

Application of Different Vegetable Oils as Processing Aids in Industrial Rubber Composites: A Sustainable Approach

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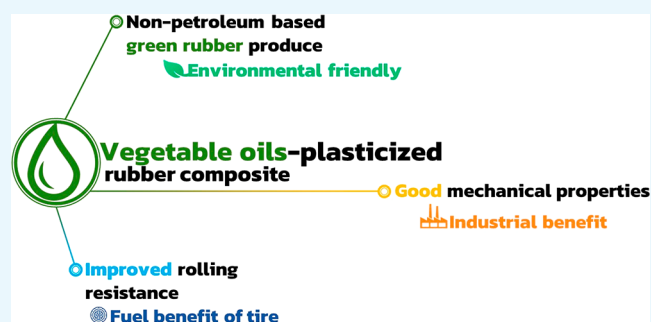
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ABSTRACT: Rubber composites based on renewable vegetable oils are being increasingly developed, as these materials significantly reduce the use of petroleum-based carcinogenic oils as plasticizers in rubber products. Apart from renewability, vegetable oils have some major advantages, such as easy availability, biodegradability, and environmentally friendly nature. Until now, vegetable oils, such as palm oil, soybean oil, and linseed oil, have been successfully used as processing oils to replace petroleum-based oils in engineered rubber composites. So far, the concept of a vegetable-oil-based plasticizer has been applied to rubber composites containing different industrially important fillers, like carbon black, silica, calcium carbonate, and expandable graphite. In the near future, the trend of utilizing vegetable-oil-based plasticizers may bring considerable advancements in the performance of filled rubber composites in an environmentally acceptable and sustainable manner.



1. INTRODUCTION

The successful application of different reinforcing fillers is an important invention in the rubber industry in order to get rubber composites with appropriate mechanical properties and thermal stability.¹ In this regard, excellent interaction between the rubber and filler is the most important criteria to ensure the quality of filled rubber composites.¹ The use of processing oils or plasticizers is by far the most effective way to enhance the interaction between the rubber and filler by increasing the compatibility.² Petroleum oils with polycyclic aromatic hydrocarbons (PAHs) are generated via the petroleum refining process.² Based on their chemical composition, petroleum-based processing oils can be classified into different categories, such as aromatic, paraffinic, and naphthenic. Traditionally, petroleum-based oils have played a crucial role as plasticizers or extenders in the rubber industry because of their low price and excellent compatibility with most of the available rubbers.³ However, petroleum-based aromatic oils with high PAH content are highly carcinogenic in nature.³ Thus, the use of these petroleum-based aromatic oils in the rubber industry can cause severe environmental pollution and water contamination.^{3,4} Furthermore, the Council of the European Communities has suggested complete prohibition of the use of PAH-rich petroleum oils for industrial and marketing purposes.^{3,5}

Vegetable oils are mainly composed of triglycerides.^{6,7} The main structural parts of triglycerides are esters produced from glycerol and various fatty acids.⁷ In different types of vegetable oil, the fatty acid chain is comprised of carbon atoms ranging from 8 to 24 and carbon–carbon double bonds ranging from 0

to 5.⁷ Simply, depending on the composition of the fatty acid, one vegetable oil differs from the other. Plant seeds are considered as a sustainable and perpetual source of vegetable oils. As reported by the USDA-FSA, there is a day to day increase in the global production of vegetable oil.⁸ Among the different vegetable oils, globally important vegetable oils are palm oil, soybean oil, and rapeseed oil because of their high worldwide production and reasonable prices for large-scale application in industrial purposes.⁶ In the past few years, the application of vegetable oils was found to be of great interest in different small- and large-scale industries, such as soaps, lubricants, biofuels, paints, etc.⁹

In the past decade of the 21st century, the idea of a sustainable circular economy has attracted a lot of attention from environmental, social, and economic viewpoints. Actually, a sustainable circular economy provides environmental and economical benefits to present and future generations by proper utilization of green and renewable materials in different industrial purposes.¹⁰ The present paper aims to review the up-to-date advancements in the application of renewable vegetable oils instead of nonrenewable petroleum-based oils as

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processing aids for the manufacturing of commercially suitable sustainable rubber products.

