Journal of Materials Exploration and Findings (JMEF)

Volume 2 | Issue 1 Article 3

5-2-2023

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Recommended Citation
Sianturi, Krisma Yessi; Nugraha, Adam Febriyanto; kristaura, Belle; and Chalid, Mochamad (2023) "Enhancing Compatibility and Mechanical Properties of Natural Rubber Composites," *Journal of Materials Exploration and Findings (JMEF)*: Vol. 2: Iss. 1, Article 3.
DOI: 10.7454/jmef.v2i1.1029
Available at: https://scholarhub.ui.ac.id/jmef/vol2/iss1/3

Journal of Materials Exploration and Findings (JMEF)
Vol. 02, Issue/No. 01, May 2, 2023

Enhancing Compatibility and Mechanical Properties of Oil Palm Empty Fruit Bunch (OPEFB) Fiber-Reinforced Natural Rubber Composites with Latex-Starch Hybrid Coupling Agent

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Received: 8th April 2023; Revised: 20th April 2023; Accepted: 27th April 2023;
Available Online: 2nd May 2022

Abstract. Pure natural rubber (NR) exhibits low mechanical properties, necessitating the incorporation of additives like vulcanizing agents and fillers. Carbon black and silica, conventional fillers, are relatively expensive and not environmentally friendly. This study explores using Oil Palm Empty Fruit Bunch (OPEFB) fiber as an affordable, abundant, and biodegradable alternative filler for NR. However, compatibility issues arise between the nonpolar NR and the polar OPEFB fiber. A latex-starch hybrid coupling agent (CA (NR-St)) was added to the composite formulation to address this. NR, OPEFB fiber, and the coupling agent were mixed using an open roll mill with a 10 phr OPEFB filler loading and coupling agent concentrations of 0, 1, 2, and 3 phr. Fourier-transform infrared spectroscopy (FTIR), rheology, and mechanical property tests revealed that the coupling agent improved the compatibility between NR and OPEFB fibers, as evidenced by increased tensile strength and stiffness. The composite with 3-phr coupling agent exhibited the best performance with tensile strength and stiffness values of 25.6 MPa and 3.7 MPa, respectively. This increase in mechanical properties has the potential to act as a catalyst for increasing the use of renewable materials in the rubber industrial sector, especially the automotive industry.

INTRODUCTION

Natural rubber is a natural polymer that has limited mechanical properties and is, therefore, not used in its pure form [1, 2]. In order to enhance the mechanical properties, additives such as vulcanizing and fillers are required [3, 4]. Filler-reinforced rubber composites have numerous applications in the rubber industry, including tires, hoses, dock and ship fenders, condoms, footwear, O-rings, conveyor belts, fireproofing materials, bearings, etc. [5–7]. Carbon black is a common filler for NR, and among rubber manufacturers, it ranks as the most widely used reinforcing filling. Due to the environmental pollution caused by its production, carbon black derived from petroleum is both prohibitively costly and counterproductive to advancing environmentally friendly technologies due to the depletion of petroleum reserves, increased greenhouse gas concentrations, and global warming [8, 9]. In addition to carbon black, another common filler is silica, which is also quite expensive [10, 11]. Due to its polar silica surface, silica is not easy to distribute in the non-polar rubber matrix, both of which have poor interfacial compatibility. [3, 12].

Biodegradable materials are becoming increasingly popular for numerous uses because of their recyclability, longevity, and low impact on the ecosystem [13–15]. Due to its exceptional properties and renewability, natural fiber has the potential to be used as a reinforcing agent for polymers such as NR [7, 16, 17]. Oil Palm Empty Fruit Bunch (OPEFB) is a source of natural fiber that is abundantly available in many countries and has a number of benefits, including being cheap, having high specific strength, being a thermal insulator, and having regenerative capacity [18]. The combination of NR and OPEFB fiber is expected to produce better mechanical properties, resulting in wider product applications. However, the use of OPEFB fiber as a filler for NR has a significant issue, namely the incompatibility between NR and fiber because NR is a nonpolar polymer and fiber is a polar polymer. The inhomogeneous dispersion of fiber particles into the natural rubber matrix is affected by this polarity difference. This can be overcome by modifying the surface, chemical modification, and adding a compatibilizer or coupling agent [19–22]. A coupling agent was chosen to increase the interaction of the fiber and NR matrix, in which the coupling agent has a polar and nonpolar structure that functions as a bridge to connect natural rubber and fiber. In this experiment, the coupling agent used was a latex-starch hybrid coupling agent (CA (NR-St)), which was conducted by Kirana (2019) and found a high percentage of reactions [23]. The objective of this study is to find out how CA (NR-St)) affects the compatibility of the composite obtained from FTIR testing to see its functional groups, rheology, or curing characteristics, which will affect its mechanical properties.

