

Improvement of Filler–Rubber Interaction by the Coupling Action of Vegetable Oil in Carbon Black Reinforced Rubber

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ABSTRACT: Vegetable oil has been added in small amount to the rubber compound during mixing. It has been observed that the extent of cure obtained from the rheometric torque is lower for vegetable oil-containing compounds. This has been manifested from their physical and tensile properties. The lower abrasion and hardness of vegetable oil-containing compounds may be due to better plasticization and lower crosslink density. The lower $\tan \delta$ at maximum torque indicates lower loss and heat generation. The vegetable oil-containing compounds shows lower modulus, higher tensile strength, and elongation. All the compounds containing vegetable oil shows lower compression set and higher rebound resilience, tear strength, and flex cracking compared to the standard compound containing no vegetable oil. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 735–739, 2000

Key words: vegetable oil; surface modification of carbon black; crosslink density; modulus; flexing and rebound resilience

INTRODUCTION

Carbon black is used in rubber compounding due to its ability to enhance the ultimate properties like tear strength. By the incorporation of carbon black in rubber, the properties affected are tensile strength and fatigue life. Due to its rigidity, the modulus of carbon black is high compared to the elastomeric matrix. Thus, the elastomeric matrix has to deform to a larger extent than the macroscopic strain applied to the sample.¹ This causes strain amplification into the rubbery matrix. The measurement of strain amplification given by Medalia² depends on the volume of rubber that is occluded, i.e., which resides within the indentation of the particle aggregates, which is also protected from the strain field of the elastomeric matrix and does not participate in the deformation process. The effective immobilization of rub-

ber portion acting as a part of the carbon black rather than the rubber matrix³ increases the effective volume of the carbon black beyond the value calculated from mass and density. The effective immobilization of the rubber by filler depends on the strength of the rubber–filler interaction^{4–6} at the surface of filler. The carbon black surface is characterized by the dispersive and specific (polar) components of surface energy.⁷ The specific components of surface energy arises due to the presence of polar groups at the surface. Donnet⁸ reported on surface modification of carbon black by that silane coupling agent leads to lowering in reinforcement, thus deteriorates in ultimate properties, whereas Bras and Papirer⁹ reported an improvement in ultimate properties upon grafting of rubber onto the carbon black surface. Kundu et al. has reported the measurement of filler–rubber interactions through the studies of rheometric¹⁰ and physical¹¹ properties. The use of oils in the rubber compound reduces its cost as well as plasticises the surface between the

Table I Compounding Ingredients in phr

Compounding Ingredients	Compound-1 (Standard Compd.)	Compound-2	Compound-3	Compound-4
HAF black	50.0	49.5	49.1	48.5
Vegetable oil	0.0	0.5	0.9	1.5

All the compounds contain (in phr) NR (RMA-IX): 70, PBR: 30, Zinc Oxide (ZnO): 4.5, Stearic acid: 1.5, 6 PPD (Antidegradant): 1.0, H.S. beads: 1.5, Parafin wax: 2.0, Elasto 710: 10.0, Cyclohexyl Benzsulphenamide: 1.0, Sulphur: 1.5.

carbon black and the polymers. The industrially used oils are originally from petroleum. This may cause them to be costlier than vegetable oils. The aim of this article is to study the effect of using a small amount of vegetable oils in addition to petroleum oils (like aliphatic, aromatic, etc.) on the properties of rubber.

EXPERIMENTAL

Materials Used

Natural rubber (RMA-1X): Moisture content 1%, ash content 0.4%, specific gravity 0.85, and Mooney viscosity (ML, 1 + 4 at 100°C) 60; Polybutadiene rubber: moisture content 1%, ash content 1.5%, specific gravity 0.93, and Mooney viscosity (ML, 1 + 4 at 100°C) 45; HAF carbon black: DBP absorption 102 cc/100 g. Procured from Ralson Carbon, India; 6 PPD: antidegradant, M.W. 268. Procured from ICI LTD. Elasto 710: Sp. gravity 0.98, flash point 220°C, aniline point 47°C; stearic acid: m.p. 62°C, acid value 192–204; Vegetable oil (propitery chemical): aniline point 25°C.