2. VEGETABLE-OIL-BASED RUBBER COMPOSITES

The increasing environmental consciousness has forced rubber researchers to search for more environmentally friendly additives for the preparation of rubber products. For this purpose, the rising trend of utilizing vegetable oils as a green extender or plasticizer has become the most interesting approach in the rubber industry. Table 1 enlists the examples of different filled rubber composites based on vegetable oils.^{2,3,11–24}

Table 1. Rubber Composites Prepared by Using Different Vegetable Oils as a Plasticizer

vegetable oils	rubber composite systems	refs
epoxidized palm oil (EPMO) and epoxidized soybean oil (ESBO)	carbon black (CB) filled natural rubber (NR) and styrene butadiene rubber (SBR) blend	11
esterified and epoxidized soybean oil	silica-filled styrene butadiene rubber (SBR)/butadiene rubber (BR) composite	12
soybean oil (SBO), palm oil (PMO), sunflower oil (SFO)	CB-filled NR composite	13
orange peel oil (OPO) and olive oil (OO)	CB-filled acrylonitrile–butadiene rubber (NBR) composite	14
polymerized soybean oil (PSBO)	CB-filled NR/SBR blend	15
polymerized soybean oil (PSBO)	CB-filled ethylene propylene diene monomer (EPDM) composite	16
transgenic soybean oil (TSO)	CB-filled EPDM composite	17
castor oil (CAO) and jatropha oil (JO)	CB-filled SBR composite	3
epoxidized palm oil (EPMO)	CB-filled SBR composite	18
palm oil (PMO)	CB-filled EPDM composite	19
palm oil (PMO)	CB-filled NR composite	2
tea oil (TO), palm oil (PMO), and coconut oil (CO)	silica-filled NR composite	20
moringa oil (MO) and niger oil (NO)	silica-filled NR composite	21
linseed oil (LO)	nanocalcium carbonate filled NR composite	22
linseed oil (LO)	nanocalcium carbonate filled NBR composite	23
linseed oil (LO)	expandable graphite (EG) filled NR composite	24

2.1. Application of Vegetable Oils in Carbon-Black-Filled Rubber Composites. Carbon black (CB) filled rubber composites based on various vegetable oils, such as palm oil, epoxidized palm oil, soybean oil, epoxidized soybean oil, polymerized soybean oil, transgenic soybean oil, sunflower oil, orange peel oil, olive oil, castor oil, and jatropha oil, have been prepared in recent years.^{2,3,11,13–19}

Wang et al.¹⁹ have done systematic research on the plasticization effects of green palm oil (PMO) in CB-filled ethylene propylene diene monomer (EPDM) composites. In this study, the authors have mainly focused on the possible replacement of petroleum-based paraffin oil (PO) by renewable PMO as a plasticizer in EPDM/CB compounds. Initially, 2 phr (parts per hundred parts of rubber) dicumyl peroxide (DCP) was used as a cross-linking agent in this work. The maximum torque decreased constantly with an increasing amount of processing oil in EPDM/CB composites, which was thought to be due to the plasticizing effects of PMO and PO. The EPDM/CB composites based on PMO showed lower

cross-link density than the EPDM/CB composites based on PO. As a result, EPDM/CB composites with PMO had a lower value of modulus at 100% elongation (M_{100}) than EPDM/CB composites with PO. The stress–strain curves of EPDM composites in the presence of different plasticizers are shown in Figure 1. In Figure 1, different EPDM composites are

