bioresources.com

Lignin in Place of Carbon Black for Ethylene-Propylene-Diene-Monomer Based Automotive Sealing Profiles

Bayram Poyraz,[a,*] Yusuf Güner,[b] Ayhan Tozluoğlu,[c] Rıdvan Yamanoğlu,[d] Zeki Candan,[d] and Murat Şen [f,g]

This study examined the effects of lignin used in EPDM elastomer composites in place of carbon black. For that purpose, lignin was added in amounts of 3.5, 7, and 10.5 phr to investigate the chemical, thermal, rheological, mechanical, and morphological properties of the EPDM elastomers. At the end of the study, tear strength and elongation were enhanced, whereas thermal stability was lowered due to the lignin. The lignin facilitated the vulcanization process and improved the torque values. In the morphology, the lignin was dispersed homogeneously in the matrix, and no voids or cracks were observed except with 10.5 phr. In conclusion, when incorporated at a specified ratio, lignin is economical and provides ecological benefits. Its use as a natural filler can be recommended to automotive industries to provide enhanced properties and ecological properties as a substitute for carbon black.

Contact information: a: Department of Civil Engineering, Faculty of Engineering, Düzce University, Düzce, Turkey, b: Research and Development Center, Standard Profil Corporation, Duzce, Turkey; c: Department of MEtallurgy and Material Engineering, Faculty of Engineering, Kocaeli University, Department of Forest Product Engineering, Faculty of Forestry, Düzce University, Düzce, Turkey, d: Department of Forest Products Enginering, Istanbul University-Cerrahpasa, Sariyer, 34772, IStanbul, Turkey e: Hacettepe University, Department of Chemistry, Polymer Chemistry Division, 06800 Ankara, Turkey; f: Hacettepe University, Institute of Science, Polymer Science and Technology Division, 06800;
* Corresponding author: bayrampoyraz@duzce.edu.tr

INTRODUCTION

Elastomer composites incorporated with green materials have been encountered in many applications ranging from automotive parts to smart devices (Sen *et al.* 2015; Meng *et al.* 2019). Thus, a number of studies continue to be carried out in the search of novel high-performance elastomer composites in order to expand their application range (Chung and Washburn 2013; Priyodip *et al.* 2013; Fuke *et al.* 2019). Ethylene-propylene-diene-monomer (EPDM), a nonpolar polyolefin structure, is one of these rubbers. It is mostly used in sealing profiles. These are used to create the shaped closures for car windows, as well as for the automotive components such as doors, windows, hoods, and trunks (Alagar *et al.* 2006). Recently, however, manufacturers have focused on biodegradable materials because of biocompatible features. The usage of environmentally harmful substances has begun to be restricted in many places and thus, investigations into bio-compatible materials continue (Ashori 2008). Lignin is a biodegradable polymer consisting of the three phenylpropanoid units p-hydroxyphenyl (H), guaiacyl alcohol (G), and syringyl alcohol (S), which are attached to one another by a series of characteristic linkages (β-O-4, β-5, β-

β) as a randomized structure in a three-dimensional network inside the cell wall. The H/G/S ratio is 0–5/95–100/0 in softwood, 0–8/25–50/46–75 in hardwood, and 5–33/33–80/20–54 in grasses. As a result, lignin can interact with different polymer matrices and ingredients. Today, lignin is one of the most frequently researched materials after cellulose, owing to its renewability, abundance, sustainability, and unique mechanical properties, as well as other features such as its stabilizing effect, reinforcing effect, and UV absorption (Jiang *et al.* 2013; Thakur and Thakur 2015; Kun and Pukanszky 2017).

Many studies have been devoted to lignin to improve the thermoplastic performance of thermosets and the respective properties of elastomers. Kim *et al.* (2014) investigated lignin's effect on the thermal and mechanical properties of an alkyl-chain modified PLA matrix. In that study, composites with modified lignin exhibited different thermal properties due to the fact having various alkyl chains. Rozman *et al.* (2000) studied the impact of lignin as a compatibilizer on the physical properties of coconut fiber-PP composites. They revealed that composites with lignin as a compatibilizer possessed higher flexural properties. However, tensile properties exhibited no improvement after lignin incorporation. Park *et al*. (2018) prepared lignin and modified lignin/polycaprolactone (p-lignin) composites. The p-lignin was better dispersed in the PCL compared to the neat lignin, and the p-lignin/PCL composites revealed a homogenously fractured surface. An increase in the lignin or p-lignin content decreased the tensile strength and elastic moduli.

Lignin has also been applied in some thermosetting polymers. Hirose *et al.* (2003) prepared composites using epoxy resin and lignin in the presence of ester-carboxylic acid derivatives. The Tg value of the polymers revealed an increase in parallel with the increase of the ester-carboxylic acid derivative contents. Moreover, the thermal degradation temperatures of the epoxy resin decreased slightly with increasing ester carboxylic acid derivative contents. In another study, Wu *et al.* (2019) blended diphenylmethane diisocynate resin and cellulose-lignin to investigate the curing rate of polymeric diphenylmethane diisocynate (PMDI). They showed that adding lignin-containing cellulose reduced the Ea value of the PMDI curing reaction and rendered it fast-curing. Feghali *et al*. (2018) reviewed lignin-based model compounds and depolymerized lignin bio-oils with a focus on thermosetting materials.

In addition to thermoplastic and thermoset polymers, lignin was revealed as a potential candidate in elastomeric applications. Sun *et al.* (2021) studied the effect of lignin as a filler on the structure, thermostability, mechanical performance, and self-healing properties of polyurethane elastomers (Sun *et al.* 2021). The observed properties were significantly enhanced after the introduction of lignin, especially the maximum tensile strength and elongation at break increased. Goliszek *et al.* (2019) used kraft lignin, which was obtained from softwood and hardwood, together with styrene, divinylbenzene polymeric microspheres to reveal its influence on the structural and thermal properties on the microspheres. The introduction of lignin enabled the highly porous functionalized microspheres to increase their sorption capability. Chung and Washburn (2012) investigated lignin-based polyurethane composites in order to improve their respective properties, as well. They observed considerable improvements on the modulus after the addition of lignin. This was attributed to the better integration of the modified lignin into the covalent polymer network resulting from the higher concentration of the hydroxyl groups. In another study, Şen *et al.* (2020) studied the effect of ionizing radiation on the mechanical properties of NBR elastomers reinforced with lignin. They observed that gamma irradiation had a significant effect on the tensile properties of NBR elastomer containing 0.5 phr lignin.

