

## Research Article

# Investigation of Epoxidized Palm Oils as Green Processing Aids and Activators in Rubber Composites

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Epoxidized palm oil (EPO) is environmentally friendly, biodegradable, and a relatively less costly processing aid. In this study, we investigated the suitability of EPO in place of aromatic processing oils in styrene butadiene rubber. The curing properties, mechanical properties, abrasion resistance, and heat buildup properties of rubber composites with EPO were compared with those of the standard with aromatic oils. The rubber composites with EPO showed enhanced mechanical properties including modulus, tensile strength, and elongation at break. This is ascribed to the improved dispersion of fillers in the rubber matrix and interaction between the filler and the polymer. Furthermore, EPO in the rubber matrix showed remarkable abrasion resistance, rebound resilience, and heat buildup at low loadings. EPO in a rubber composite presents feasibility as a renewable raw material that can serve as an alternative to petrochemical oils in various applications.

## 1. Introduction

Petroleum oils, which originate as derivatives of the petrochemical industry, have been conventionally used as plasticizers for natural and synthetic rubbers in the tire industry [1–3]. Among petroleum oils, aromatic, naphthenic, and paraffin oils are frequently used as processing aids with peroxides being the crosslinking agents [4]. However, it is noteworthy that petroleum oils are depleted and have adverse effects on human health. In response, there has been growing demand to find alternative oils that are renewable, safe, sustainable, and environmentally friendly [5].

Vegetable oils are an attractive natural resource for the synthesis of bio-based polymers due to their stability, low cost, environment friendliness, and biodegradability [6, 7]. The use of these oils is of particular interest to researchers due to their potential as substitutes to petrochemical derivatives in the plastic and rubber industries as excellent plasticizers. Dasgupta et al. reported that palm oil (PO) in a rubber matrix shows better processing properties by enhancing the interaction between rubber and fillers and the

dispersion properties as an eco-friendly processing aid [8]. Kuriakose and Varghese found that vegetable oil exhibited enhanced mechanical properties in comparison to those of paraffinic oil at a fixed dose (1 phr). Rice bran oil with free fatty acids enhances the physical properties of carbon black-filled natural rubber and polychloroprene blends [9].

In recent years, modified vegetable oils have been used to modify thermoset polymers and to synthesize new polymers in efforts to enhance the efficiency of the manufacturing method of linoleum floor cloth [10–12]. In general, it is considered that epoxidized palm oil (EPO) chemically modifies and transforms the triglyceride into a reactive group via epoxidation and acrylation of the epoxide reaction with maleic anhydride [13–16]. Epoxidation of palm oil is done by introducing palm oil through an oxidation process. The epoxidation process is a chemical reaction of converting carbon-carbon double bond to the epoxide functional group in vegetable oil, which is a cyclic ether with three ring atoms. It is a very important process nowadays because epoxides obtained from vegetable oil can be used as high temperature of raw materials for alcohol or glycols. EPO not only

improves the stability of the oil but also provides adequate reactivity to form chemical linkages with other polymers. Rosli et al. studied the curing of an EPO-cycloaliphatic diepoxide system with an oxirane ring as a curing agent to form polymer composites using UV radiation [17]. Also, to improve the impact strength of polymer composites, Jayewardhana et al. used epoxidized soybean oil in epoxy resin as a toughening agent [18]. Therefore, it is possible for researchers to incorporate with the epoxy network system as a processing aid. However, while the reinforcement of plastic polymers by exploiting the effects of EPO has sparked significant interest, few works have been devoted to using the same effects in a rubber matrix. In this light, it is necessary to investigate the chemical and physical interactions of EPO with styrene butadiene rubber in order to assess its suitability as a processing aid and as an activator.

In this study, we selected styrene butadiene rubber (SBR) as the rubber matrix and successfully prepared SBR/EPO-based multifunctional rubber composites. EPO is a promising elastomer additive because it enhanced the modulus, tensile strength, and elongation at break. Also, the improved dispersion of fillers in the elastomer matrix produced a remarkable synergetic effect that significantly enhanced abrasion resistance, heat buildup, and rebound resilience properties. Based on these results, we confirm that palm oil-based hybrid oils may be used as multipurpose additives in elastomer composites.

## 2. Experimental Section

**2.1. Materials.** SBR (styrene butadiene rubber, SBR 1500) consisting of styrene of 23% and butadiene of 77% as the matrix material was purchased from Kumho Petrochemical Co. Ltd., Korea. Also, carbon black (N 330) was obtained from OCI Co. Ltd., Korea and N-tert-butyl-benzothiazole sulfonamide (TBBS) were purchased from Shandong Shanyan Co. Ltd., China. Zinc oxide (ZnO), stearic acid (S/A), and sulfur were purchased from Sigma-Aldrich. AO, TDAE, PO, and EPO were purchased from Kumho Petrochemical Co. Ltd., Korea.

