

# Effect of the Doses and Nature of Vegetable Oil on Carbon Black/Rubber Interactions: Studies on Castor Oil and Other Vegetable Oils

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**ABSTRACT:** The effects of additives in various vegetable oils on the physical, mechanical, and adhesion properties of carbon black/rubber compounds were studied. Various doses of castor oil and some other oils such as paraffin oil, vegetable oil 1, and cashew nut shell liquid (CNSL) at a fixed dose (1 phr) were used. With an increase in the castor oil content, the modulus, tear strength, and tensile strength increased, whereas the hardness and adhesive strength exhibited little variation up to 1 phr. Beyond 1 phr castor oil, the modulus, tear strength, and hardness decreased, whereas the adhesive and tensile strengths increased up to 2.5–3 phr and then decreased. Therefore, castor oil seemed to behave as a coupling agent up to 1 phr and as a coupling

agent and a plasticizer in the range of 1–3 phr; beyond that, the main role of castor oil was plasticization. When various oils at a fixed dose (1 phr) were compared, it was found that the vegetable oils exhibited enhanced properties in comparison with those of paraffin oil. In addition, both of the unsaturated oils (castor oil and vegetable oil 1) enhanced physical and mechanical properties in comparison with saturated paraffin oil. CNSL exhibited the best adhesion properties against mild steel and galvanized iron substrates. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 1574–1578, 2003

**Key words:** additives; adhesion; mechanical properties

## INTRODUCTION

Carbon blacks are widely used in rubber compounding because of their unique reinforcing properties with respect to other fillers. This reinforcement of rubber properties by the incorporation of carbon black is due to the presence of active polar groups such as phenol, carboxyl, quinone, and lactone on the carbon black surfaces.<sup>1–4</sup> These polar groups at the carbon black surfaces interact with rubbers, and the interaction is higher with polar rubber than with hydrocarbon rubber. This is due to the polar–polar interaction.<sup>5,6</sup> For hydrocarbon rubbers such as natural rubber (NR) and styrene–butadiene rubber, the possible interactions with carbon black are physical and physicochemical through double bonds of the main chain. The interactions between hydrocarbon rubbers and carbon black can be improved greatly by the introduction of the coupling action of some particular additives.<sup>7,8</sup> It has been reported elsewhere<sup>9–11</sup> that vegetable oils can act

as coupling agents between carbon black and rubber interfaces, leading to improved properties.

In this article, the effects of various doses of castor oil as an additive for carbon black/rubber compounds on the physical, mechanical, and adhesion properties were studied. The effects of various oils such as paraffin oil, vegetable oil 1, castor oil, and cashew nut shell liquid (CNSL) at a fixed dose (1 phr) to the carbon black/rubber compounds were compared in terms of the physical and mechanical properties. The chosen fixed dose was based on our earlier study in which vegetable oils exhibited optimum coupling action at 1 phr.<sup>9</sup>

## EXPERIMENTAL

### Materials

NR (RMA 1X) had a moisture content of 1%, an ash content of 0.4%, a specific gravity of 0.85, and a Mooney viscosity (ML<sub>1+4</sub> at 100°C) of 60. Polybutadiene rubber (PBR) had a moisture content of 1%, an ash content of 1.5%, a specific gravity of 0.93, and a Mooney viscosity (ML<sub>1+4</sub> at 100°C) of 45. High-abrasion-furnace (HAF) carbon black had di-*n*-butyl phthalate absorption of 102 cc/100 g was procured from Ralson Carbon (India). 2,5-Diphenyl-1,3,4-oxadiazole derivative (6-PPD) was an antidegradant (molecular weight = 268) and was procured from ICI, Ltd. (Calcutta, India). Stearic acid had a melt-

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**TABLE I**  
**Compound Formulations**

Contents of plasticizers (phr) in formulated compounds								
Variable doses of castor oil					Fixed dose of various plasticizers			
Compound 1	Compound 2	Compound 3	Compound 4	Compound 5	Compound 6	Compound 7	Compound 8	Compound 9
0	1	2	3	4	5	1	1	1

Compounds 7, 8 and 9 were formulated for paraffin oil, vegetable oil 1, and CNSL, respectively. In addition to the plasticizers, all of the formulated compounds contained NR (RMA-1X), 70, PBR: 30, carbon black, HAF (reinforcing agent): 50, ZnO: 4.5, stearic acid: 1.5, 6 PPD: 1, H. S. beads (polymerized 1,2-dihydro-2,4 trimethylquinoline, ICI, Calcutta, India) (antioxidant): 1.5, paraffin wax: 2, cyclohexyl benzsulphenamide (accelerator), and sulfur: 1.5 phr.