Although a number of matrix types have been used with the lignin, only limited study has been carried out with EPDM elastomers. Mei *et al.* (2019) studied the relation between the EPDM and lignin. They demonstrated the ability of lignin to simultaneously improve the modulus, strength, and toughness in the lignin/EPDM composites without sacrificing extensibility. In another study, Xu *et al*. (2015) examined lignin as a coupling agent in order to observe the thermal, morphological, and mechanical properties of EPDM rubber in the presence of triethoxy silane. The results revealed that the mechanical properties were better than those of the pure rubber in the presence of triethoxysilane. Higher thermal stability was also observed in the EPDM that contained lignin. In the morphology, the inter-phase cohesion between the lignin molecule and EPDM particles was enhanced. A patent by Benjelloun and Delmas (2014) revealed the interaction between EPDM and lignin as well as improved the mechanical properties.

A number of ingredients have been incorporated into the EPDM formula. One of these is carbon black, which consists of small particles (10 to 300 nm) in a grape-like aggregate. Carbon black has been used as a reinforcing agent and to ensure the retarded vulcanization of rubber mixtures as well as to increase the strength of the resulting rubbers due to the fact that having advanced mechanical properties such as abrasion resistance and hardness (Chen *et al.* 2017). Although carbon black can easily be prepared from waste woody materials at a low cost, its production mostly has been carried out *via* synthetic sources, and it could have been costly. Therefore, the use of a different and green-based reinforcing agent in the formula have become necessary (Nagornaya *et al.* 2006). However, lignin by itself would be presumably incapable of providing such mechanical features; thus the direct substitution of the carbon black by lignin seems not suitable. For that reason, the authors prefer to substitute it at a certain value to maintain standard values (TL 52345 standard).

The present study investigated the influence of lignin by observing the alteration in the EPDM's chemical, thermal, curing, mechanical, rheological, and morphological properties. For that purpose, lignin was used at 3.5, 7 and 10.5 phr in the EPDM rubber formula instead of carbon black.

EXPERIMENTAL

Materials

EPDM rubber (ML (1+8 min), Mooney Viscosity: 60 MU at 150 °C, C2 (ethylene: 44% and ENB: 9.0%)(Arlenxeo, Netherlands) which were mixed with carbon black (CTAB 43 ± 5 m2/g, OAN 121 ± 5 cm3/1000gr, (FEF N550, India), white filler (Micronised Calcium Carbonate d50: 2 μ), oil (parafinic process oil, 40 °C: 105 ± 5 mm2/s), sulphur and activators (accelerators) (Sulphur+Thiazole+Dithio Carbamate+ Dithio Phosphate) was provided by Standart Profile with a formula given in Table 1.

Lignin (MCC) which is also used in place of carbon black in a certain amount was supplied by Sigma (alkali, Powder, 370959).

Methods

Three plates for each material, and three different compounds were prepared by adding 3.5 phr, 7 phr, and 10.5 phr lignin to EPDM compounds (E, E-Lig1, E-Lig2 and E-Lig3) instead of carbon black (Table 1).

Table 1. The Recipes of the E, E-Lig1, E-Lig2, and E-Lig3.(phr)

Compound Name	EPDM	Lignin	Carbon Black	White Filler and Oil	Sulphur + Activators
E	100	-	120	108	11
E-Lig1	100	3.5	116.5	108	11
E-Lig2	100	7	113	108	11
E-Lig3	100	10.5	109.5	108	11

Compounds were mixed in a lab-scale mixer (Intermix Mixer, Carter Bros 1.5 L) for 5 min, (47 rpm rotor speed) with EPDM: 30 sec +C Black+Oil+White Filler: 50 sec and S+Accelerators: 30 sec respectively with an internal temperature change (23±2 °C) after the mixtures had been passed through the lab-scale cylinder (ESER). Then, the prepared plates were pressed for 7.5 min at 180 °C with a compression press (ESER). Temperature of compressing press was chosen as it is in the standard method. Also, this temperature is the lignin softening temperature. It was thought that softening of lignin facilitates the penetration of EPDM rubber. Afterward, mechanical, thermal, chemical, morphological, and aging tests were carried out.

Analysis of Chemical Structure

Chemical alterations were investigated with ATR-FTIR (IR Prestige-21, Shimadzu). For this analysis, elastomers were gently put on the attachment to investigate and elucidate chemical alterations as vibrations in the range of 4000 to 600 cm^{-1}, resolution of 4 cm^{-1}, and 20 scans. Also, the total crystalline index (TCI) was calculated from the ratio of the intensity of the absorbance bands at 1372 and 2892 cm^{-1} (A1372/A2892).

Thermal Properties

Thermal stability was determined with a thermogravimetric analysis (TGA) device equipped with a thermal analysis data station (Shimadzu, DTG 60). For that purpose, 5 to 10 mg of elastomers were gently placed in the Pt pan. Then, elastomers was exposed to heat from 25 to 600 °C at a 10 °C/min heating rate and under a 75 ml/min N2 (nitrogen) atmosphere.

Mechanical Properties

Plates obtained from EPDM compounds were analyzed in that tensile, tear, and elongation test in this part. The tensile and elongation specimens were investigated according to DIN standard, while the tear specimens were tested according to DIN ISO 34-1 standard. Tests were carried out at room temperature with a cross-head speed of 200 mm/min using a universal testing machine. Five samples were tested to ensure reliable results.