**2.2. Preparation of Rubber Composites.** Composites of carbon black and elastomers produced by Banbury internal mixing were prepared with epoxidized palm oil (EPO) for comparison with composites with diverse oils such as aromatic oil (AO), treated distillate aromatic extracted oil (TDAE), and unmodified palm oil (PO). Different oil/SBR composites were prepared by following the standard procedure outlined in Table 1. First, SBR (100 phr; parts per hundred rubber by weight) was mixed with 50 phr carbon black with 3 phr diverse oils at a rotor speed of 60 rpm in a Banbury mixer. And then, the vulcanization agents and additives were mixed at the end to start the curing process of the compounds. The compounds were placed in an aluminum mold and cured at 160°C for  $t_{90}$  (vulcanization optimum) by a rheometer under pressure (0.45 MPa). The formulations of the diverse oil/SBR composites are summarized in Table 1 [19].

TABLE 1: Formulations of the diverse oil/SBR composites (unit: phr).

Materials	AO	TDAE	PO	EPO
SBR	100	100	100	100
Carbon black	50	50	50	50
Stearic acid	1	1	1	1
AO	3	—	—	—
TDAE	—	3	—	—
PO	—	—	3	—
EPO	—	—	—	3
Sulfur	1.75	1.75	1.75	1.75
ZnO	2	2	2	2
TBBS	1	1	1	1

**2.3. Thermal Degradation Method.** Dumbbell-shaped samples with a thickness of 0.5 mm were prepared from the elastomer composites with different oils. All the samples (AO/SBR, TDAE/SBR, PO/SBR, and EPO/SBR) were placed in an oven at 100°C for thermal degradation reactions conducted during 168 hrs.

**2.4. Characterization.** Curing characteristics were carried out using a moving-die rheometer (DRM-100(LP-171)) over 30 min periods at 160°C. Also, Shore A hardness was conducted by using a hand-held Shore A durometer according to TECLOCK. Tensile tests were measured at a crosshead speed of 500 mm/min in an Instron tensile machine (Instron Co., UK). The dumbbell shape samples were 100 mm in length and 5 mm in width. At least four tests were conducted for each case. Dynamic tests were carried out using a dynamic mechanical analyzer (model DMA 50N01Db; Metravib, France) in tensile mode. The temperature dependence (temperature sweep) of the storage modulus and the loss factor ( $\tan \delta$ , defined as the ratio of the loss modulus to the storage modulus) were measured from -50 to 100°C at a heating rate of 3°C/min and a frequency of 10 Hz. The fatigue properties of the composites were characterized by using Demattia (Ueshima, D430-06(ASTM)). The abrasion resistance and rebound resilience of the rubber composites were determined by a DIN rubber abrasion resistance tester (GT-KB02, D3389-19 (ASTM)) and a rebound resilience tester (RB 3000), respectively.

## 3. Results and Discussion

The processability of the composites with diverse oils such as aromatic oil (AO), treated distillate aromatic extracted oil (TDAE), and unmodified palm oil (PO) is important and was determined by evaluating curing characteristics such as cure time, Mooney viscosity, and maximum and minimum torque. Generally, as an indicator of processability for elastomer composites, Mooney viscosity is used. The EPO reduced the Mooney viscosity and apparent shear viscosity of the elastomer composites, which facilitated the manufacturing process of the elastomer composites, as indicated in Figure 1(a). The curing properties based on  $t_{40}$  (scorch time)