Sample Preparation

The compounds formulated are shown in Table I. The first column of Table I are taken as standard compounds (compound 1). The other compounds are formulated by using excess plasticiser (0.5, 0.9, and 1.5 phr) as vegetable oil in compound 2, compound 3, and compound 4, keeping constant the total amount of plasticiser and carbon black. The required amount of vegetable oil is taken in acetone, along with the necessary amount of carbon black, and they are agitated slowly to get them properly mixed. The acetone is then evaporated at 40°C. The rubbers, vegetable oil-modified carbon black, and other compounding ingredients are mixed on a two-roll mill according the standard practice. The compounds are moulded on a press at 160°C and 15 MPa pressure for 9 min for

different test samples. All the test samples are prepared using treated carbon black. It is expected that these vegetable oil-treated carbon black compounds are superior compared to the compounds obtained by a direct addition of carbon black and vegetable oil to the two-roll mill. This may be due to proper physical mixing and adsorption of vegetable oil onto the carbon black surface without the hindrance to penetration caused by rubbers in case of direct addition. This is also experimentally verified, as the added vegetable oil only acts as a plasticiser.

Mechanical Properties

Dumbbell-shaped test samples were punched out from the molded sheets. The thickness of the sample was measured with a bench thickness gauge. The test method described was measured, and ASTM-D-412-51 was followed. The test was carried out on a Tensile Testing Machine at 25°C and at a crosshead speed of 500 mm/min.

Hardness

Hardness was tested with a Shore-A Durometer according to ASTM-D-2240. The Durometer was kept on a stand under a constant load.

Abrasion Loss

The loss due to abrasion was tested with Din Abrader according to ASTM D 1242.

Compression Set

These properties were measured at 70°C for 22 h according to ASTM D 395.

Tear Strength

They were measured on a tensile tester according to ASTM D 624.

Curing Test

The curing tests were performed on a Monsanto Moving Disc Rheometer (MDR-2000) at 150°C, according to ASTM D 2084-81.

Flex Crack

The flex crack properties were tested on a Goodrich Flexometer according to ASTM-D 671. The test results were taken in Kilocycles only when pinholes were created by flexing.

RESULTS AND DISCUSSION

The maximum extent of cure and $\tan \delta$ at maximum torque obtained from the torque (kg-m) and time (minutes) curve of the MDR-2000 are plotted against content of vegetable oil in phr in the rubber compounds in Figure 1. The maximum extent of the cure, which is equivalent to maximum torque minus minimum torque ($D_{\max} - D_{\min}$), decreases linearly with increasing the content of the vegetable oil. $\tan \delta$ also decreases, but the trend is different. Initially, the rate of decrease in $\tan \delta$ is higher followed by an asymptotic trend.

The groups like ester and double bonds of the vegetable oil can interact with black, and the hydrocarbon part can be easily blended with the rubber. Thus, the vegetable oil will act as a coupling as well as a plasticising agent. The double bonds present in the vegetable oil may also participate in the physicochemical bond formation between the carbon black and rubber. Due to the

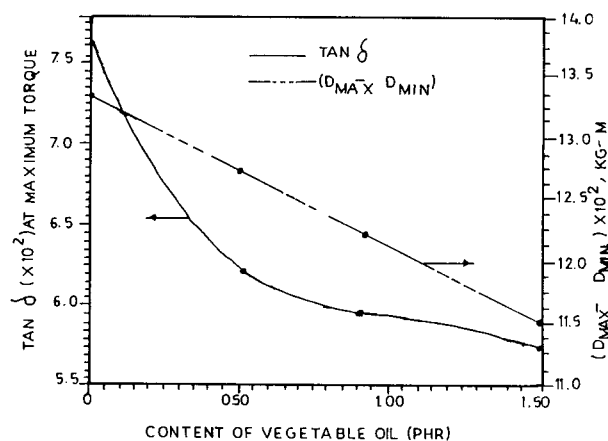


Figure 1 Plots of maximum extent of curing, ($D_{\max} - D_{\min}$) in kg-m and $\tan \delta$ vs. content of the vegetable oil in phr.