Curing Properties

Moving die rheometer (MDR) and scorch tests were carried out according to ASTM 1646 in order to determine rheological properties (ALPHA Technologies MDR 2000). Mooney viscosity was investigated at 1+4 min at 100 °C to determine the flow, motion,

and shape-taking properties during the time spent in the extruder. Likewise, scorch tests were performed at 1+20 min at 121 °C.

The MDR tests were carried out at 180 °C for 2.5 min in order to measure and analyze the vulcanization times of $ts2$ (scorch time) and $t90$ (the 90 % optimum vulcanization time of rubber). The specimens were measured after aging 22h+2h at 100 °C with a gauge (Miuyoto) according to the DBL 5571 standard.

The deformation values for determining the permanent sets were calculated according to,

$$\text{Permanent set (\%)} = \frac{hi - ho}{hi - ho} * 100 \tag{1}$$

where h_i is the sample height before thermal aging, h_f is the sample height after aging, and h_o is the compression distance. Three replicates were specified to ensure reliable results.

Morphological Analysis

Morphological analysis of specimens was carried out with an SEM (Quanta 250, FEI) in order to investigate the surfaces and cross-sectional distribution of EPDM plate and Lignin-based EPDM plates.

RESULTS AND DISCUSSION

Chemical Characterization

FT-IR spectra of the elastomers are given in the Fig. 1. C-H asymmetric and symmetric vibrations sourced from interactions related to methylene groups originated from the lignin, carbon black, accelerating agent, additives oil, and EPDM rubber terpolymer structure were observed in all elastomers. These vibrations were at approximately 2928 and 2860 cm^{-1}. There was no considerable shift in those vibrations, though those intensities were altered.

The OH groups, observed in the 3300 cm^{-1} attributable to the hydroxyl ends in the lignin were not specifically observed in the spectra due the removal of moisture. C-S bonds that create crosslinking were observed at 2310 and 2095 cm^{-1} (Sanchez *et al.* 2015). Many vibrations coming from EPDM and other ingredients were observed between at 1010 and 1720 cm^{-1} (Derkacheva and Sukhov 2008). C-H tensile vibration which is seen at 1371 cm^{-1}, shifted to the higher wavenumbers and those vibrations were seen at 1372 and 1373 cm^{-1} for E-Lig elastomers, respectively.

In the same way, C-H bending vibrations that were seen at 1336 cm^{-1} shifted to higher wave numbers and were observed at 1338 cm^{-1}. This circumstance could be ascribed to a change in crystallinity level. The total crystalline index (A_{1372}/A_{2892}), which is proportional to the crystallinity degree of elastomers, decreased after adding the lignin. These structural alterations did not considerably improve the compability between the EPDM matrix and the lignin in order to obtain composites with improved tensile properties (Colom *et al.* 2022). It could be said that the more lignin found in the elastomer structure, the more entanglement of the network occurred, owing to lignin's 3-D entangled network structure.
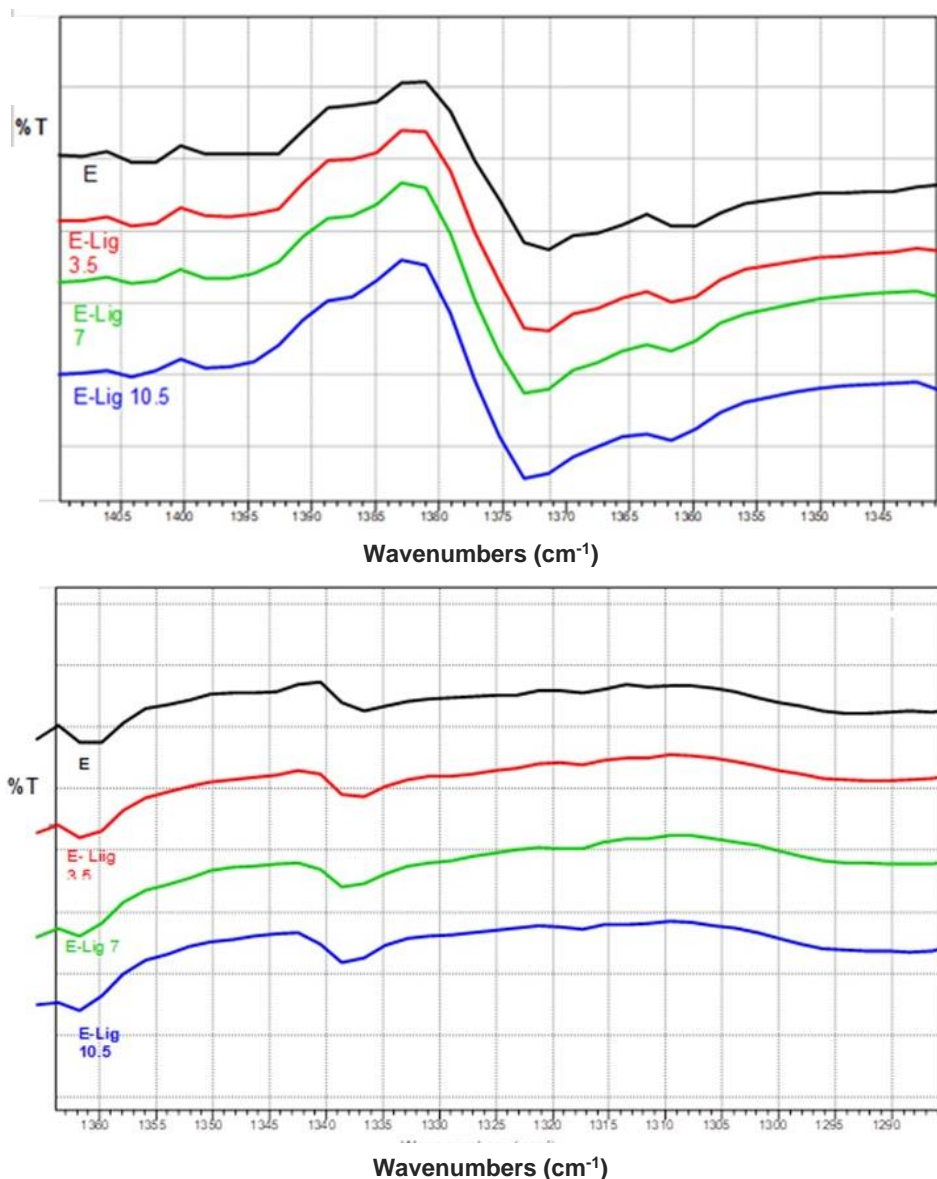
Fig. 1. FT-IR spectra of the E, E-Lig3.5, E-Lig7, and E-Lig10.5

Thermal Characterization

Thermograms of lignin-based EPDM elastomers give insights thermal stability of elastomers. The obtained thermograms are given in Fig. 2.