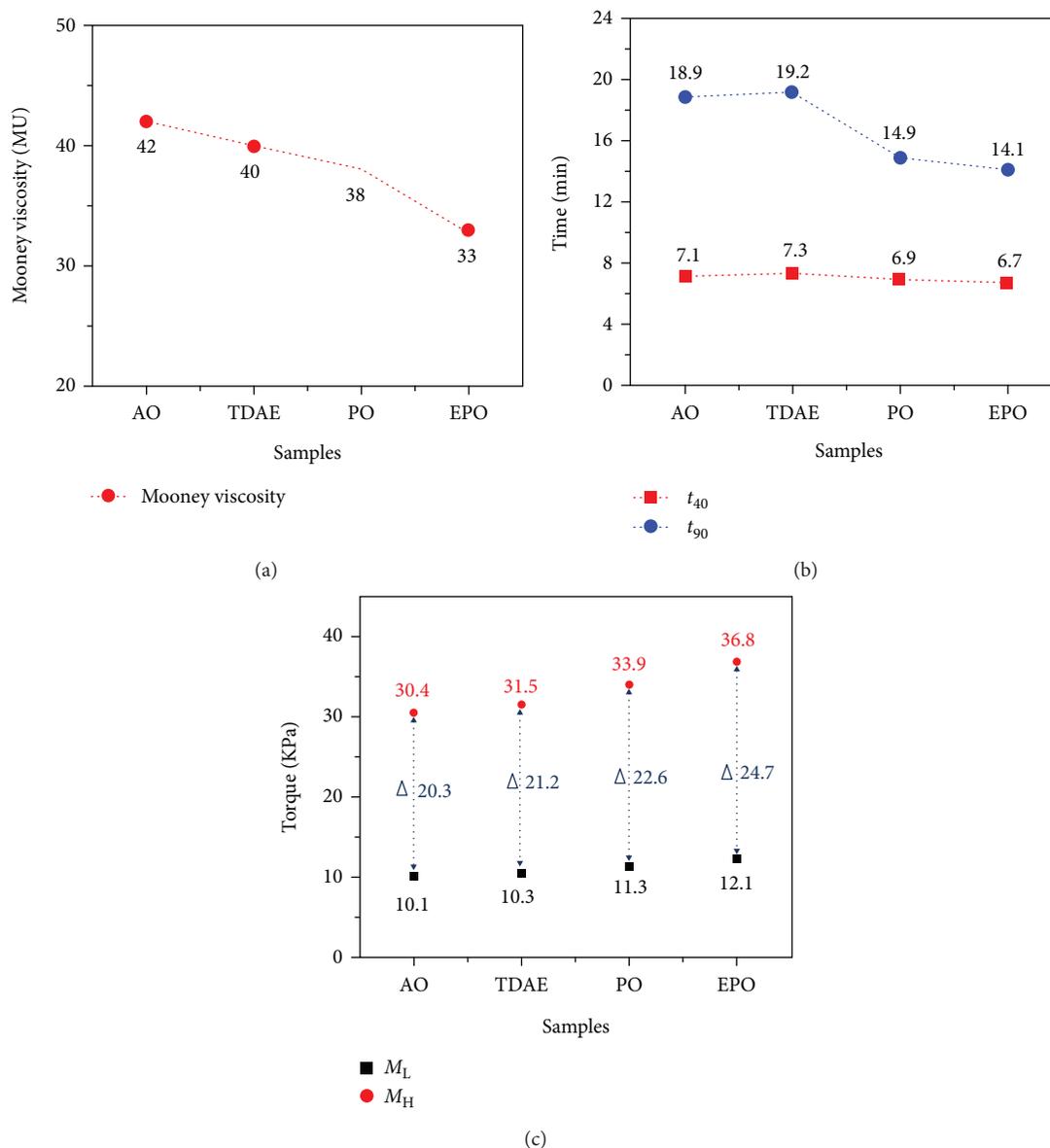


FIGURE 1: Curing properties of rubber composites. (a) Curing properties of rubber composites with different oils. (b) Mooney viscosity of rubber composites with different oils. (c) Torque of rubber composites with different oils.

and  $t_{90}$  (cure time) of different oil-filled elastomer are shown in Figure 1(b). The scorch and cure times of the elastomer composites with PO and EPO are shorter than those of other elastomer composites, because the epoxy group is able to form active vulcanizing agents [20] in Figure 1(b). A comparison of torque in the elastomer composites with different oils is showed in Figure 1(c). The  $M_H - M_L$  ( $\Delta$  torque) value (24.7 MPa) of the elastomer composites with EPO, the crosslink density of vulcanization, was increased compared to the composites with other elastomer composites [21–24]. EPO was more compatible with SBR due to the characteristic polarity of the oils and the stronger crosslinking with rubber by the epoxy groups of EPO during vulcanization by enhancing the dispersion of fillers in the rubber matrix. This explains the improved mechanical properties of the elastomer composites shown in Figure 2.