EXPERIMENTAL

Materials

NR latex with 55 wt% dry rubber content, starch (powder), and an electrolyte solution of sodium sulfate (Na_2SO_4) for the manufacture of coupling agents. Following are the materials for making rubber compounds, consisting of the matrix, which is NR SIR 20, and additional materials as activators: powdered zinc oxide (ZnO) and stearic acid; as accelerators, n-cyclohexyl-2-benzothiazole sulfonamide (CBS); and as vulcanizing agents, sulfur. Both SIR 20 and the additional materials were obtained from the Indonesian Rubber Research Institute (IRRI), Bogor, Indonesia, and as a filler, OPEFB fibers were obtained from the Green Polymer Technology Laboratory, University of Indonesia.

Procedure

Preparation of the coupling agent begins by preparing a solution consisting of natural rubber latex, which is diluted to 1 wt% from the original 55 wt% by adding distilled water, then adding starch 25 wt% by weight to the dry latex mass, along with 0.02 M Na_2SO_4. Latex dilution aims to increase the dispersion between starch and electrolyte (Na_2SO_4) in latex. The main instrument used in making latex-starch hybrids is the plasma electrolysis reactor. In this reactor, air injection is given through an air shroud to provide a gas supply in the form of oxygen and nitrogen to help form an air shroud around the anode. The anode used is a solid cylindrical anode with a diameter of 6 mm and made of tungsten or titania, while the cathode is made of stainless steel SS-314 or carbon. The electric power used is 200-500 watts, and the operating temperature is 65ºC. The highest percentage reaction yield from research by Kirana (2019) was chosen as the coupling agent to be used [24].

Preparation of Empty Palm Oil Bunches Fiber OPEFB fiber begins with heating at 80 °C for 6 hours, cleaning of impurities, crushing, and sieving in a crusher machine to obtain a fiber size of approximately 100 mesh.

The mastication and compounding process uses an open roll mill machine located at the Indonesian Rubber Research Institute (IRRI), Bogor. The CA (NR-St) used to make the compound will be varied, and Table 1 provides information regarding the composition of the compound's other materials, including NR (SIR 20), ZnO, Stearic Acid, and CBS, as well as sulfur. In order to produce rubber composites at the end of the process, homogenous mixtures of rubber compounds were cured in a rubber vulcanizing press machine at a temperature of 150 ºC for a period of time based on rheological measurements.

TABLE 1. Composition of composite (in phr)

Sample	NR	OPEFB fiber	CA (NR-St)	ZnO	Stearic acid	CBS	Sulfur
B0	100	10	0	6	0.5	0.7	2.5
B1	100	10	1	6	0.5	0.7	2.5
B2	100	10	2	6	0.5	0.7	2.5
B3	100	10	3	6	0.5	0.7	2.5

In order to characterize the composites, an FTIR Perkin Elmer L1600400 was utilized to investigate the functional groups of compounds. Rheological testing was carried out with a Moving Die Rheometer (MDR) Alpha 2000 at a temperature of 150 °C in order to determine the scorch time (t_{s2}), the optimal curing time (t_{90}), the maximum torque (M_H), and the minimum torque (M_L). The LF1207 Universal Testing Machine from Lloyd Instrument, coupled with NEXYGEN Material Testing Software, was utilized in order to evaluate the material's mechanical properties.