Thermal degradation curves revealed mostly similar behavior for all elastomers. As can be seen in Fig. 2, the first plateau, seen up to 350 °C, started to degrade faster after incorporating the lignin. Therefore, it could be seen that thermal stability was decreased in all elastomers after the lignin addition. This suggests that lignin enabled faster heat transfer owing to filling the gaps in the EPDM matrix (Shimazaki *et al.* 2007). This finding was supported by the TCI values calculated in the FT-IR. In addition, this circumstance may be attributed a branching effect, a nucleation effect, and a size and surface effect (Peng *et al.* 2007).
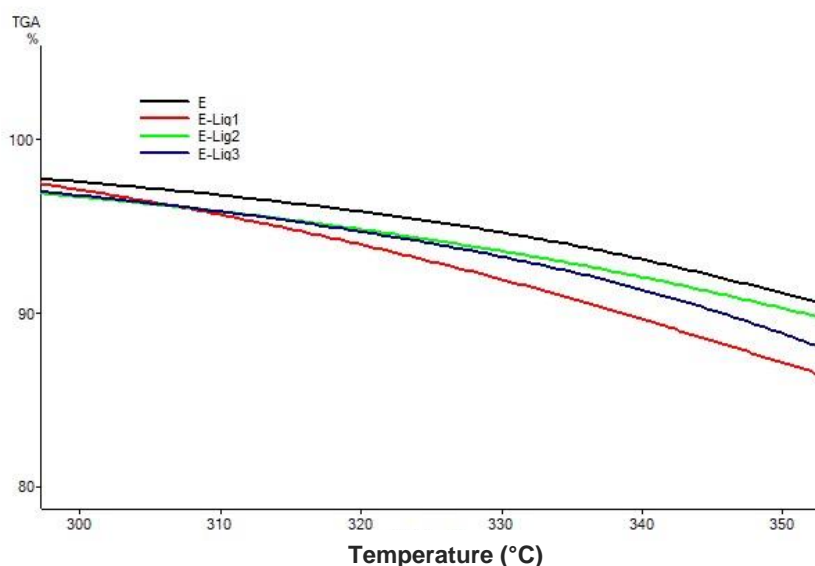
Fig. 2. Thermogram of the E-Lig3.5, E-Lig7, and E-Lig10.5

However, in another study, Sun *et al.* (2021) revealed that higher energy was needed to destroy the interaction between lignin and polyurethane molecular chains, which resulted in an increase in T_{first}. This may be attributed to the fact that lignin contained a large amount of aromatic structures, as well as the polymer chains, which required higher energy to move.

Mechanical Properties

Lignin-based EPDM elastomers and EPDM were analyzed with respect to tensile strength, elongation, and tear strength after weathering to elucidate mechanical alteration. The obtained results after weathering are given in Fig. 3.

In the case of tensile strength, the highest value was seen in the E-Lig3.5 as 8.32 MPa (Fig. 3). This level is notable compared to the elastomer without lignin (E) (7.78 MPa). However, tensile stress revealed a decrease with further loadings at 7 phr and 10.5 phr. This distinction can be attributed to two factors: lignin became less well dispersed in the EPDM matrix. The lignin became partly agglomerated due to the stirring level applied higher frequency of collisions for higher solids levels. Secondly, Goash (2022) stated that this circumstance may be attributed to the presence of a more non-crosslinked lignin phase. To account for the reduction in strength, the lignin particles were no longer adequately separated or wetted by the EPDM matrix, and this phenomenon made the stress transmission difficult from the matrix to lignin (Sarkawi and Aziz 2003).