The mechanical properties of the elastomer composites with EPO with other integrated oils were examined in Figure 2. Hardness does not show a large difference in any of the samples in Figure 2(a). Figure 2(b) shows the modulus and tensile strength of the elastomer composites with different embedded oils. The tensile strength (T/S) of the composites with EPO showed an increase of as much as 3% and 2% relative to those of OA and PO composites, respectively. This enhancement was due to the improved dispersion and strong interfacial bonding of the fillers within the elastomer matrix by epoxy groups of EPO. Furthermore, the elongation at break of the elastomer composite with EPO (430%) was improved compared to that of the composite with OA (330%) in Figure 2(c). The enhanced reinforcement is attributed to the restriction of the motion of the elastomer chains and improved interfacial adhesion between the fillers and

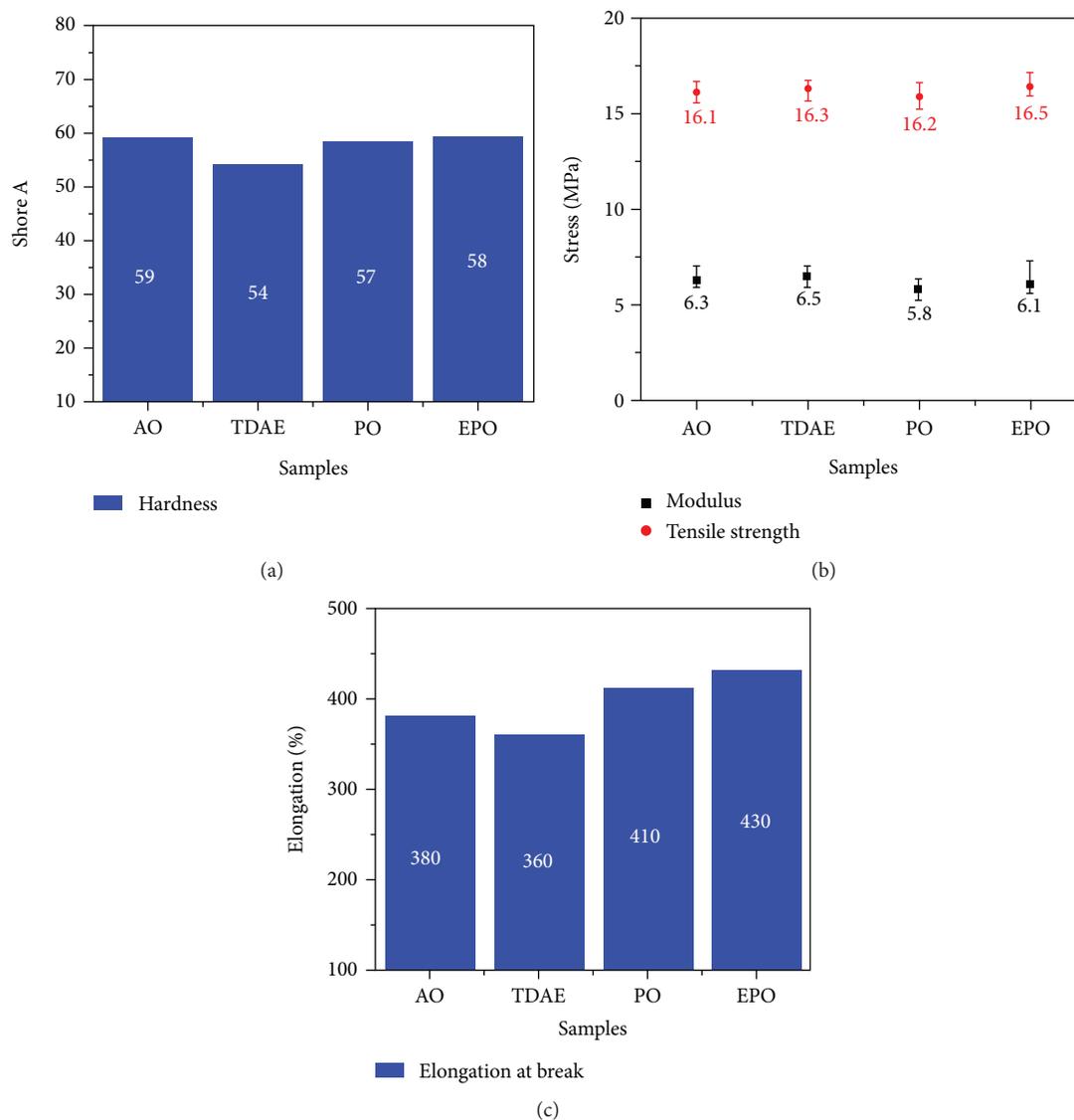


FIGURE 2: Mechanical properties of rubber composites. (a) Hardness of rubber composites with different oils. (b) Elastic modulus and tensile strength of rubber composites with different oils. (c) Elongation of rubber composites with different oils.

elastomer by the enhanced dispersion of the fillers within the elastomer by the EPO. The tensile strength of the elastomer composite with EPO (3 phr) was much higher than that of the other composites. This indicates that an applied mechanical load may transfer to fillers through interfacial interactions and uniform dispersion [17].

