfeiting application.

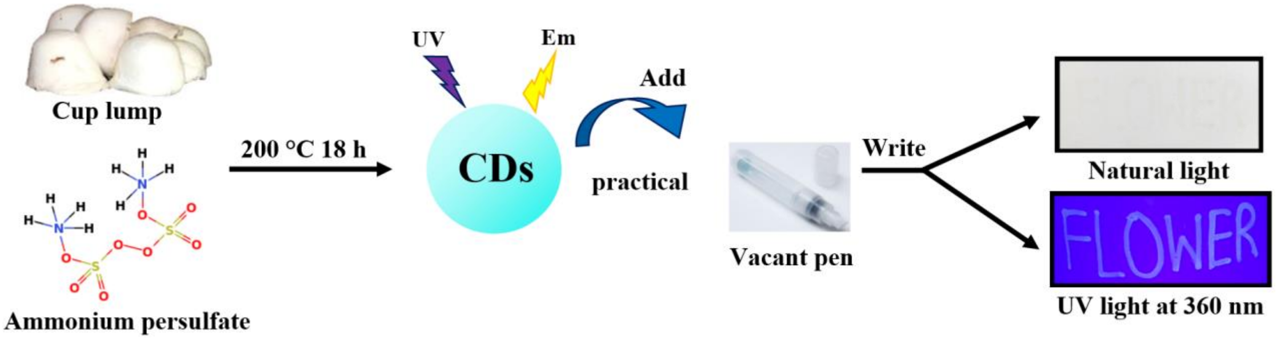

Figure 1. Formation of carbon dots from cup lump via hydrothermal process.

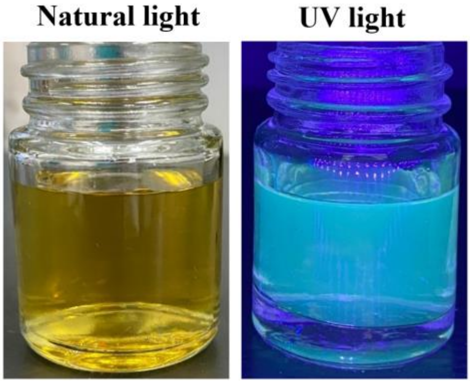

Figure 2. Obtained carbon dots under natural and UV lights at 200°C for 18 h.

Acknowledgement

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Thermo-responsive Shape Memory Polymer Network with Outstanding Thermal Conductivity

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Keywords: reactive mesogen; shape memory polymer; thermal conductivity; thermoactuator.

In this research, a novel polymerizable additive with a tetrathiafulvalene (TTF) core and flexible chain is synthesized to enhance the thermal conductivity of a shape memory polymer network (SMPN).[1] The TTF-based reactive molecule is analyzed for its thermal, optical, and structural properties using a variety of experimental techniques. The SMPN is fabricated at high temperatures without the need for any catalysts, simplifying the fabrication process and enhancing the efficiency of the method.

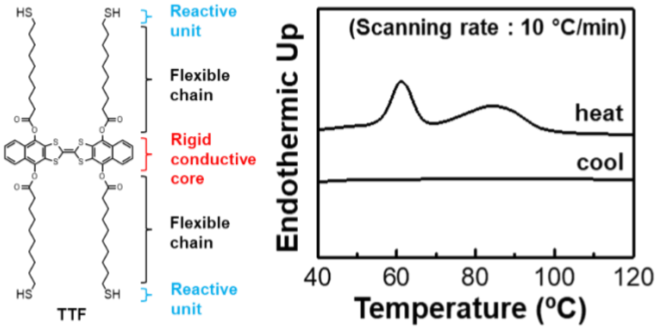

Figure 1. Chemical structure and differential scanning calorimetry of TTF reactive mesogen

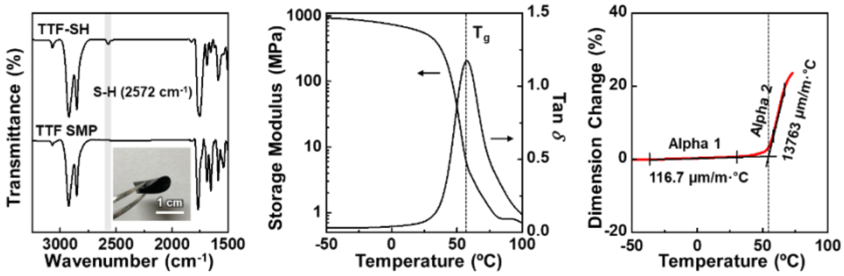

Figure 2. FT-IR of TTF monomer and SMP, photo image of TTF SMP (inset). DMA and TMA curve of TTF SMP.

The TTF-based SMPN exhibits high shape memory properties, with a fixing ratio of 99.42% and a recovery ratio of 99.98%, demonstrating the effectiveness of the TTF-based reactive molecule for the performance of the SMPN. In addition, the SMPN shows an excellent thermal conductivity of 1.12 W/mK, which is significantly higher than that of conventional shape memory polymers. This high thermal conductivity is crucial for applications that require rapid heat transfer, such as thermoactuators.