Addition of lignin led to increased elongation. This increase was remarkable, especially at 3.5 phr and 10.5 phr, and the highest value was seen at the 10.5 phr E-Lig10.5 (285). This can be attributed to lignin's polyaromatic ring structures. This lignin's 3-d structure provided rigidity and more interactions between lignin and EPDM molecular segments (Sun *et al.* 2021). Therefore, lignin makes the rubber more elastic due to the strong adhesion between lignin and the EPDM matrix (Miao and Hamad 2013; Mathew and Joseph 2007).
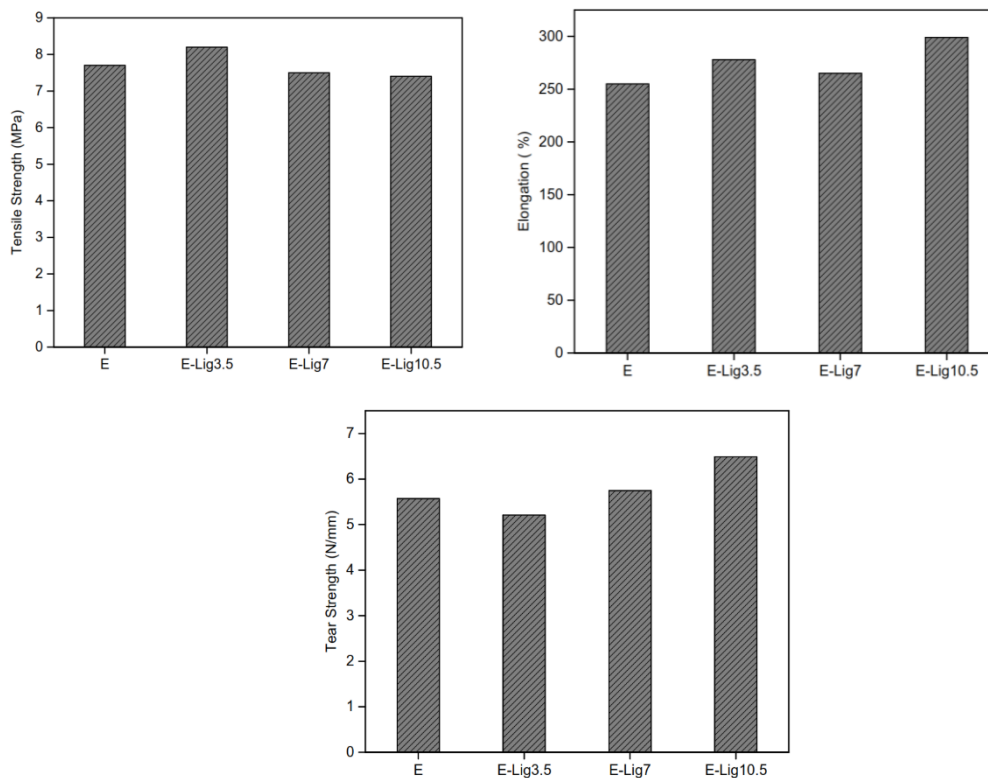
Fig. 3. Mechanical Properties of the E-Lig3.5, E-Lig7, and E-Lig10.5

Test results revealed a general increase in the tear strength. This increase likely resulted from the molecular chain of the EPDM rubber, which is able to orient in the direction of the strain uploading. The ability to orient and slip around the lignin probably originated from the high aspect ratio of the lignin that this dimensional property enabled an increased contact surface with the EPDM, which supported a better transfer of stress (Nabil *et al.* 2013).

According to customer specification, TL 52345 standard, the obtained values in the mechanical properties remained in the standard tolerances.

Rheological Properties

The influence of lignin on the rheological properties is represented by the comparison of the Mooney viscosity, Mooney scorch, and vulcanisation times as t_{s2} (scorch time) and t_{s90} (optimum cure time) values of the EPDM elastomers in the figure.

As can be seen from Fig. 4, both Mooney viscosity values (Mi), (Mf) and the $t_{0,5}$ values in Mooney scorch decreased with increasing lignin content. It seems that the needed torque values for the vulcanization process decreased. Decreasing in viscosity is known to be associated with an increase in the molecular movement of EPDM elastomer, which was probably due to the presence of weak EPDM-lignin interaction. With decreased viscosity, lower shear forces are needed to rotate the rotor. Also, the maximum torque value was seen at 10.5 phr lignin. This phenomenon means that the increased lignin decreased the stiffness of EPDM elastomers, consequently increased the torque value recorded (Che Mat *et al.* 2016). Also, the $ts2$ (scorch time) and $t90$ (optimum cure time) values were similarly influenced by the lignin that was considerably decreased with increasing lignin loading.

Lignin enabled earlier vulcanization, hence providing faster production. It can be inferred that lignin acted as an activating agent to reduce scorch time. This is ascribed in faster heat transfer due to homogenously lignin distribution and friction between filler and EPDM in the matrix (Ismail *et al.* 2002). Overall, the vulcanization process is accelerated with the incorporation lignin with respect to that of EPDM. Though this similar influence is generally seen in the inorganic-based filler such as Si and bentonite, the used organic-based lignin in this study revealed the close influence on the rheological and curing parameters (Amin *et al.* 2018).
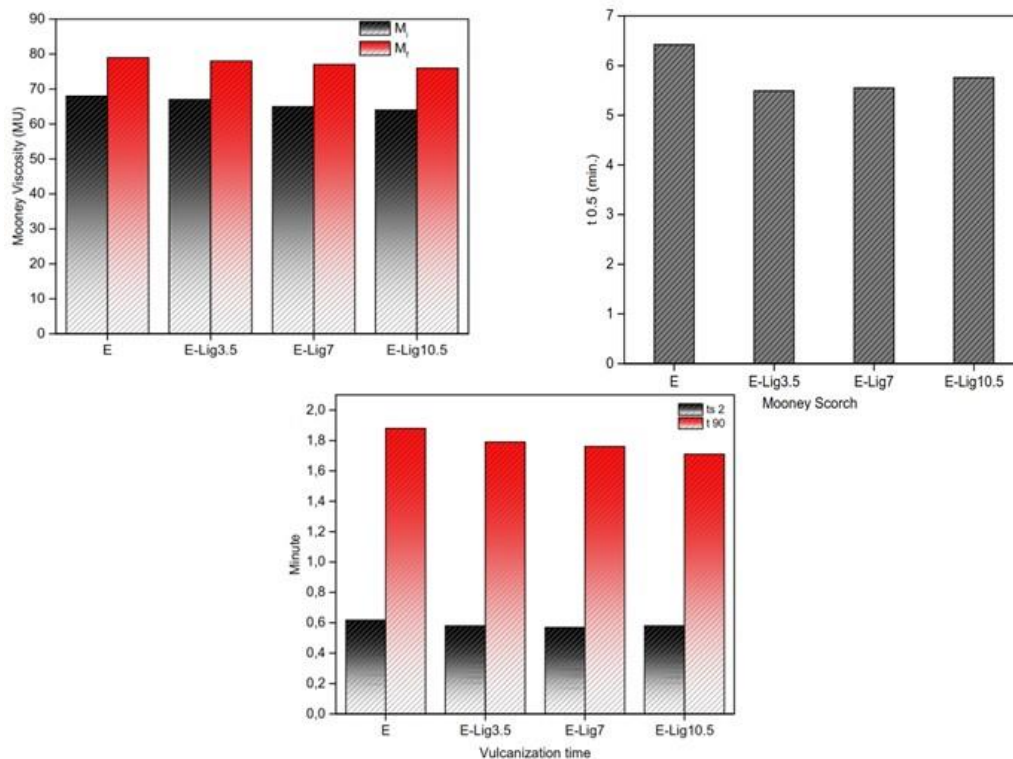