In the FT-IR spectra of epoxidized palm oils (EPO), four characteristic peaks related to C-O-C stretching, C=C stretching,  $-\text{CH}_2$  stretching, and  $-\text{CH}_3$  stretching are seen in Figure S1. Furthermore, we directly show carbon black dispersion in the elastomer matrix by TEM analysis in Figure S2. In the rubber composite without oil, these carbon black fillers are observed as globular aggregates of various sizes, ranging from several microns to submicronic clusters. However, with the rubber composite with EPO, the large aggregates are not observed any more but the carbon black occurs to be well distributed throughout the rubber

matrix as smaller clusters of a micron or less in length in Figure S2.

Generally, because many engineering elastomers receive dynamic loading, dynamic mechanical properties (DMA) are important. The DMA of the elastomer composites, such as  $\tan \delta$  (the ratio of loss modulus to storage modulus) of the SBR composites with diverse oils versus temperature, are showed in Figure 3(a) [25]. The DMA results of elastomer composites were used to predict both wet traction properties and rolling resistance. With the addition of EPO, the  $\tan \delta$  of  $0^\circ\text{C}$  was about 14% higher than that of OA, as seen in Figure 3(a), indicating pneumatic grip tire performance. Also, in Figure 3(a), the  $60^\circ\text{C}$   $\tan \delta$  of the pneumatic tire with EPO was about 22% lower than that of the SBR with OA, which correlates with an improved rolling resistance tire with the use of EPO. Moreover, the addition of EPO to the rubber matrix increases  $T_g$  to  $27.9^\circ\text{C}$  from the value of  $-29.0^\circ\text{C}$  of

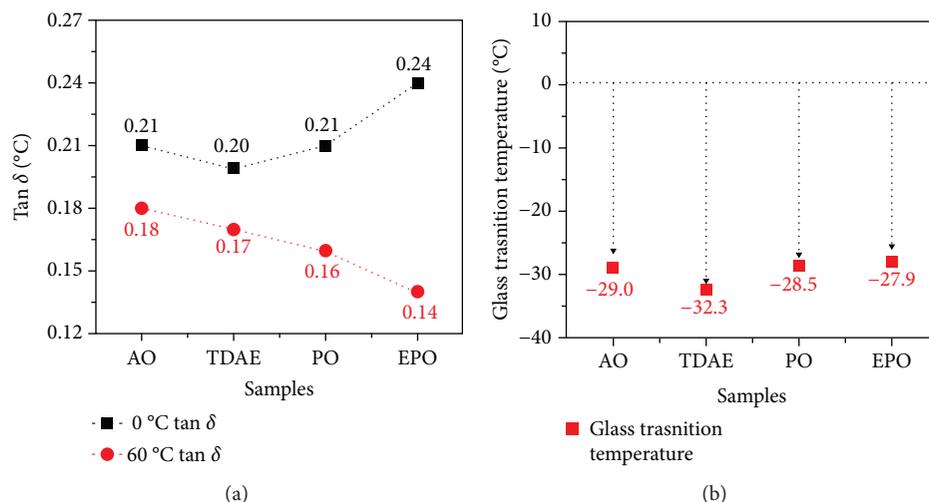


FIGURE 3: Dynamic properties of elastomer composites. (a)  $\tan \delta$  of rubber composites with different oils. (b) Glass transition temperature ( $T_g$ ) of rubber composites with different oils.