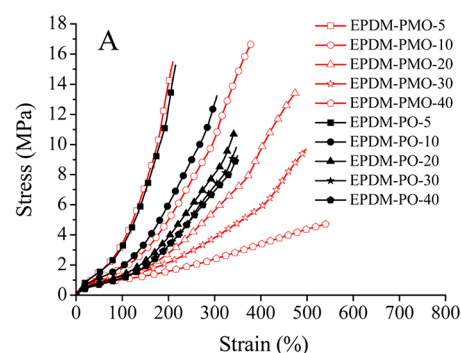


Figure 1. Stress–strain curves of EPDM composites based on PMO and PO. Reprinted with permission from Wang, Z.; Peng, Y.; Zhang, L.; Zhao, Y.; Vyzhimov, R.; Tan, T.; Fong, H. Investigation of palm oil as green plasticizer on the processing and mechanical properties of ethylene propylene diene monomer rubber. *Ind. Eng. Chem. Res.* **2016**, *55*, 2784–2789. Copyright 2016 American Chemical Society.

represented as EPDM–plasticizer oil- x , where x stands for the amount of plasticizer in phr. At 10 phr loading of processing oil, the PMO-based EPDM/CB composite showed considerably higher tensile strength than the PO-based EPDM/CB composite. However, the EPDM/CB composite with 40 phr PMO had very poor tensile strength, which was due to the interaction between double bonds in PMO and DCP. The tensile strength of the 40 phr PMO-plasticized EPDM/CB composite can be adjusted by increasing the amount of cross-linking agent (DCP). As claimed by the authors, the 40 phr PMO-plasticized EPDM/CB composite showed excellent tensile strength in the presence of 4 phr cross-linking agent (DCP). In another study, the plasticizing effect of epoxidized palm oil (EPMO) was compared with that of PMO and petroleum-based aromatic oil (AO) in CB-filled styrene butadiene rubber (SBR) composites.¹⁸ At 3 phr loading of processing oil, the tensile strength of an EPMO-plasticized SBR/CB composite was comparable with that of an AO-plasticized SBR/CB composite. The reduction in the value of tangent delta ($\tan \delta$) at 60 °C indicates improved rolling resistance, i.e., fuel benefit of tire compounds.²⁵ The $\tan \delta$ value at 60 °C indicated that the EPMO-plasticized SBR/CB composite showed better fuel consumption efficiency as compared to either a PMO-plasticized SBR/CB composite or AO-plasticized SBR/CB composite.

The processing and mechanical properties of soybean oil (SBO)-based rubber composites have been explored by different research groups.^{11,13,15–17} Petrović et al.¹⁵ have suggested the importance of solubility parameters to determine the compatibility between rubber and plasticizers. The authors predicted that SBO and polymerized soybean oil (PSBO) have better compatibility with natural rubber (NR) or SBR as compared to petroleum-based naphthenic oil (NTO). The value of maximum torque indicated that SBO has a higher plasticizing effect than either PSBO or NTO. As a result, the mechanical properties showed remarkable reduction for SBO-plasticized NR/SBR composites at a higher level of plasticizer

(40 to 60 phr). Throughout the whole plasticizer loading level (higher or lower), PSBO-plasticized NR/SBR composites had comparable mechanical properties with those of NTO-plasticized NR/SBR composites. This is the most interesting point regarding the replacement of petroleum-based NTO by renewable PSBO as a plasticizer in NR/SBR formulations. On the other hand, at an up to 15 phr plasticizer loading level, transgenic soybean oil (TSO)-plasticized EPDM/CB composites showed higher mechanical properties and thermal stability than paraffin-oil-plasticized EPDM/CB composites.¹⁷ However, at 20 phr plasticizer loading level, the mechanical properties of the TSO-plasticized EPDM/CB composite were found to be very poor due to the common interaction between double bonds of TSO and cross-linking agent (DCP). At a lower plasticizer loading level (0 to 9 phr), some other vegetable oils, such as jatropha oil and castor oil, can be used as a replacement of commonly used petroleum-based AO in SBR composites.³ The tensile strength values of these vegetable-oil-plasticized SBR composites were almost comparable with the tensile strength of AO-plasticized SBR composites (Figure 2). However, the efficiency of both jatropha oil and castor oil is not clear at a higher plasticizer loading level.