ing point of 62°C and an acid value of 192–204. The oils included paraffin oil (a plasticizer), a long-chain hydrocarbon oil, castor oil (iodine value = 85.8), vegetable oil 1 (a proprietary chemical, with an aniline point of 22°C, that was more unsaturated than the reported oil),<sup>6</sup> and CNSL (a long-chain styrenated phenol with some unsaturated fatty ester but little in comparison with conventional vegetable oil.<sup>12</sup> Brass-coated (70% Cu and 30% Zn) mild steel (MS) was used as a substrate for testing the adhesive strength of metal–rubber interfaces.

### Sample preparation

The compounds were formulated as shown in Table I. The formulated compounds were mixed on a two-roll mill according to the standard procedure. The oils were first mixed with carbon black for its pretreatment and then added to rubber on the mixing mill. The procedure for the pretreatment of carbon black with vegetable or paraffin oil was described elsewhere.<sup>6</sup> Suitable specimens for the measurement of the rheometric, hardness, abrasion, tear, and tensile strength properties were prepared with the aforementioned formulated compounds.

### Treatment of the metal surfaces for adhesion

The surfaces of brass-coated MS and galvanized iron (GI) were cleaned through rubbing with emery paper. For MS, the surface was treated with concentrated hydrochloric acid, which was followed by a phosphate solution. The surface of MS was then dried and kept in a dirt-free atmosphere. After proper treatment, the surfaces of MS and GI were covered with a primer coat of Chemlok 202, and a final coat of Chemlok 215 (Chemloks are epoxy-based adhesives, Lord Coop., North Carolina) was applied.

### Molding

The molding of rubber sheets was employed on a laboratory hydraulic press (Moore, London, UK) at 160°C and 15 MPa for 15 min. Under the same conditions, a strip type of the specimen was also molded for adhesion.

### Testing

#### Hardness

The hardness was tested on a shore A durometer (Wallace Instruments, Kingston, UK) according to ASTM Standard D 2240.

#### Tensile properties

Dumbbell-shaped specimens were punched out from the molded sheets. The thickness was measured with a bench thickness gauge. The mechanical properties were measured on an Instron 4301 universal tensile testing machine (UTM) (Instron Korea Co. Ltd., Seoul, Korea) according to ASTM Standard D 412-51 at 25°C and at a crosshead speed of 500 mm/min.

#### Adhesive strength

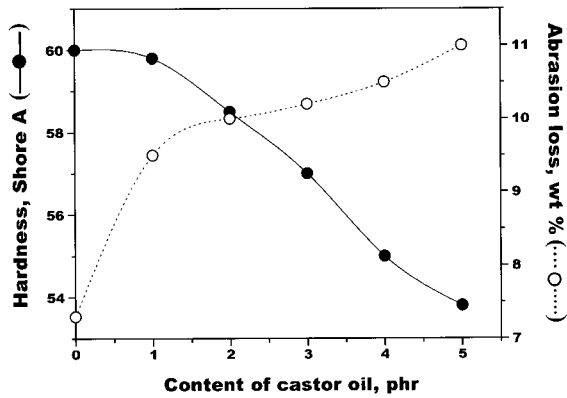
The specimen prepared in the form of a strip was stretched on a UTM for the adhesion strength according to ASTM Standard D 4393 at room temperature and at a humidity of 60%.

#### Tear strength

The tear strength was measured on a UTM according to ASTM Standard D 624.

## RESULTS AND DISCUSSION

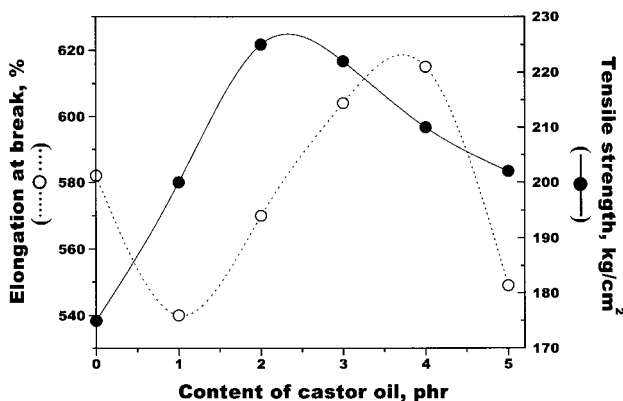
The variations in the hardness (shore A) and abrasion loss (wt %) are plotted against the content of castor oil (phr) in Figure 1. The hardness decreased but the abrasion loss increased with the content of castor oil. The abrasion loss depended on the softness of the rubber surface, the dispersity of carbon black, and the crosslink density of the rubber compounds. The hardness of the rubber compound decreased with the castor oil: this may be the plasticization effect of castor oil at the carbon black/rubber interface. In contrast, the crosslink density could increase because of the active participation of castor oil through its double bonds. In this case, the increase in the abrasion loss with castor