The correlation between the shape recovery speed and thermal conductivity is demonstrated, providing valuable insights into the performance of the SMPN. This correlation confirms the effectiveness of the TTF-based reactive molecule as an additive in enhancing the thermal conductivity of the SMPN, thereby improving its shape recovery speed.

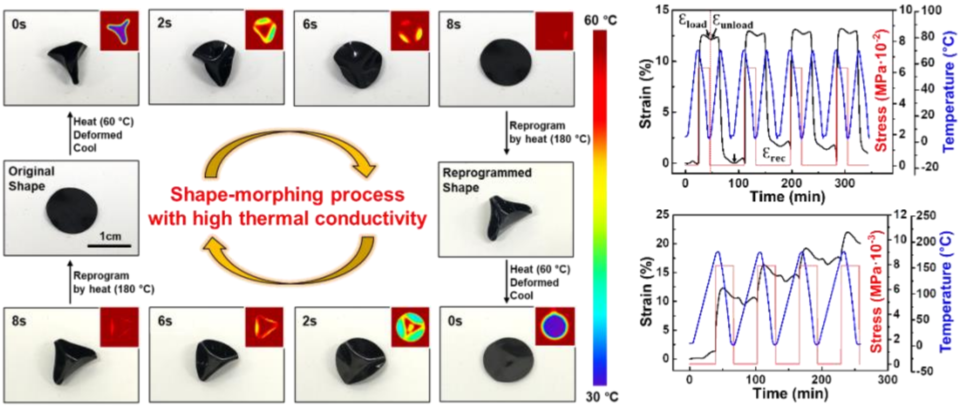

Figure 3. Qualitative and quantitative verification of TTF shape memory polymer with high thermal conductvity.

The applicability of the TTF-based SMPN is confirmed through the successful fabrication of a thermoactuator. The thermoactuator shows a fast shape-morphing response due to its excellent thermal conductivity, demonstrating the potential of the TTF-based SMPN in practical applications.

Potential applications of the TTF-based SMPN include a warning sensor for device overheating and a smart sunshade for solar energy management. These applications highlight the versatility of the TTF-based SMPN and its potential to contribute to various fields, including electronics, energy management, and smart materials.

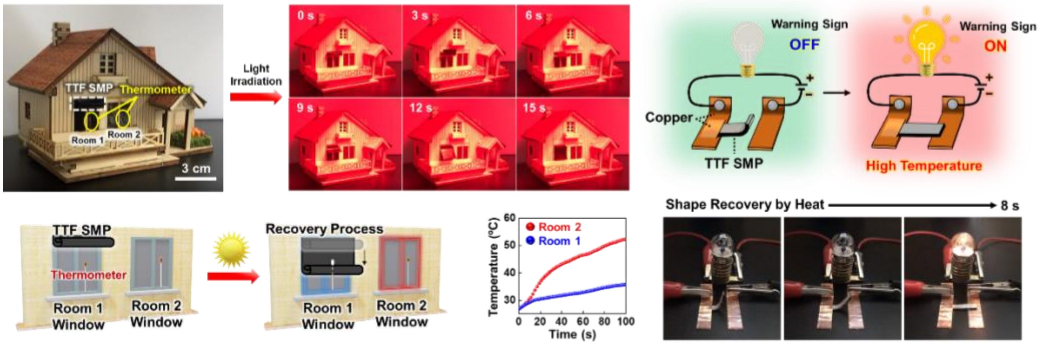

Figure 4. Practical application of TTF SMPN.

Acknowledgement

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How does heat development affect the cut and chip wear of rubber?

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Keywords: Tire; Wear; Cut and Chip; Heat

Tire wear is a complex system of interlinked mechanisms which have a decisive impact on the length of the service life of a tire. When a tire is exposed to the most severe conditions resulting in Cut and Chip (CC) mechanism a rapid heating process is triggered due to the friction caused by the viscoelastic rubber sliding over an uneven surface and sharp asperities. This takes place particularly in areas of high stress concentration in the tire contact patch and locally around the tips of the bumps, heating the material and transferring the heat to the surrounding areas in the tire, subsequently affecting wear process. However, the extend of heat generation and its specific effects on rubber wear during CC mechanism have not yet been investigated. Therefore, this work presents the first study that primarily deals with the detailed characterization of the influence of heat development on the CC wear of a styrene-butadiene rubber (SBR), which is used as a synthetic rubber in tire treads.

The investigations were carried out using the Instrumented Cut and Chip Analyzer (ICCA, Coesfeld GmbH & Co. KG, Germany) in combination with a high-precision on-site measurement of temperature development using high-speed thermography shown in Figure 1. The mechanical ICCA testing conditions consisted of two loading normal forces 110 N and 150 N with constant rotation speed 203 rpm and constant impact frequency 2 Hz. Conditions for high-speed thermography were set to sampling rate of 625 Hz recording initial three impacts and subsequent impacts after 1000, 2000 and 3000 cycles of the ICCA measurement.