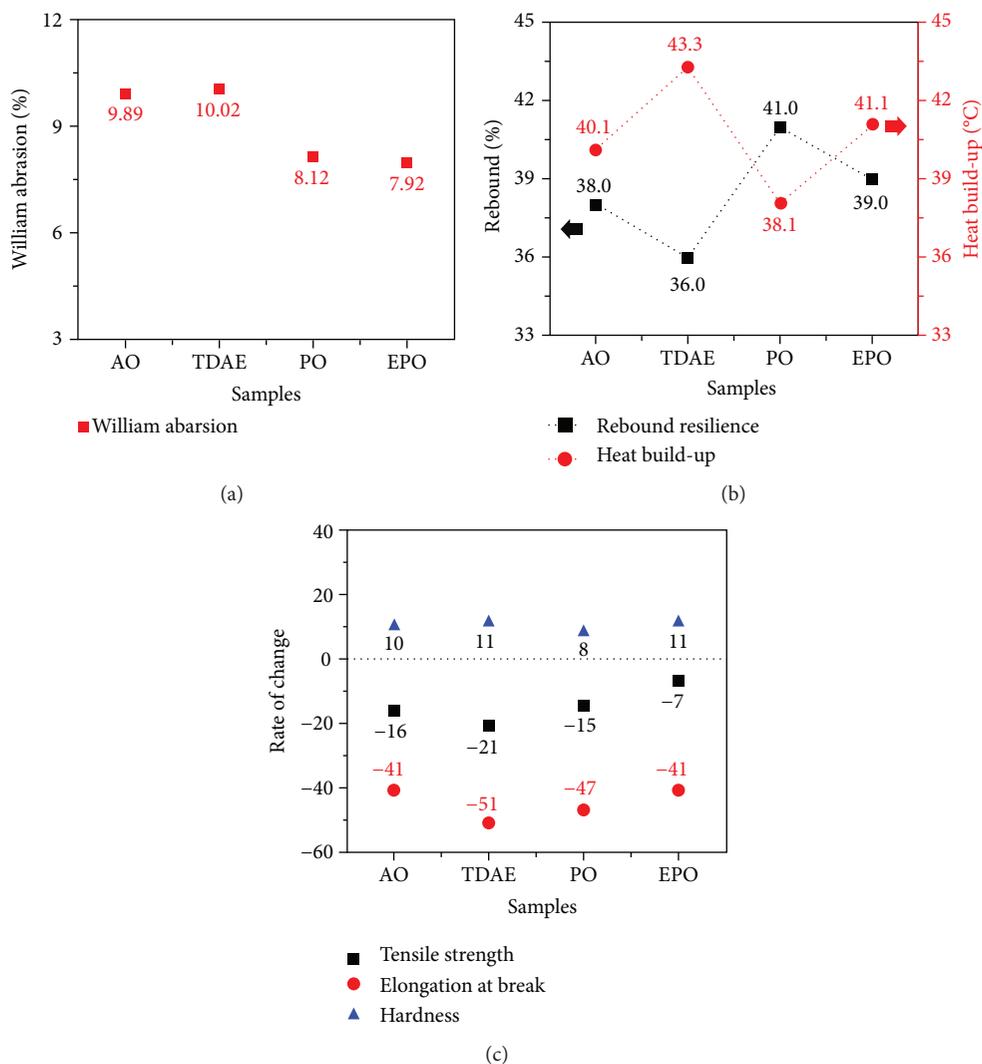


FIGURE 4: Abrasion, rebound resilience, heat buildup, and aging properties of rubber composites. (a) William abrasion of rubber composites with different oils. (b) Rebound resilience and heat buildup of rubber composites with different oils. (c) Hardness, tensile strength, and elongation at break of rubber composites with different oils at 168 hrs, 100 °C.

that of SBR with AO and is comparable with a  $T_g \sim 28.5^\circ\text{C}$  of the PO/SBR composite. This enhances interfacial adhesion and restricts the motion of the SBR segmental chains in Figure 3(b) [26]. Furthermore, these results are consistent with the mechanical properties of the composites in Figure 2.

The abrasion properties of elastomer composites with different oils are shown in Figure 4(a). For the SBR composites with EPO, the William abrasion property was enhanced by improving the dispersion of fillers in the elastomer matrix. Furthermore, the abrasion of the composites using EPO was much lower than that using AO, implying effective alleviation of heat buildup and the damping capability of the elastomer systems. In Figure 4(b), the SBR composites using EPO had a lower heat buildup of  $41.1^\circ\text{C}$ ; the SBR/TDAE composite had a higher value of  $43.4^\circ\text{C}$ , while the rebound properties of elastomer composites showed the opposite tendency. Also, the heat buildup result supports the abrasion results of the rubber composites. Interestingly, the rubber composites with EPO showed improved retardation of thermal degradation. The thermal degradation of polymers that contain polybutadiene groups, such as butadiene rubber (BR) [27], nitrile rubber (NBR) [28], acrylonitrile butadiene styrene (ABS) [27, 29], and styrene-butadiene rubber (SBR) [29, 30], has been studied by several groups. It has been suggested that thermal degradation is mainly controlled by the reactivity of the 1,2-butadiene of the cis and trans-1,4-butadiene isomers. After thermal degradation, since the chains lose their ability to move as individual rubber chains, the molecular motion reduces the interaction of the dipole moments, and consequently, the cross-polarization is a slow process [31]. However, in the SBR composites with EPO, the interaction between the rubber chains and the epoxy functional group of EPO becomes more rigid during thermal treatments. Therefore, the hardness, tensile strength, and elongation at break of rubber composites with EPO decreased less than those of the other rubber composites.

The SBR with EPO composites exhibited remarkable improvements in mechanical properties such as tensile strength and elongation properties, even at low loadings, which are ascribed to the enhanced interfacial bonding and homogeneous dispersion between the filler in the elastomer matrix. Moreover, the incorporation of EPO in the SBR matrix also significantly improved abrasion, heat buildup, and rebound resilience properties. Therefore, we can confirm that our approach provides remarkable potential for scalable and commercial polymer engineering.