Fig. 4. Mooney Viscosity, Mooney Scorch, and Vulcanization time of the E-Lig3.5, E-Lig7, and E-Lig10.5

Permanent Set

One of the most important properties of rubber is the percentage of permanent set, which is the deformation that stay on the material once the applied stress is removed. The value is an important that materials could be exposed to mechanical stress which formed in the external conditions. The obtained results are given in the Fig. 5. As can be seen in the figure, higher permanent set values were almost seen in E-Lig3.5, E-Lig7, and E-Lig10.5 elastomers samples in comparison with the EPDM rubber. It can be said that the lignin caused an increase in the percentage of permanent set values.

When compared biopolymers (cellulose, lignin, and hemicellulose) which can be extracted from vegetable sources, the highest Young's modulus was seen with the lignin. Therefore, the produced lignin-based elastomers do not show rubbery behavior due to lignin's prospective highly branched and aromatic chemical structure. In other words, increasing the lignin provides solid-like behavior.
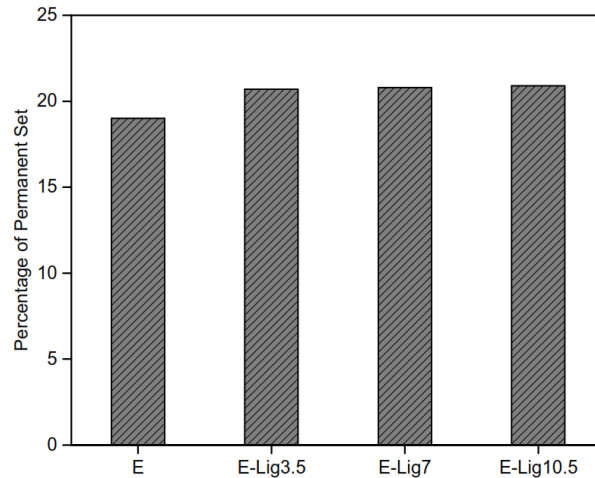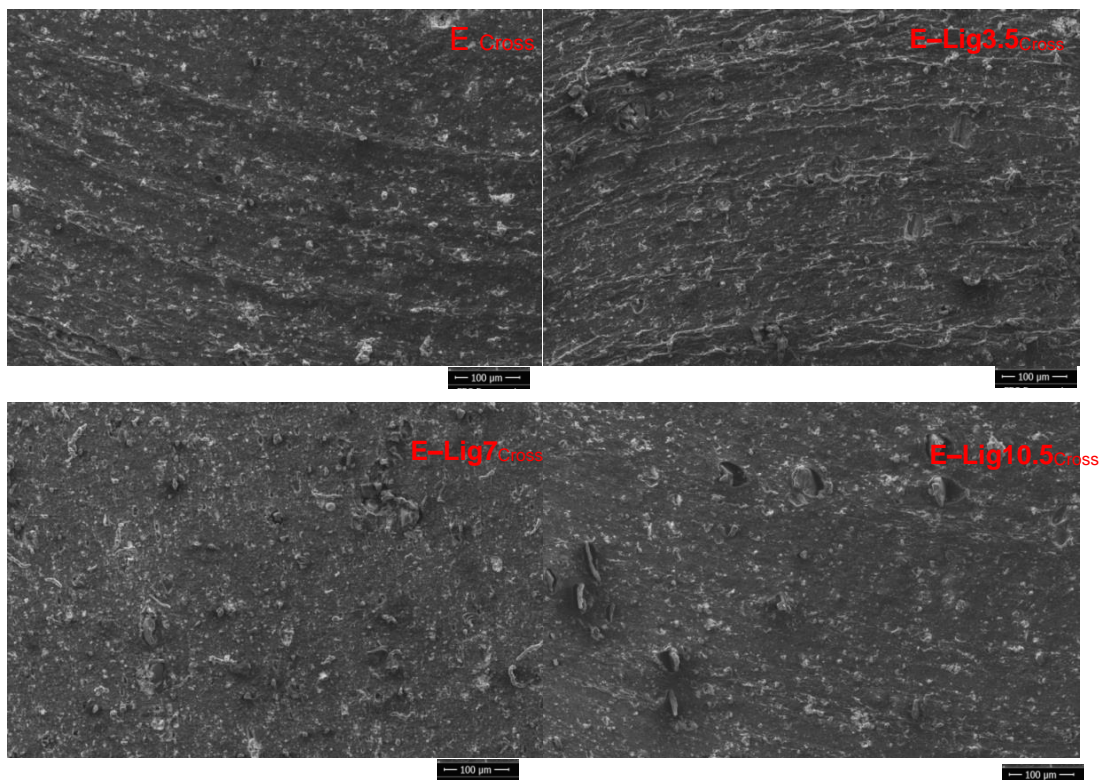
Fig. 5. Percentages of Permanent Set of the E-Lig3.5, E-Lig7, and E-Lig10.5