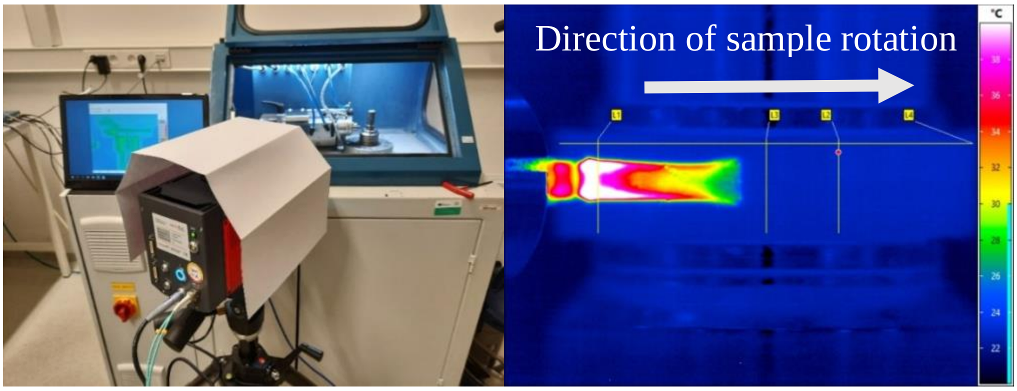

Figure 5. ICCA testing set-up with high-speed thermo-camera (left), thermographic record of the CC process (right).

In terms of mechanical behavior study showed that the higher the applied load, the higher the CC wear of the SBR rubber, which is consistent with previous findings on the resistance of synthetic rubber to CC wear. [1-2] However, from a thermal point of view, it is surprising to find that the heat development during CC wear of SBR rubber is completely independent of the applied load. It was also found that at the beginning of the CC wear process, the initial temperature value depends on the applied load, but the temperature rise during the first CC wear phase does not. Last but not least, it has been demonstrated unanimously that during CC wear the temperature rises up to a certain level and then the temperature does not rise any further, but the generated heat leaves the surroundings.

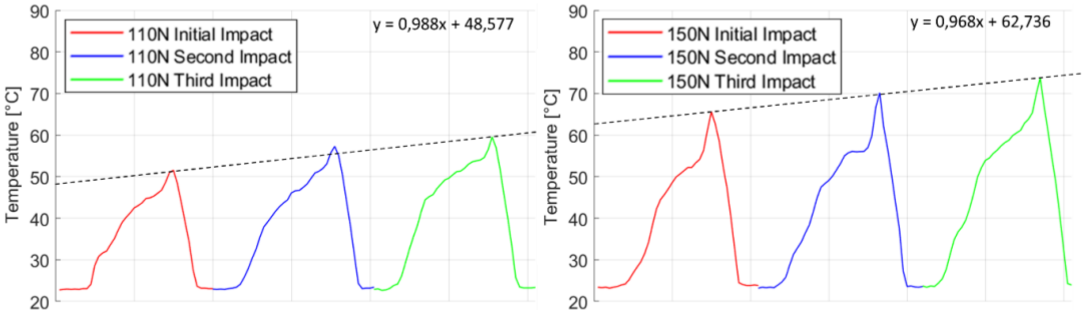

Figure 6. Temperature data of the first three sequential impacts.

The findings suggest interesting load-independence of heat evolution of SBR rubber within the investigated CC loading conditions. Therefore, the future study will focus on more detailed heat development description using increased cycle resolution during CC abrasion of different materials. Such data could then be used for advanced numerical simulations of different tire wear processes or, for example, off-segment tires for CC of conveyor belt tread wear, as well as for intelligent optimization of rubber compounds to improve the wear resistance of these different applications.

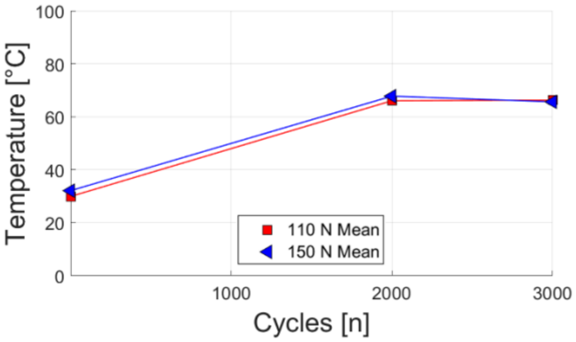

Figure 7. Temperature over number of cycles.

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Evaluation and Characterization of Resistance of Polyacrylate (ACM) Under Different Types Application Areas

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Keywords: Polyacrylate (ACM); oils; elongation at break; volumetric change.

Polyacrylate (ACM) type rubbers have wide range of usage areas in different industries likewise gaskets, o-rings, beltings, shaft seals, plastics, piping etc...Different usage areas have different working conditions. Additionally, different working conditions could include different oil, grease and fuel contact areas. According to contacted petroleum product different stability characteristics could be developed by the ACM product. In this study, we have been evaluated different characteristics of ACM type rubber under two different types of engine oils, gasoline fuel, diesel fuel, two different types of differantial oils, hydraulic oil and grease conditions. Along with these UV stability of ACM with petroleum products have been evaluated also. Elongation at break, volumetric changes, density changes and Shore A values of ACM samples have been evaluated and characterisation results have been reported and concluded.