#### 4. Conclusion

In conclusion, we have demonstrated a novel approach to prepare elastomer composites containing EPO with an epoxy group. Elastomer nanocomposites prepared with EPO showed enhanced mechanical, abrasion, heat buildup, and dynamic properties by improving interfacial interaction. The results showed that EPO was a more effective oil than AO, TDAE, and PO for producing rubber composites at low loading levels. Furthermore, the elastomer composites with EPO showed the most improved performance for thermal degradation among the evaluated composites. This study

opens a new avenue for high-performance elastomer composites for various engineering applications.

#### Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

#### Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

#### Acknowledgments

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#### Supplementary Materials

Figure S1: FT-IR spectra of epoxidized palm oil. Figure S2: TEM images of elastomer composites with epoxidized palm oil. (*Supplementary Materials*)

#### References

- [1] M. J. Wang, H. Y. Gong, and G. Z. Xue, *Handbook of Rubber Industry*, Chemical Industry Press, 2nd edition, 1989.
- [2] R. Faez and M.-A. de Paoli, "Elastic polyaniline with EPDM and dodecylbenzenesulfonic acid as plasticizers," *Journal of Applied Polymer Science*, vol. 82, no. 7, pp. 1768–1775, 2001.
- [3] G. Wypych, *Handbook of Plasticizers*, Chem Tec Publishing, Canada, 2004.
- [4] J. W. ten Brinke, S. C. Debnath, L. A. E. M. Reuvekamp, and J. W. M. Noordermeer, "Mechanistic aspects of the role of coupling agents in silica-rubber composites," *Composites Science and Technology*, vol. 63, no. 8, pp. 1165–1174, 2003.
- [5] S. Dasgupta, S. L. Agrawal, S. Bandyopadhyay et al., "Characterization of eco-friendly processing aids for rubber compound," *Polymer Testing*, vol. 26, no. 4, pp. 489–500, 2007.
- [6] L. G. Parks, J. S. Ostby, C. R. Lambright et al., "The plasticizer diethylhexyl phthalate induces malformations by decreasing fetal testosterone synthesis during sexual differentiation in the male rat," *Toxicological Sciences*, vol. 58, no. 2, pp. 339–349, 2000.
- [7] M. Rahman and C. S. Brazel, "Review: an assessment of traditional plasticizers and research trends for development of novel plasticizers," *Progress in Polymer Science*, vol. 29, no. 12, pp. 1223–1248, 2004.
- [8] S. Dasgupta, S. L. Agrawal, S. Bandyopadhyay, R. Mukhopadhyay, R. K. Malkani, and S. C. Ameta, "Improved polymer–filler interaction with an ecofriendly processing aid. Part 1," *Progress in Rubber, Plastics and Recycling Technology*, vol. 25, no. 3, pp. 141–164, 2009.
- [9] A. P. Kuriakose and M. Varghese, "Use of rice bran oil and epoxidized rice bran oil in carbon black-filled natural rubber