Morphological Properties

Pictures of the produced elastomers were taken with SEM as surface (a) and cross sectional (b). The obtained results are given in Fig. 6.
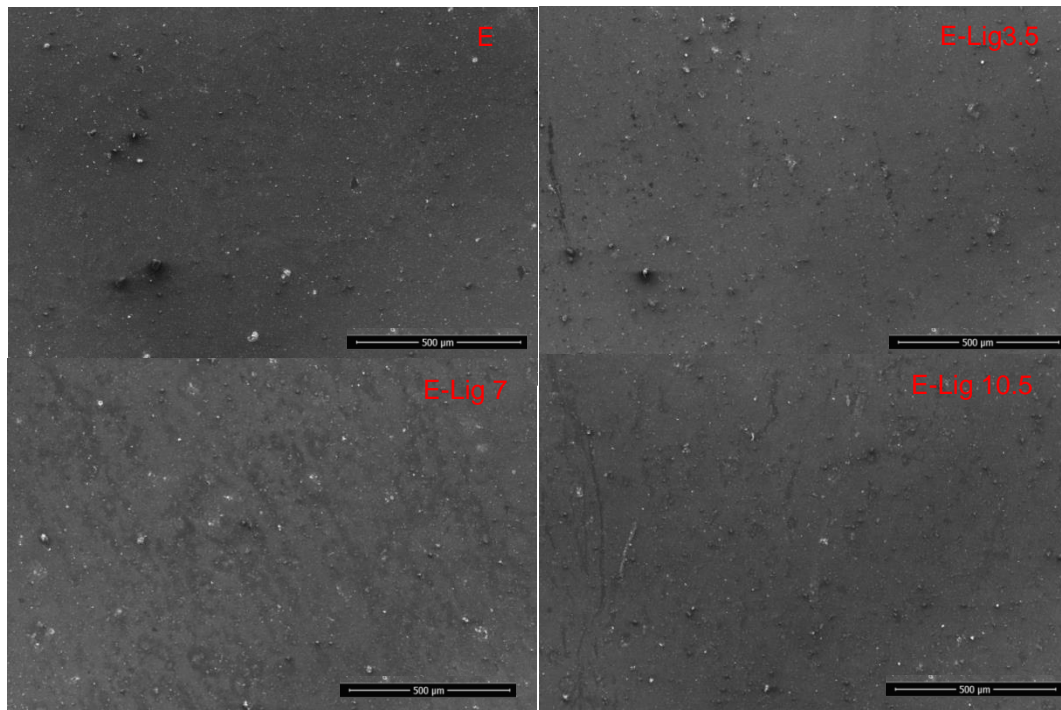
Fig. 6-a). Pictures of E-Lig3.5, E-Lig7, and E-Lig10.5 (Surface)

Fig. 6-b). Pictures of E-Lig3.5, E-Lig7, and E-Lig10.5 (Cross-section)

The lignin started to be observable after its addition. Also, as the lignin present increased in the elastomer, the higher lignin concentration was found in the EPDM matrix. Overall, the dimensions of the lignin ranged approximately from 1 to 45 μm. However, some agglomeration, as well as individual fibrils were observed in the E-Lig3 when checking the cross-sectional dimensions in comparison with E-Lig1 and E-Lig2 elastomers. This circumstance can be ascribed in lignin's chemical nature and process conditions. However, it can be concluded that the lignin mostly dispersed homogenously in the matrix and no considerable cracks and voids were observed except of the E-Lig3 elastomer.

CONCLUSIONS

1. Ethylene-propylene-diene-monomer (EPDM) (E) and lignin-based EPDM (E-Lig3.5, E-Lig7, and E-Lig10.5) elastomer composites were successfully prepared.

2. Lignin-based EPDM elastomer composites showed a good combination of mechanical properties.

3. The lignin dispersed homogeneously in the EPDM matrix at proportions up to 10 phr.

4. The lignin enabled lower thermal stability than the matrix.

5. The lignin noticeably facilitated the vulcanization process.

In the end of the study, the produced lignin-based EPDM elastomer composites not only conformed to the TL 52345 standard but also demonstrated an overall high mechanical

performance. This may provide economic and ecological advantages to automotive industries. For that reason, lignin can be recommended instead of carbon black for industries run on EPDM elastomer composites.

ACKNOWLEDGMENTS

REFERENCES CITED

Alagar, M., Abdul Majeed, S.M., Selvaganapathi, A., Gnanasundaram. P. (2006). "Studies on thermal, thermal aging and morphological characteristics of EPDM-g-VTES/LLDPE," *European Polymer Journal*. 42(2), 336-347.

Amin, A., Kandil, H., Rabia, M., Nashar, D., and İsmail, M. N. (2018). "Enhancing the mechanical and dielectric properties of EPDM filled with nanosized rice husk powder," *Polymer-Plastics Technology and Engineering* 57(17), 1733-1742.

Ashori, A. (2008). "Wood plastic composites as promising green-composites for automotive industries," *Bioresource Technology* 99(11), 4661-4667.

Benjelloun-Myalah, B., and Delmas, M. (2014). "Use of lignin for the mechanical reinforcement of elastomers, and elastomer thus strengthened," Patent No. WO2014012924A.

Che Mat, N. S., Ismail, H., and Othman, N. (2016). "Curing characteristics and tear properties of bentonite filled ethylene propylene diene (EPDM) rubber composites," *Procedia Chemistry* 19, 394-400.

Chung, H., and Washburn, N. (2013). "Chemistry of lignin based materials," *Green Materials* 1, 138-158.

Chung, H. Y., and Washburn, N. R. (2012). "Improved lignin polyurethane properties with Lewis acid treatment," *ACS Applied Material Interface* 4, 2840-2846.

Derkacheva, O., and Sukhov. D., (2008). "Investigation of lignins by FTIR spectroscopy," *Macromol. Symp.* 265, 61-68.

Feghali, E., Torr, K., Pas, D., Vanbroekhoven, K., Eevers, W., and Vendamme, R. (2018). "Thermosetting polymers from lignin model compounds and depolymerized lignins," *Topics in Current Chemistry* 376, 32-40.

Fuke, C. A., Mahanwar, P. A., and Chowdhury, S. R. (2019). "Modified ethylene-propylene-diene elastomer (EPDM)-contained silicone rubber/ethylene-propylene-diene elastomer (EPDM) blends: Effect of composition and electron beam crosslinking on mechanical, heat shrinkability, electrical, and morphological properties," *Journal of Applied Polymer Science* 136(29), 47787-47796.

Goash, A. (2022). "Organosolv lignin improved thermoplastic elastomeric behavior of polyethylene/polyisoprene blend," *ACS Omega* 7(10), 8483-8492.