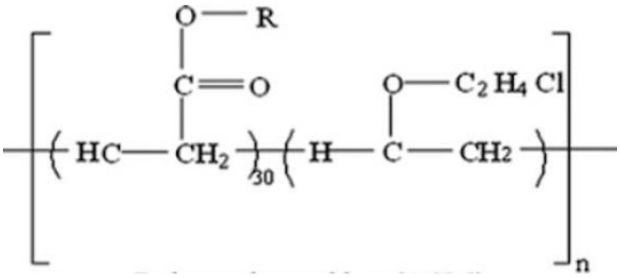

Figure 1. Chemical structure of Polyacrylate (ACM) type rubbers

Table 1. Sample compositions

Components [phr]	**Sample notations**			
	N1	**N2**	**N3**	**N4**
ACM[a]	100	100	100	100
Engine Oil I	A	A	A	A
Engine Oil II	B	B	B	B
Fuel Oil	C	C	C	C
Gasoline	D	D	D	D
Hydraulic Oil	E	E	E	E
Grease	F	F	F	F

[a] Polyacrylate rubber

Acknowledgement

Thanks to the Petrol Ofisi A.Ş. for contributions to the study.

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Investigation of the Effects of the Use of UV Stabilizers in Process Oils on EPDM Based Rubber Compounds

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Keywords: EPDM based rubber; process oils; elongation at break; volumetric change, rheometric measurements

In this study, we have been investigated the effect of UV stabilizer usage in process oils on EPDM based rubber compounds. This study was carried out by Petrol Ofisi A.Ş. The aim of this study is to evaluate the usability of the "PO White Oil" product, currently produced by A.Ş., as a paraffinic-based process oil that can provide effective UV resistance in EPDM-based and light-colored rubber compounds.

For this purpose PO White Oil; Petrol Ofisi A.Ş. It was compared with the process oil provided by and defined as the closest competing product in terms of the material properties in question. It was evaluated separately for its effectiveness in peroxide and sulfur cooking systems, using a light colored EPDM paste formulation created as a reference. In order to improve the UV resistance of EPDM dough, it was investigated by adding two different commercial UV stabilizers that are widely used. At this stage, the situations of adding UV stabilizers directly to the dough and adding them by pre-mixing with PO White Oil are discussed separately.

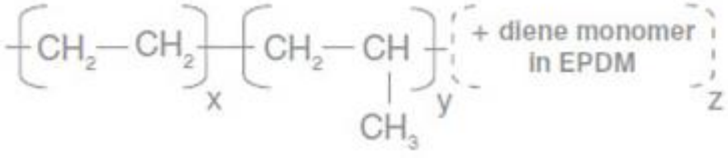

Figure 1. Chemical structure of EPDM type rubbers

Table 1. Sample compositions

Components [phr]	**Sample notations**					
	S-REF	**R-S**	**UV-1 SD**	**UV-2 SD**	**UV-1 SID**	**UV-2 SID**
EPDM[a]	100	100	100	100	100	100
PO White Oil	A	-	A	A	-	-
PO White Oil-UV 1	-	-	-	-	B	-
PO White Oil-UV 2	-	-	-	-	-	C
TiO_2[b]	D	D	D	D	D	D
ZnO[b]	E	E	E	E	E	E
Sulphur	F	F	F	F	F	F

[a] Ethylene-Propylene-Diene-Monomer
[b] Titanium Dioxide
[c]Zinc Oxide

When the rheometer curves and numerical values of rheological properties of dough baked with sulfur are examined, it is seen that PO White Oil and competing process oil do not make a difference in terms of baking properties in EPDM-based control dough.

Other important findings obtained were that the cooking system did not have a noticeable effect on the rheological properties in the selected dough composition, and that minor changes in rheological properties were observed both in the case of comparing PO White Oil with the competing process oil and in the case of the use of UV stabilizer, for both cooking systems. that it is at the same level.

Acknowledgement

Thanks to the grant sponsors and/or people who contribute to the study

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Anti-reversion agents for preventing marching cure of chloroprene rubber

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Keywords: Anti-reversion agents, Chloroprene rubber, Kinetic modelling, Marching cure, Vulcanization.

Vulcanization is a process, in which rubber compound is irreversibly turned into an elastic structure using chemical crosslinking agents by means of heat and pressure. Vulcanization reaction can usually be monitored on a moving die rheometer equipment. Vulcanization reaction may undergo plateau, reversion or marching cure depending on type of rubber, vulcanization temperature and duration of the reaction. In marching cure type vulcanization, torque value increases continuously, reaction takes too long, and no stable plateau can be reached. High reaction times also restrict industrial feasibility. Besides, for marching cure type vulcanization reactions, scorch time (t_{s2}) and optimum cure time (t_{90}) cannot be determined properly due to indefinite cure time (t_{MH}) time and therefore it is not likely to obtain sufficient performance for the final cured product. Chloroprene rubber (CR), chlorosulfonated polyethylene (CSM), nitrile rubber (NBR) and styrene-butadiene rubber (SBR) are the examples for those which usually exhibit marching cure type vulcanization behaviour.