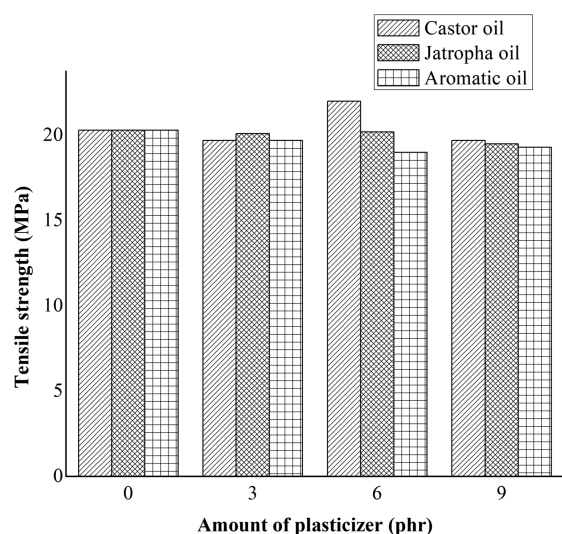


Figure 2. Tensile strength values of SBR composites plasticized with castor oil, jatropha oil, and aromatic oil. Adapted with permission from Pechurai, W.; Chiangta, W.; Tharuen, P. Effect of vegetable oils as processing aids in SBR compounds. *Macromol. Symp.* **2015**, *354*, 191–196. Copyright 2015 John Wiley and Sons.

Undoubtedly, palm oil and soybean oil are the two interesting green plasticizers in CB-filled rubber composites. Thus, it is quite reasonable to compare the plasticizing effect of palm oil and soybean oil in CB-filled rubber compounds. In an interesting research work, Sahakaro et al.¹¹ have compared the effect of epoxidized palm oil (EPMO) and epoxidized soybean oil (ESBO) in CB-filled NR/SBR composites at 10 phr plasticizer loading level. The mechanical properties of the EPMO-plasticized NR/SBR composite were comparable with those of the conventional distillate aromatic extract (DAE)-plasticized NR/SBR composite. However, the mechanical properties of the ESBO-plasticized NR/SBR composite were found to be much lower than the EPMO-plasticized NR/SBR composite. More interestingly, the rolling resistance and wet grip properties of the EPMO-plasticized SBR composite were

slightly better as compared to the DAE-plasticized SBR composite. Thus, EPMO was found to be a far better choice than ESBO as a replacement for petroleum-based DAE in CB-filled rubber composites.

2.2. Application of Vegetable Oils in Silica-Filled Rubber Composites. Siwarote et al.²⁰ have investigated the suitability of three different vegetable oils (tea oil, palm oil, and coconut oil) as a plasticizer in silica-filled NR composites. For comparison, the authors have used petroleum-based naphthenic oil (NTO) as a reference. Because of the good interaction between the polar ester groups of vegetable oils and silanol groups of silica, vegetable-oil-based NR/silica composites showed better dispersion of silica within the rubber matrix than NTO-based NR/silica composites. As a result, the mixing energies of vegetable-oil-based NR/silica composites were found to be lower than NTO-based NR/silica composites. The concept of the Payne effect is very important to determine the filler–filler interaction in filled rubber compounds. The lowering in the value of the Payne effect indicates improved filler dispersion within a rubber matrix. The value of the Payne effect of the rubber sample is commonly calculated from the difference of the storage modulus at high and low strains. The authors stated that vegetable-oil-based NR/silica composites showed lower Payne effect than NTO-plasticized NR/silica composites at the same plasticizer loading level, which indicated excellent dispersion of silica within an NR matrix in the presence of vegetable-oil-based plasticizers.

Another attractive way to replace petroleum-based NTOs in NR/silica composites is to use new vegetable oils, such as niger oil (NO) and moringa oil (MO).²¹ At lower plasticizer loading level (0 to 9 phr), the values of torque difference and mechanical properties were found to be higher for vegetable oil (NO or MO)-based NR/silica composites than NTO-based NR/silica composites. As shown in Figure 3, the chemical interaction between polar ester groups of vegetable oils and silanol groups of silica led to satisfactory dispersion of silica within the NR matrix. The same research group has also reported that the use of MO or NO as a plasticizer led to the better rolling resistance performance of NR/silica materials than petroleum-based NTO. Recently, Hayichelaeh et al.⁵ have suggested the efficiency of amine-modified epoxidized palm oil (AMEPMO) as a processing oil in silica-filled NR composites. The amine group of AMEPMO can enhance the cross-linking density of NR/silica composites by promoting a cure reaction. As a result, the AMEPMO-based NR/silica composite showed better mechanical properties than the DAE-based NR/silica composite.