Goliszek, M., Podkoscielna, B., Sevastyanova, O., Gawdzik, B., and Chabros, A. (2019). "The influence of lignin diversity on the structural and thermal properties of

polymeric microspheres derived from lignin, styrene, and/or divinylbenzene," *Materials* 12, 2847.

Hirose, S., Hatakeyama, T., and Hatakeyama, H. (2003). "Synthesis and thermal properties of epoxy resins from ester-carboxylic acid derivative of alcoholysis lignin," *Macromol Symp.* 197, 157-169.

Ismail, H., Edyham, M., and Wirjosentono, B. (2002). "Fibre filled natural rubber composites: The effects of filler loading and bonding agent," *Polymer Testing* 21(2), 139-144.

Jiang, C., He, H., Jiang, H., Ma, L., and Jia, M. (2013). "Nano-lignin filled natural rubber composites: Preparation and Characterization*," eXPRESS Polymer Letters* 7(5), 480-493.

Kim, S., Oh, S., Lee, J., Ahn, N., Roh, H., Cho, J., Chun, B., and Park, J. (2014). "Effect of alkyl-chain-modified lignin in the PLA matrix," *Fibers and Polymers* 15, 2458-2465.

Kramavo, Z., Alexy, P., Chodak, I., and Duracka, M. (2007). "Biopolymers as fillers for rubber blends," *Polymers for Advanced Technologies* 18(2), 135.

Kun, D., and Pukanszky B. (2017). "Polymer/lignin blends: Interactions, properties, application," *European Polymer Journal* 93, 618-641.

Mathew, L., and Joseph, R. (2007). "Mechanical properties of short -ısora-fiber reinforced natural rubber composites: Effects of fiber length, orientation, and loading: Alkali treatment, and bonding agent," *Journal of Applied Polymer Science* 103, 1640-1650.

Mei, J., Liu, F., Huang, J., and Qiu, X. (2019). "Lignin-reinforced ethylene-propylene-diene copolymer elastomer via hydrogen bonding interactions," *Macromolecules Material Engineering* 304, article no. 1800689.

Meng, Q., Liu, Z., Han, S., Xu, L., Araby, S., Cai, R., Zhao, Y., Lu, S., and Li, T. (2019). "A facile approach to fabricate highly sensitive, flexible strain sensor based on elastomeric/graphene platelet composite film," *Journal of Material Science* 54,10856-10870.

Miao, C., and Hamad, W. Y. (2013). "Cellulose reinforced polymer composites and nanocomposites: A critical review," *Cellulose* 20(5), 2221-2262.

Nabil, H., İsmail, H., and Azura, A. R. (2013). "Compounding, mechanical and morphological properties of carbon-black filled natural/recycled ethylene-propylene-diene monomer blends," *Polymer Testing* 32, 385-393.

Nagornaya, M. N., Razdyakonova, G. I., and Khodakova, S. (2006). "The effect of functional groups of carbon black on rubber properties," *Procedia Engineering* 152, 563-569.

Park, C., Youe, W., Namgung, H., Han, S., Seo, P., Chae, H., and Lee, S. (2018). "Effect of lignocellulose nanofibril and polymeric methylene diphenyl diisocyanate addition on plasticized lignin/polycaprolactone composites," *BioResources* 13(3), 6802-6817.

Peng, Z., Kong, L., Li, S. D., Chen, Y., and Huang, M. F. (2007). "Self-assembled natural rubber/silica nanocomposites: Its preparation and characterization," *Composites Science and Technology* 67, 3130-3139.

Priyodip, P., Balaji, S., and Vijaya, K. (2013). "Physio-chemico-thermo-mechanical properties of selected biodegradable polymers," *Green Materials* 1(3), 191-200.

Rozman, H. D., Tan, K. W., Kumar, R. N., Abubakar, A., Ishak, Z. A. M., and Ismail, H. (2000). "The effect of lignin as a compatiblizer on the physical properties of coconut fiber-polypropylene composites," *European Polymer Journal* 36, 1483-1494.

Sanchez, N., Cassu, S., and Dutra, R. C. L. (2015). "TG/FT-IR characterization of additives typically employed in EPDM formulations," *Polimeros* 25(3) 247-255.

Sarkawi, S. S., and Aziz, Y. (2003). "Ground rice husk as filler in rubber compounding," *J. Teknol., Keluaran Khas. Dis.* 39(A), 135-148.

Sen, S., Patil, S., and Argyropoulos, D. S. (2015). "Thermal properties of lignin in copolymers, blends, and composites: A review," *Green Chem.* 17, 4862-4887.

Şen, M., Aksüt, D., and Karağaç, B. (2020). "The effect of ionizing radiation on the mechanical properties of NBR elastomers reinforced by lignin," *Radiation Physics and Chemistry* 168, 108626-108630.

Shimazaki, Y., Miyazaki, Y., Takezawa, Y., Nogi, M., Abe, K., Ifuku, S., and Yano, H. (2007). "Excellent thermal conductivity of transparent cellulose nanofiber/epoxy resin nanocomposites," *Biomacromolecules* 8, 2976-2978.

Sun, N., Di, M., and Liu, Y. (2021). "Lignin-containing polyurethane elastomers with enhanced mechanical properties via hydrogen bond interactions," *International Journal of Biological Macromolecules* 184, 1-8.

Thakur, V. K., and Thakur, M. K. (2015). "Recent advances in green hydrogels from lignin: A review," *International Journal of Biological Macromolecules* 72, 834-847.

Wu, G., Feng, X., Kong, Z., and Wang, S. (2019). "Effect of lignin-containing cellulose nanofibrils on the curing kinetics of polymeric diphenylmethane diisocyanate (PMDI) resin," *Holzforschung* 73(9), 879-887.

Xu, G., Yan, G., and Zhang, J. (2015). "Lignin as coupling agent in EPDM rubber: Thermal and mechanical properties," *Polymer Bulletin* 72, 2389-2398.