In this study, 1,3-bis (citraconimidomethyl) benzene (CIMB), N-N'-m-phenylenedimaleimide (HVA-2) and epoxidized natural rubber (ENR) were evaluated for stabilizing crosslinks and so for preventing marching cure in CR based rubber compounds. CIMB and HVA-2, which are commonly used as anti-reversion agents for natural rubber, were incorporated to CR compounds in various amounts and cure characteristics of these compounds were studied. Physical, mechanical, structural, thermal and morphological properties of the compounds were measured after vulcanization. Besides, cure kinetics of the compounds was investigated by fitting the cure curves to a common non-linear kinetic model. Conventional anti-reversion agents have been considered for preventing marching cure as the first time in this study. It was concluded that, CIMB and HVA-2 could effectively be used for stabilizing crosslinks in CR based rubber compounds.

Acknowledgements

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Mussel-inspired environmentally friendly dipping system for aramid fiber and its interfacial adhesive mechanism with rubber

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Keywords: Surface modification, Fiber, Adhesion, Dopamine.

Aramid fiber (AF), which has the excellent properties of high specific strength, high specific modulus, cut resistance, as well as low density, is widely used in rubber reinforcement, aerospace, bulletproof and other fields. However, AF has a smooth and crystalline surface, resulting poor interfacial adhesion properties when used in reinforcing rubber matrix [1]. In the rubber industry, in order to bond fiber cord with rubber, the most commonly used method is the resorcinol-formaldehyde-latex (RFL) dipping treatment of the fiber skeleton materials. The hydroxymethyl and hydroxyl groups in the resorcinol-formaldehyde resin phase can be chemically linked to the fiber surface, and the rubber latex can participate in the vulcanization of the rubber matrix, thereby forming a good interfacial interactions between fiber and rubber [2]. On the other hand, however, the development of a new environmentally friendly dipping system for fibers to replace the toxic and harmful RFL dipping system is imminent.

In this work, inspired by versatile mussel adhesion protein and mimicking adhesive molecule [3,4], polyethyleneimine/pyrogallic acid (PEI/PG) adhesive was employed to replace toxic and carcinogenic resorcinol and formaldehyde to make the dipping process safe and environmentally friendly. Due to the chemically inert surface of the AF, we use blocked isocyanate and epoxy aqueous solution to activate AF, and then conduct dipping treatment. We have investigated the interfacial adhesion, chemical compositions and surface topography under different conditions, and developed a novel environmentally friendly dipping system which reaches the level of traditional RFL dipping system. The detailed chemical ractions are illustrated in Fig. 1.

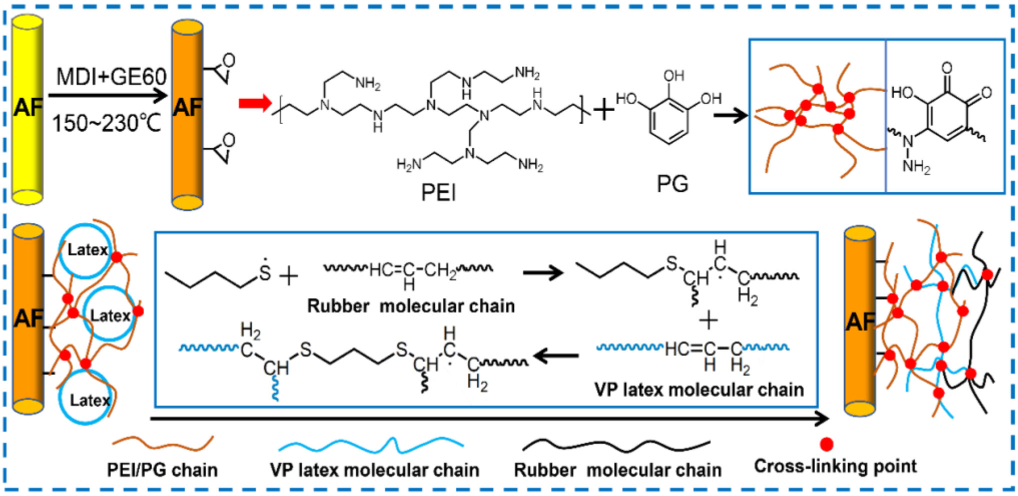

Fig. 1. The illustration of chemical interactions between AF-EP-PAL and rubber.

As shown in Fig. 2(a-c), Nano-IR is used to study the interfacial microchemical structure of AF/rubber composites. the results of AF-EP-PAL/rubber composites is found to be 147 N, which is near to the result of the AF-EP-RFL/rubber composites (154 N)(Fig. 2(d-f)). After the dipping treatment of AF, there is no obvious further decrease in breaking strength, which shows that the dipping solution will not cause damage to the mechanical properties of the fiber. Elongation at break of the fiber is mainly caused by the activation step of the epoxy and isocyanate, which is due to the destruction of the amide structure in the fiber backbone. These results show that the PAL dipping solution can effectively replace the RFL dipping solution which contains harmful resorcinol and formaldehyde, thereby reducing damage to the human body and the environment.