RESULTS AND DISCUSSIONS

Molecular interaction

The FTIR spectra of functional groups from the composite based on Table 1 are presented in Figure 1. In NR, there is a distinctive peak at 2960-2851 cm^{-1} for the asymmetric strain vibration of the CH_3 methyl group, the symmetric strain vibration of methylene CH_2, and for the C=C carbon double bond found in NR located at 1645 cm^{-1}, Peak 1380-1460 cm^{-1} also shows C–H bending [16, 24]. The FTIR spectra between B0 and the other composites did not show a significant difference. OPEFB fiber contains biomass such as starch, cellulose, lignin, and hemicellulose as its main components. The addition of CA (NR-St) is expected to increase the compatibility of the NR and OPEFB fiber composite, which can be determined from the hydroxyl functional groups (-OH) in the range 3300 – 3600 cm^{-1} [24, 25]. Based on Figure 1, there is an OH peak, stretching the hydroxyl group at 3359-3360 cm^{-1}. The interaction between CA (NR-St) and NR-OPEFB fiber composite, shows that the nonpolar side of CA (NR-St) will interact with the NR matrix, while the polar side will form intermolecular hydrogen bonds between CA (NR-St) and OPEFB fiber, as reported by Chalid et al. [16]. The transmittance of B0, B1, B2, and B3 were 94.77 %, 94.58 %, 94.56 % and 94.38 %, respectively. For B3, the lowest transmittance value implies more -OH functional group.

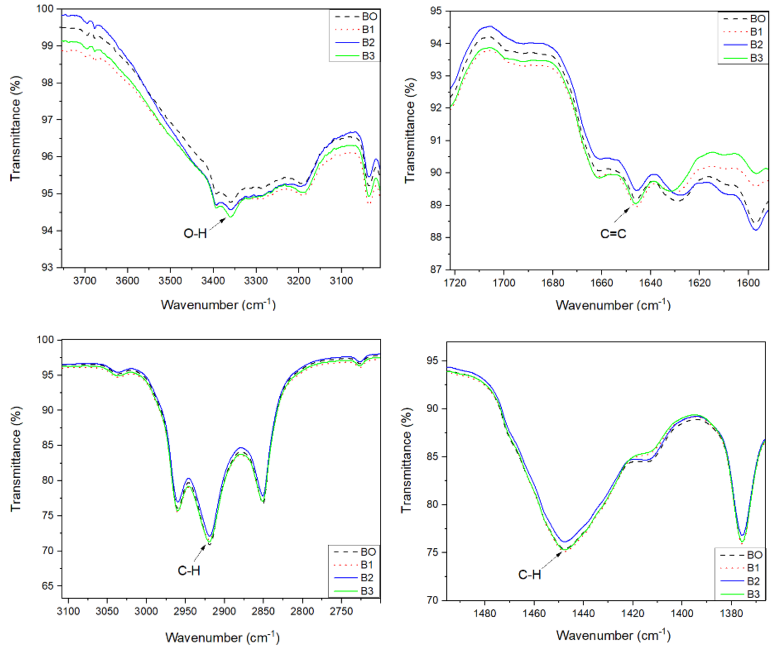


FIGURE 1. FTIR spectra of composite

Curing characteristics

Figures 2 and 3 show the curing characteristics for maximum torque (M_H), cure time (t_{90}), and scorch time (t_{s2}) of composites, respectively. The maximum torque (M_H) increases with CA (NR-St) loading, as shown in Figure 2. Maximum torque (M_H) values are 8.3, 8.33, 8.36, and 8.54 dNm for B0, B1, B2, and B3, respectively. The composite with the highest M_H value, B3, may contain the largest quantity of coupling agent. Due to the fact that the coupling agent has polar and nonpolar surfaces, it increases the crosslinking between NR and OPEFB fibers, thereby reducing the mobility of the macromolecular chain. This results in a composite rubber that is harder and stiffer. Inhibition of this mobility may also result from the formation of hydrogen bonds between the OPEFB fiber and the coupling agent [16].

Evaluating the time parameter on the rheological curve is an additional method for determining how a coupling agent's presence influences composites' crosslinking behavior during the curing reaction. The composites' scorch time (ts2) and optimum crosslinking time (t90) tend to decrease as the coupling agent load increases. (Figure 3). The shortest time is B3, which contains the most CA (NR-St). This was due to the increasing number of cross-links between NR and fiber due to the bridging action performed by the coupling agent, thereby decreasing the time required to reach 90% M_H [16, 26].