- polychloroprene blends,” *Journal of Applied Polymer Science*, vol. 90, no. 14, pp. 4084–4092, 2003.
- [10] J. Xu, Z. Liu, S. Z. Erhan, and C. J. Carriere, “A potential biodegradable rubber—viscoelastic properties of a soybean oil-based composite,” *Journal of the American Oil Chemists’ Society*, vol. 79, no. 6, pp. 593–596, 2002.
- [11] H. Miyagawa, R. J. Jurek, A. K. Mohanty, M. Misra, and L. T. Drzal, “Biobased epoxy/clay nanocomposites as a new matrix for CFRP,” *Composites Part A: Applied Science and Manufacturing*, vol. 37, no. 1, pp. 54–62, 2006.
- [12] I. Hilker, D. Bothe, J. Prüss, and H. J. Warnecke, “Chemoenzymatic epoxidation of unsaturated plant oils,” *Chemical Engineering Science*, vol. 56, no. 2, pp. 427–432, 2001.
- [13] B. Lin, L. Yang, H. Dai, and A. Yi, “Kinetic studies on oxirane cleavage of epoxidized soybean oil by methanol and characterization of polyols,” *Journal of the American Oil Chemists’ Society*, vol. 85, no. 2, pp. 113–117, 2008.
- [14] W. He, Z. Fang, D. Ji et al., “Epoxidation of soybean oil by continuous micro-flow system with continuous separation,” *Organic Process Research & Development*, vol. 17, no. 9, pp. 1137–1141, 2013.
- [15] M. Jacob, S. Thomas, and K. T. Varughese, “Mechanical properties of sisal/oil palm hybrid fiber reinforced natural rubber composites,” *Composites Science and Technology*, vol. 64, no. 7–8, pp. 955–965, 2004.
- [16] M. Rüschen Klaas and S. Warwel, “Complete and partial epoxidation of plant oils by lipase-catalyzed perhydrolysis,” *Industrial Crops and Products*, vol. 9, no. 2, pp. 125–132, 1999.
- [17] W. D. W. Rosli, R. N. Kumar, S. M. Zah, and M. M. Hilmi, “UV radiation curing of epoxidized palm oil-cycloaliphatic diepoxide system induced by cationic photoinitiators for surface coatings,” *European Polymer Journal*, vol. 39, no. 3, pp. 593–600, 2003.
- [18] W. G. D. Jayewardhana, G. M. Perera, D. G. Edirisinghe, and L. Karunanayake, “Study on natural oils as alternative processing aids and activators in carbon black filled natural rubber,” *Journal of the National Science Foundation of Sri Lanka*, vol. 37, no. 3, pp. 187–193, 2009.
- [19] S. H. Song, “The effect of palm oil-based hybrid oils as green multifunctional oils on the properties of elastomer composites,” *Polymers*, vol. 10, no. 9, pp. 1045–1054, 2018.
- [20] G. Chandrasekara, M. K. Mahanama, D. G. Edirisinghe, and L. Karunanayake, “Epoxidized vegetable oils as processing aids and activators in carbon-black filled natural rubber compounds,” *Journal of the National Science Foundation of Sri Lanka*, vol. 39, no. 3, pp. 243–250, 2011.
- [21] S. H. Song, “Synergistic effect of clay platelets and carbon nanotubes in styrene–butadiene rubber nanocomposites,” *Macromolecular Chemistry and Physics*, vol. 217, no. 23, pp. 2617–2625, 2017.
- [22] O.-S. Kwon, D. Lee, S. P. Lee, Y. G. Kang, N. C. Kim, and S. H. Song, “Enhancing the mechanical and thermal properties of boron nitride nanoplatelets/elastomer nanocomposites by latex mixing,” *RSC Advances*, vol. 6, no. 65, pp. 59970–59975, 2016.
- [23] S. H. Song, J. M. Kim, K. H. Park et al., “High performance graphene embedded rubber composites,” *RSC Advances*, vol. 5, no. 99, pp. 81707–81712, 2015.
- [24] S. H. Song, H. K. Jeong, and Y. G. Kang, “Preparation and characterization of exfoliated graphite and Its styrene butadiene rubber nanocomposites,” *Journal of Industrial and Engineering Chemistry*, vol. 16, no. 6, pp. 1059–1065, 2010.
- [25] K. P. Menard and N. R. Menard, “Dynamic mechanical analysis in the analysis of polymers and rubbers,” *Encyclopedia of Polymer Science and Technology*, no. 42, pp. 1–33, 2015.
- [26] S. H. Song, K. H. Park, B. H. Kim et al., “Enhanced thermal conductivity of epoxy–graphene composites by using non-oxidized graphene flakes with non-covalent functionalization,” *Advanced Materials*, vol. 25, no. 5, pp. 732–737, 2013.
- [27] M. Piton and A. Rivaton, “Photo-oxidation of ABS at long wavelengths ( $\lambda > 300$  nm),” *Polymer Degradation and Stability*, vol. 55, no. 2, pp. 147–157, 1997.
- [28] F. Delor, J. Lacoste, J. Lemaire, N. Barrois-Oudin, and C. Cardinet, “Photo- and thermal ageing of polychloroprene: effect of carbon black and crosslinking,” *Polymer Degradation and Stability*, vol. 53, no. 3, pp. 361–369, 1996.
- [29] J. A. Bousquet and J. P. Fouassier, “Photo-oxidation of a random styrene-butadiene copolymer: role of hydroperoxides and behaviour of butenyl segments,” *European Polymer Journal*, vol. 23, no. 5, pp. 367–376, 1987.
- [30] C. Adam, J. Lacoste, and J. Lemaire, “Photo-oxidation of elastomeric materials: part II—photo-oxidation of styrene-butadiene copolymer,” *Polymer Degradation and Stability*, vol. 26, no. 3, pp. 269–284, 1989.
- [31] T. M. Arantes, K. V. Leao, M. I. B. Tavares, A. G. Ferreira, E. Longo, and E. R. Camargo, “NMR study of styrene-butadiene rubber (SBR) and TiO<sub>2</sub> nanocomposites,” *Polymer Testing*, vol. 28, no. 5, pp. 490–494, 2009.



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