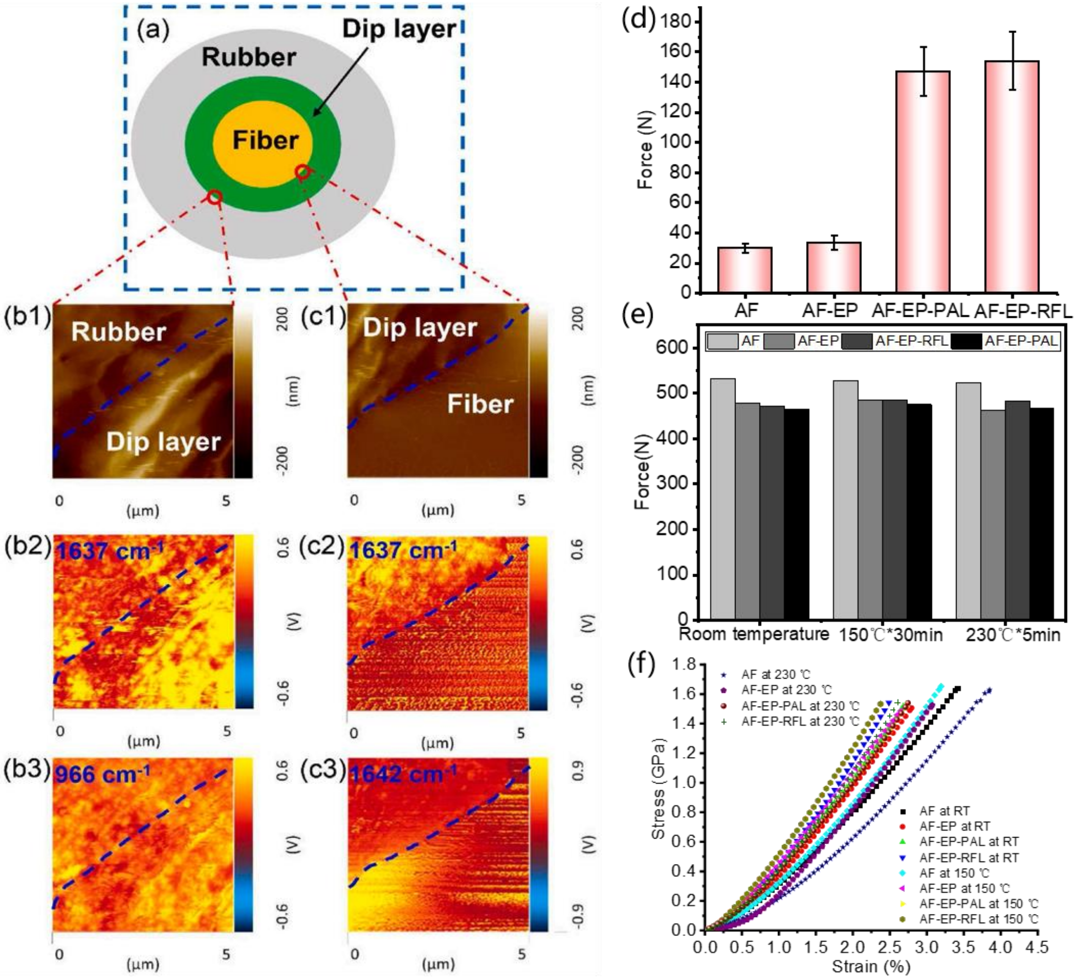

Fig. 2. (a) Schematic diagram of interface structure, Nano-IR mapping images of (b) the rubber-dip layer interface, (c) the dip layer-fiber interface, (d) H pull-out force of fiber/rubber composites, (d) breaking strength and (f) stress-strain curves of AF before and after high temperature treatment.

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Porphyrin-Based Metallomesogens for Thermal Management Materials

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Keywords: Porphyrin-Based Composites; Metallomesogen; Thermal Conductivity; Heat Management.

Thermal management is a critical issue in the development of advanced rubber composites used in various applications, ranging from automotive to electronics. Improving thermal conductivity while maintaining the material flexibility and durability is a significant challenge. This study presents the synthesis and application of novel porphyrin-based reactive metallomesogens (PorV) with dendritic alkyl chains, designed to enhance the thermal properties of rubber composites through controlled molecular architecture. (Figure 1) These metallomesogens undergo self-assembly into columnar structures, which are then polymerized using a thiol-ene click reaction, stabilizing the structure and enhancing the thermal properties. This method offers a unique opportunity to explore the impact of molecular packing structures on thermal conductivity, facilitated by the robust cross-linking provided by the thiol-ene click chemistry.