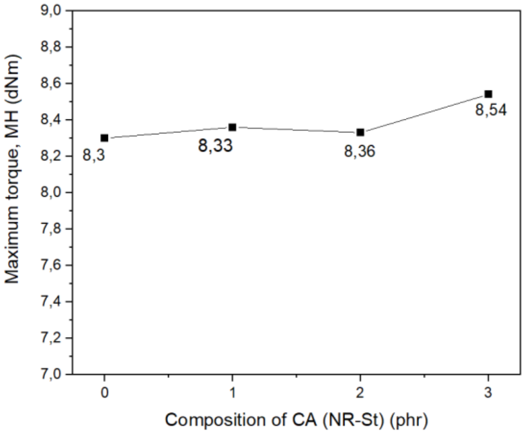
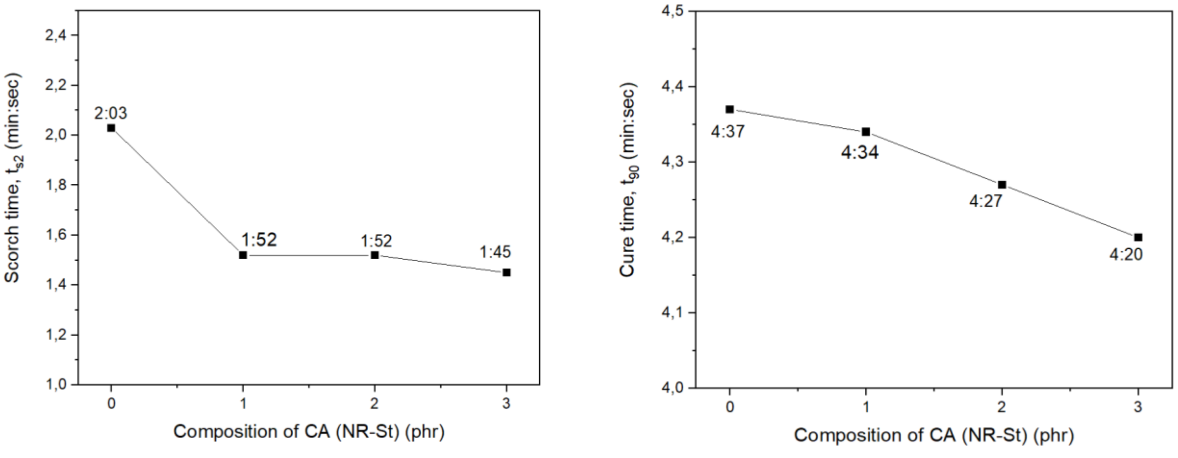


FIGURE 2. The effect of CA (NR-St) loading on maximum torque (M_H) of composites



(a) (b)

FIGURE 3. The effect of CA (NR-St) loading on (a) scorch time (t_{s2}) and (b) cure time (t_{90}) of composites

Mechanical properties

Figure 4 presents the mechanical properties of composites as tensile strength (a) and elastic modulus (b). With the addition of the coupling agent, the tensile stress increases; this is consistent with the previous discussion that there is an increase in the compatibility of the composite due to the addition of a coupling agent as a bridge between NR and OPEFB fibers so that the binding strength is increased. This phenomenon may be caused by nonpolar and polar covalent bonds in the coupling agent, which promotes the formation of intermolecular bonds between the polar portion and the OPEFB fiber [16]. In addition, in composites consisting of non-polar polymers and polar fillers, the use of a coupling agent can act as a dispersing agent to produce hydrogen bonds, thus increasing the dispersion of OPEFB fillers in the matrix [27, 28]. Several researchers also revealed that there is an increase in the tensile strength of the composite due to the incorporation of the coupling agent [26, 29, 30]. According to Figure 4 (a), coupling agents with a composition of 2-3 phr showed the highest tensile strength value, this trend was also reported in previous studies [31, 32, 33].