2.3. Application of Vegetable Oils in Calcium-Carbonate-Filled Rubber Composites. Researchers have prepared nanocalcium carbonate (CaCO_3)-filled rubber composites using linseed oil (LO) as a plasticizer.^{22,23} The mechanical properties of NR/ CaCO_3 nanocomposites increased markedly due to the incorporation of 2 phr of LO as an extender or plasticizer, which confirmed the improved dispersion of nano CaCO_3 within the NR matrix in the presence of linseed oil.²² Using a similar method, Roy et al.²³ have utilized LO as a plasticizer to develop high performance nitrile rubber/ CaCO_3 nanocomposites.

2.4. Application of Vegetable Oils in Expandable-Graphite-Filled Rubber Composites. Presently, very little information on the application of vegetable oils in expandable graphite (EG) filled rubber composites is available. The chemical interaction between ester groups of LO and EG is the

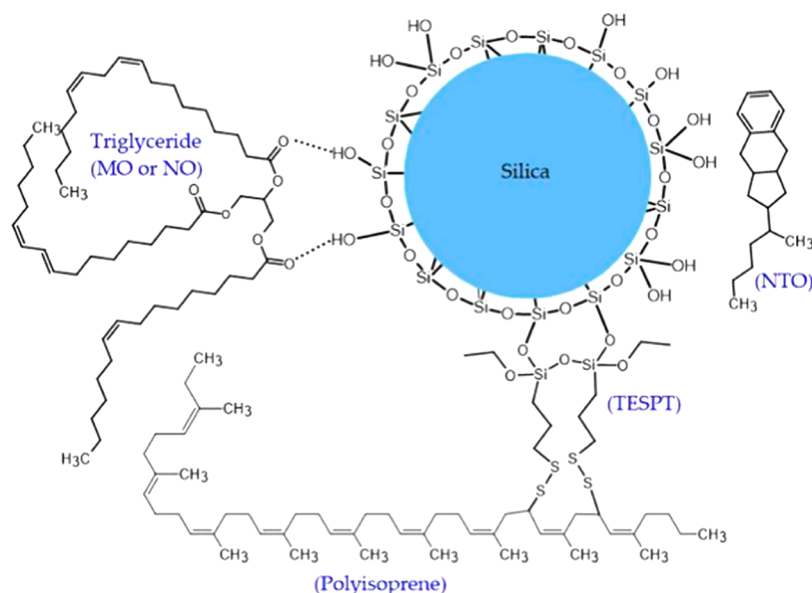


Figure 3. Possible chemical interaction between ester groups of NO or MO and silanol groups of silica. Reprinted with permission from Boonrasri, S.; Sae-Oui, P.; Reungsang, A.; Rachtanapun, P. New Vegetable Oils with Different Fatty Acids on Natural Rubber Composite Properties. *Polymers* 2021, 13, 1108. Copyright 2021, MDPI.

key factor in determining the final properties of LO-plasticized NR/EG composites.²⁴ Fernandez et al.²⁴ studied the effect of LO as a plasticizer in NR/EG composites at different plasticizer loading levels. It was found that 4 phr of LO is the optimum amount of plasticizer in 10 phr of EG-filled NR composites. For a comparative study, the authors utilized petroleum-based naphthenic oil as a reference oil. At a 4 phr plasticizer loading level, the mechanical properties and thermal stability of the LO-plasticized NR/EG composite were far better than the naphthenic-oil-plasticized NR/EG composite. Furthermore, the mechanical properties of NR/EG composites plasticized with different processing oils can be explained properly by measuring cross-link density (Figure 4). Above the 4 phr plasticizer loading level, the tensile strength of LO-plasticized NR/EG composites showed continuous reduction due to the self-vulcanization property of LO.