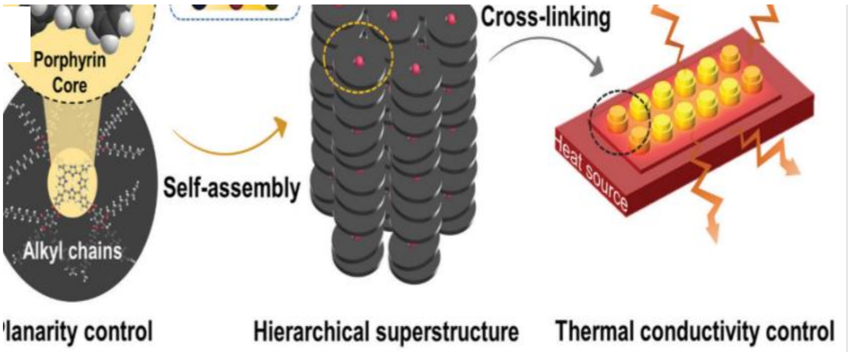

Figure 1. Schematic illustration of the control of thermal conductivity of Por-V

The research explored the substitution of various metal atoms in the porphyrin core, enhancing the crystallinity and planarity of rubber composites while maintaining their excellent mechanical properties and flexibility. Particularly, Zn substitution resulted in the highest thermal conductivity, highlighting the role of molecular planarity in thermal management. (Figure 2) This underscores the potential of metal-specific modifications to boost thermal performance in heat-sensitive rubber applications without sacrificing flexibility.

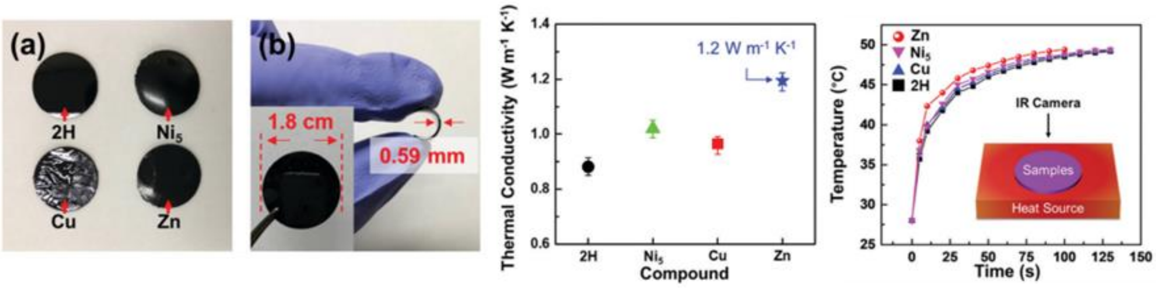

Figure 2. (a and b) Macroscopic images of the flexible PorV films. Thermal conductivities of the PorV films.

Practical applications were demonstrated by fabricating heat sinks from epoxy and PorV-Zn composites. The PorV-Zn heat sinks outperformed those made from conventional epoxy, achieving thermal equilibrium more rapidly under controlled conditions. This superior performance, driven by the optimized molecular structure of PorV-Zn, emphasizes the benefits of porphyrin-based composites in enhancing heat dissipation, pivotal for advanced thermal management solutions in the rubber industry. (Figure 3)

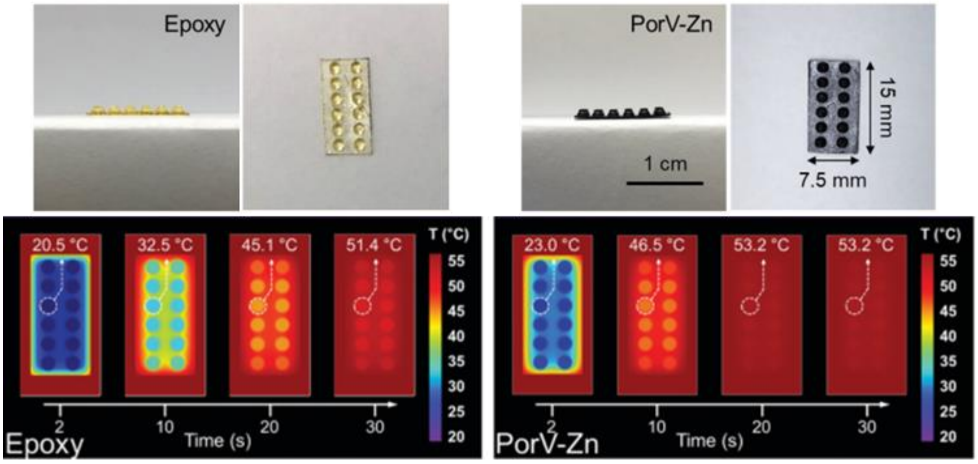

Figure 3. Photographs and IR thermal images of heat sinks consisting of Epoxy and PorV-Zn.

Our research provides valuable insights for the rubber industry, demonstrating that precise molecular-level manipulations can significantly enhance the macroscopic thermal properties of rubber composites. This study advances the understanding of heat transfer mechanisms in polymer-based systems and paves the way for designing high-performance, thermally conductive rubber materials suitable for a wide range of high-temperature applications.

Acknowledgement

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Hierarchical Superstructures of Azobenzene-Based Polynorbornenes for Smart Denpols to Remote-Controllable Actuators

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Keywords: azobenzene, dendronized polymer, photoisomerization, remote-controllable actuator.