The effect of the addition of a coupling agent on the elastic modulus was also studied, where like the tensile strength, increasing the amount of coupling agent also increased the elastic modulus. Elastic modulus, or Young's modulus, is a measure of the stiffness of an elastic material [34]. OPEFB fiber has high stiffness. Fiber added to NR will increase the density of the composite and inhibit chain movement due to the smaller intermolecular gaps in the rubber chain [35]. If a coupling agent is added, it will form intermolecular hydrogen bonds between the fiber and the coupling agent, which act as a crosslink to further inhibit the movement of the chain. Therefore, the inhibition of the movement of the molecular chains increases the stiffness of the composite.

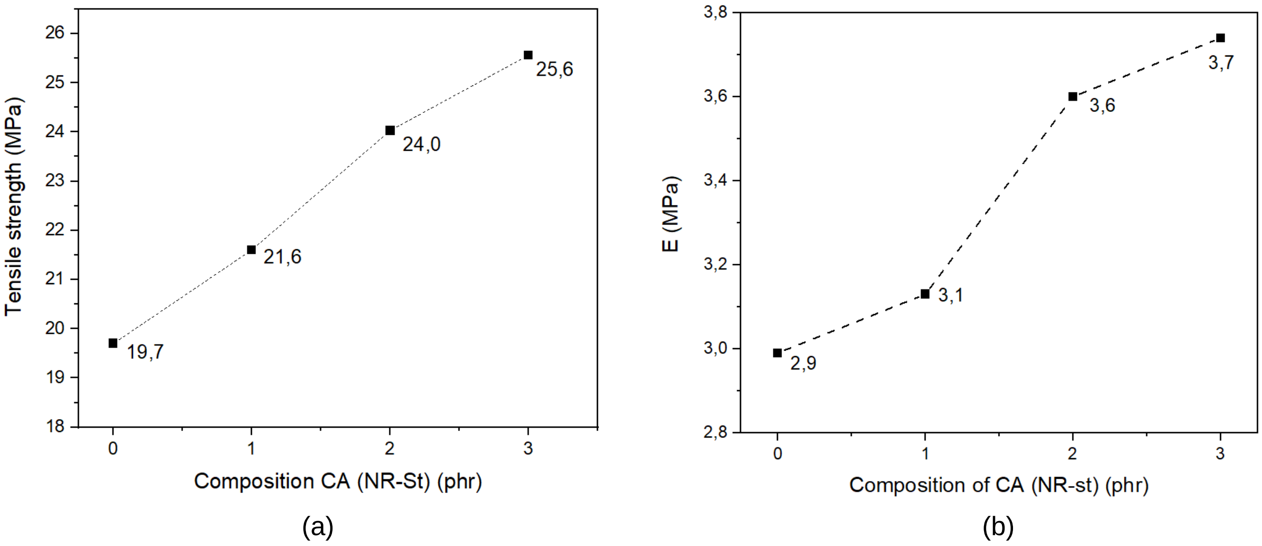


FIGURE 4. The effect of CA (NR-St) loading on the mechanical properties of composites (a) tensile strength (b) elastic modulus

CONCLUSION

In conclusion, this study demonstrates the prospect of using OPEFB fibers as an eco-friendly and sustainable reinforcing filler for natural rubber (NR) composites. Adding a latex-starch hybrid coupling agent (CA (NR-St)) effectively improves the compatibility between the NR matrix and OPEFB fibers, leading to a more homogenous dispersion and enhanced adhesion. The Fourier Transform Infrared (FTIR) analysis confirmed the presence of functional groups on the composite's surface, indicating successful interaction between the components. The rheological study revealed an increase in the maximum torque and a decrease in the scorch time and cured time with the addition of CA (NR-St), which may be attributed to improved compatibility and distribution of the fibers within the NR matrix. Mechanical testing showed that incorporating OPEFB fibers and CA (NR-St) significantly improved the tensile strength and stiffness of the NR composite. These improvements in mechanical properties suggest that the developed composite can be used for a wide range of applications, such as in the automotive, construction, and packaging industries. Further research is recommended to optimize the fiber content and CA (NR-St) concentration to achieve superior mechanical properties. Exploring other eco-friendly coupling agents and surface modification techniques for OPEFB fibers may lead to the development of even more sustainable and high-performance rubber composites.

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