In fact, the explanation of thermodynamic compatibility of rubber with vegetable oils in terms of the Flory–Huggins interaction parameter is an interesting part related to vegetable-oil-based rubber technology.^{26,27} However, so far, rubber researchers have given it very little attention at this point.

3. CONCLUSIONS AND FUTURE PERSPECTIVES

In summary, vegetable oils are gaining noteworthy importance to substitute petroleum-based carcinogenic oils in the rubber industry. Carbon-black-filled NR/SBR composites are the most important material for the preparation of high performance tires. In this regard, renewable epoxidized palm oil is a suitable substitute of petroleum-based distillate aromatic extract in carbon-black-filled NR/SBR composites. Also, polymerized soybean oil can successfully replace petroleum-based naphthenic oil in carbon-black-filled NR/SBR compound. EPDM is generally used in different nontire applications. Green palm oil can be chosen as a plasticizer in CB-filled EPDM compounds. On the other hand, silica-filled rubber composites are used for the preparation of green tires with fuel benefit in modern rubber technology. Some vegetable

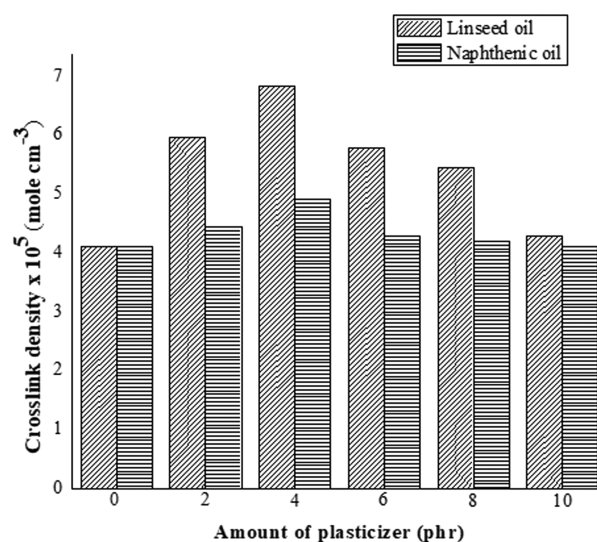


Figure 4. Cross-link density values of NR/EG composites plasticized with linseed oil and naphthenic oil. Adapted with permission from Fernandez, S. S.; Kunchandy, S.; Ghosh, S. Linseed oil plasticizer based natural rubber/expandable graphite vulcanizates: Synthesis and characterizations. *J. Polym. Environ.* 2015, 23, 526–533. Copyright 2015 Springer Nature.

oils, like niger oil and moringa oil, can substitute petroleum-based naphthenic oil in silica-filled NR composites. Besides, linseed oil is the most attractive candidate as a green plasticizer in nanoCaCO₃-filled NR composites.

In light of the up-to-date developments in this research area, there are some basic challenges that need to be overcome for the commercial application of vegetable-oil-based plasticizers in rubber-related industrial products. First, rubber researchers have given too much importance to the discovery of new vegetable-oil-based plasticizers only for carbon-black-filled rubber composites. However, researchers have given very little attention to searching for new vegetable oils for other important filled rubber systems, such as silica and calcium-

carbonate-filled rubber composites. Second, the price of the final rubber products is a key factor regarding their industrial use. So, considerable research works are necessary in the future to search for new cheaper vegetable oils in order to narrow the price gaps between vegetable oils and cheap petroleum-based oils. Third, the performance of most of the vegetable oils is not satisfactory at a higher plasticizer loading level due to some redundant interaction between double bonds of vegetable oils and a cross-linking agent.

Finally, the concept of a vegetable-oil-based plasticizer is still confined to the laboratory level. In the near future, rubber-related industries need to be willing to use vegetable-oil-based plasticizers at the commercial level.

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Notes

The authors declare no competing financial interest.

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