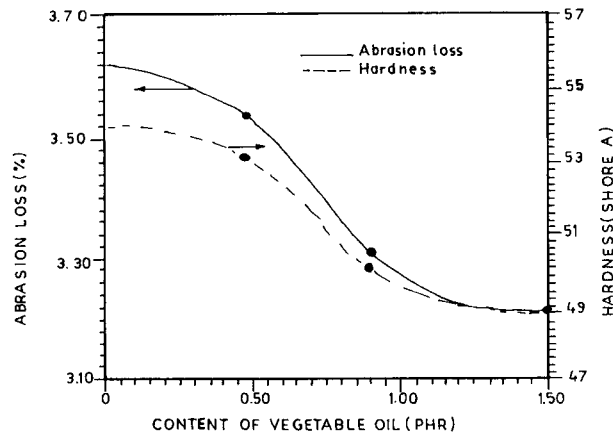


Figure 2 Plots of hardness (Shore A) and abrasion loss (%) vs. content of the vegetable oil (phr).

microplasticization of the rubber-black surface by the vegetable oil, there will be a lower amount of heat generation due to shearing at the rubber-black surface compared to the standard compound.¹ Thus, better dispersion and filler-rubber interaction due to the presence of higher amounts of vegetable oil will reduce the damping ($\tan \delta$) and increase the elastic properties.

The hardness and abrasion loss of the cured samples are plotted against the content of the vegetable oil in the compounds in Figure 2. The hardness of cured compounds decreases with an increase in content of the vegetable oil. All the compounds containing vegetable oil show lower hardness,¹² as the extra amount of vegetable oil increases microplasticization and reduces hardness. As the used vegetable oil is mainly a polyester containing three or more double bonds, it can also get cured along with the rubber during its curing. Thus, better physico-chemical bonding and plasticization at the carbon black-rubber interface will reduce the abrasion loss.^{13,14}

The tensile strength, 300% modulus and elongation at break of compounds 1, 2, 3, and 4 are plotted against vegetable oil content in the compounds in Figure 3. The tensile strength of a compound is the manifestation of its crosslink density, reinforcement by carbon black, and proper plasticization by oil. The extended molecular plasticization by vegetable oil and its active participation as a coupling agent in physico-chemical bonding between carbon black and rubber through its double bond leads to a higher tensile strength and lower modulus of the compounds containing vegetable oil (compounds 2, 3, and 4). The extra amount of vegetable oil present

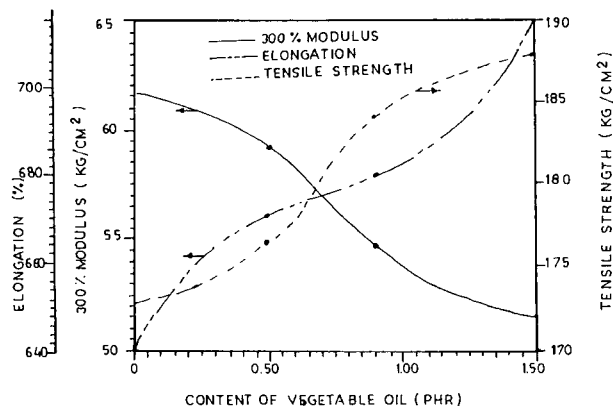


Figure 3 Plots of 300% modulus (kg/cm^2), tensile strength (kg/cm^2), and elongation (%) vs. content of the vegetable oil (phr).

in compounds 2, 3, and 4 compared to compound 1 leads to its higher plasticizing effect. This causes their higher elongation at break. For the incorporation of vegetable oil as a plasticizer, the above tensile results are the expected ones.