Photoresponsive polymers have been explored as actuators that convert light into mechanical work, with a strong focus on liquid crystalline elastomers and networks incorporating photochromic mesogens. Understanding the hierarchical superstructures formed by the self-assembly of smart denpol building blocks can provide new insights into the anisotropic bending behavior of photo actuators.

To demonstrate remote-controllable actuators, a newly designed dendronized polymer (denpol) was successfully synthesized through ring-opening metathesis polymerization of azobenzene-based macromonomers. As shown in Figure 1, incorporating azobenzene mesogens into the denpols allows for the construction of finely tuned hierarchical superstructures with anisotropic physical properties and reversible photoisomerization.

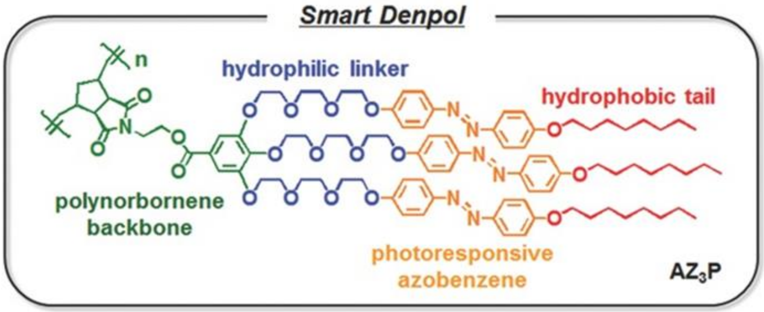

Figure 1. Chemical structure of smart denpol containing an azobenzene-functionalized dendron

The 2D WAXD was employed to investigate the details of molecular packing symmetry in the AZ_3P films (Figure 2). In uniaxially oriented films, the polynorbornene backbones and azobenzene side chains are aligned perpendicular and parallel to the layer normal, respectively.

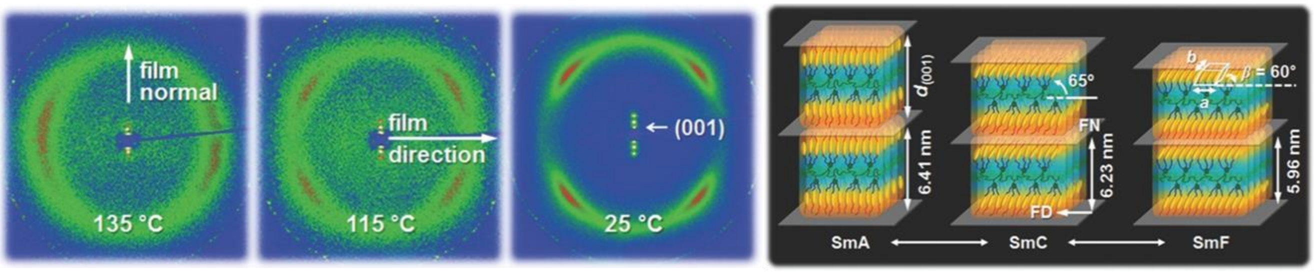

Figure 2. 2D WAXD patterns of uniaxially oriented AZ_3P film and schematic illustration of molecular arrangements

To demonstrate the photoactivaed mechanical deformations, an AZ$_3$P film was fabricated by melt scraping process. As a result, when the AZ$_3$P film is exposed to the UV light, it bends away from the light source, resulting in the AZ$_3$P film wrapping around the support pole due to the photoisomerization of azobenzene. Irradiation of visible light recovers the AZ$_3$P film to the initial floating state (Figure 3).

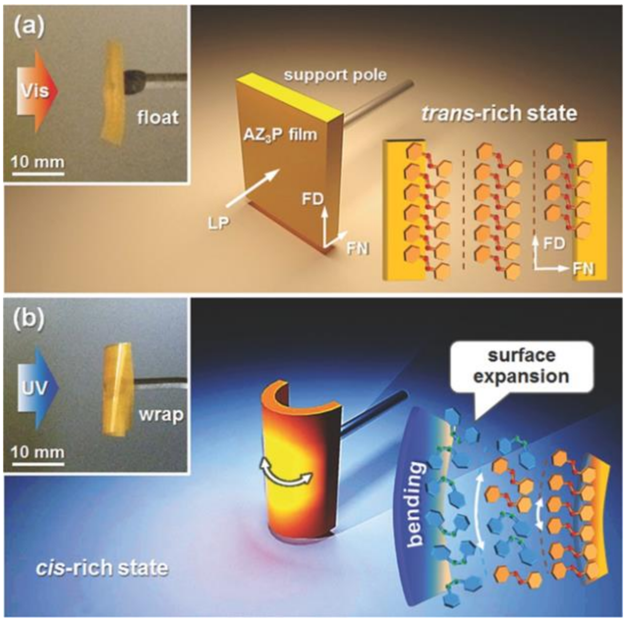

Figure 3. Schematic illustrations of photo-reversible bending mechanisms upon irradiating of vis and UV lights.

Based on photoreversible actuation experiments and diffraction results, direct relationships between the chemical structures, hierarchical superstructures, and their corresponding photomechanical behaviors are proposed. Smart denpols hold significant potential for practical applications in photoresponsive switches.

Acknowledgement

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