The tear strength and compression set properties are plotted against vegetable oil contents in compounds in Figure 4. This is a general perception that compounds containing a higher amount of vegetable oil and lower amount of carbon black should show deterioration in compression set and tear strength properties.^{13,14} The extent of cure decreases with increasing the content of the vegetable oil. Thus, it should increase the percent of the compression set and decrease the tearing energy. But the showing of a higher tear strength and lower compression set in Figure 4 with increasing the content of the vegetable oil (i.e., de-

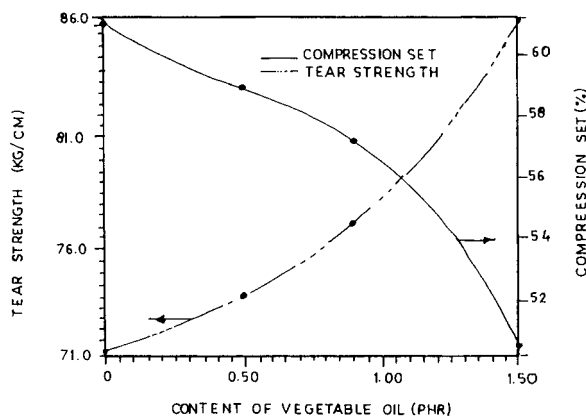


Figure 4 Plots of tear strength (kg/cm) and compression set (%) vs. content of the vegetable oil (phr).

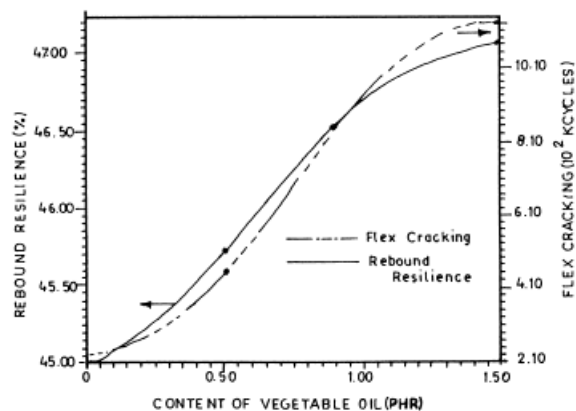


Figure 5 Plots of rebound resilience (%) and flex cracking resistance (kcycles) vs. content of the vegetable oil (phr).

creasing the content of the carbon black) is not in expected. This may be explained by the microplasticization at the carbon black–rubber interface and the coupling action of vegetable oil at this interface. The proper plasticization and dispersion of carbon black causes the elimination of propagating microcracks, leading to an improvement in tear strength and a reduction in void volume leading to a decrease in percent set.

The rebound resilience and flex crack resistance properties are plotted against vegetable oil content (phr) in Figure 5. Flex crack resistance is an ultimate failure property, depending on the propagation of cracks initiated at the tip of the carbon black surface during flexing, whereas rebound resiliency depends on the elasticity of the cured compound. Their improvement depends on proper plasticization between carbon black and rubber surfaces and the increment in filler–rubber interaction. The increasing content of vegetable oil present in compounds will increase the coupling action between carbon black and rubber interfaces by participation in physico-chemical bonding through its double bonds, leading to the formation of an extra rubber layer around the carbon black particle. All these factors will increase the elasticity of the cured compounds leading to improvement of percent rebound resilience properties. On the other hand, cyclic flexing causes shearing of rubber at the rubber–carbon black interfaces and, thus, generates heat. The secondary layer of rubber present around the carbon black particle (via coupling action of vegetable oil) will shield the shearing force.¹⁵ The better plasticization due to presence of an extra amount of plasticizer (vegetable oil) will lower the shear-

ing by proper dissipation of the heat generated by shearing. The microplasticization as well as coupling caused by vegetable oils will reduce shearing and, thus minimize the probability of tearing or cracking of rubber molecules at the carbon black-rubber interfaces. All these lead to the improvement of flex crack resistance properties upon addition of vegetable oil.

CONCLUSION

From the above results, it may be concluded that the small amount of vegetable oil added to the rubber compound during mixing has a tremendous effect on physical and tensile properties. The extent of cure obtained from the rheometric torque is lower for vegetable oil-containing compounds. This can be confirmed from their physical and tensile properties. The lower abrasion and hardness of vegetable oil-containing compounds may be due to the better plasticisation and lower crosslink density. The lower $\tan \delta$ at maximum torque indicates a lower loss or damping and heat generation. The vegetable oil-containing compounds shows a higher tensile strength and elongation and lower modulus. The lower compression set, higher rebound resilience, tear strength, and flex cracking resistance of vegetable oil-containing compounds is due to lower crosslink density, microplasticization, and coupling action of vegetable oil at the carbon black-rubber interface.

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