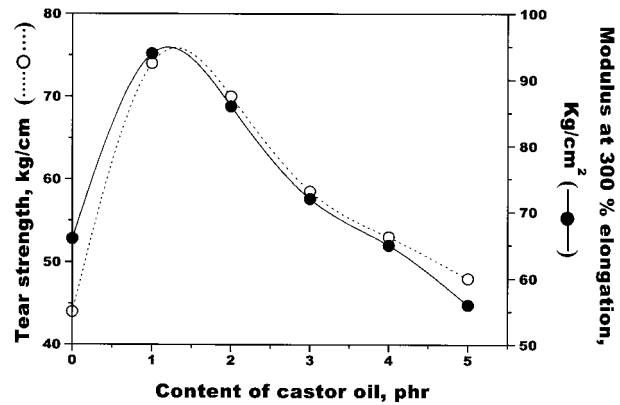
**Figure 1** Variations of the hardness (shore A) and abrasion loss (wt %) with the content of castor oil (phr) in the rubber compounds.

oil was predominantly controlled by the hardness of the compound. The abrupt increase in the abrasion loss up to 1 phr castor oil indicated the increase in the stiffness of the compound due to the active participation of castor oil during crosslinking. However, the gradual increase in the abrasion loss after 1 phr castor oil was suggested to be the effect of plasticization and coupling action.

The tensile strength ( $\text{kg}/\text{cm}^2$ ) and elongation at break (%) are plotted in Figure 2 as functions of the content of castor oil (phr). The elongation at break decreased up to 1 phr castor oil because of extensive participation in crosslinking and coupling action. This could induce improved stiffness, which was corroborated for the increase in the abrasion loss. Beyond 1 phr, the elongation at break increased up to 4 phr and then decreased. This might represent a predominance of plasticization over the coupling effect of castor oil in the range of 1–4 phr. The tensile strength increased with castor oil up to 2 phr and then gradually decreased. As a result, the castor oil was predominantly participating in crosslinking and coupling below 1 phr, in crosslinking and coupling along with plasticization in the range of 1–3 phr, and



**Figure 2** Variations of the tensile strength ( $\text{kg}/\text{cm}^2$ ) and elongation at break (%) with the content of castor oil (phr) in the rubber compounds.

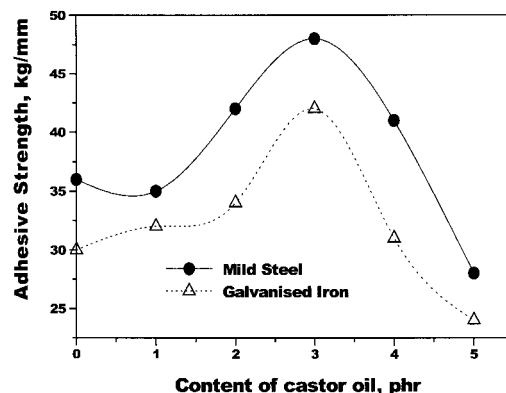


**Figure 3** Variations of the tear strength ( $\text{kg}/\text{cm}$ ) and modulus at 300% elongation ( $\text{kg}/\text{cm}^2$ ) with the content of castor oil (phr) in the rubber compounds.

then in extensive plasticization leading to a lowering of the tensile strength and elongation at break beyond 3 phr castor oil.

The variations in the modulus at 300% elongation ( $\text{kg}/\text{cm}^2$ ) and the tear strength ( $\text{kg}/\text{mm}$ ) are plotted as functions of the content of castor oil (phr) in Figure 3. Both the modulus and tear strength increased up to 1 phr castor oil. This may be explained as the coupling action of castor oil augmented by participation in curing up to 1 phr castor oil. Beyond this, there was a gradual decrease in the tear strength and modulus up to 3 phr, in which range castor oil participated in curing and acted as a plasticizer. Beyond 3 phr, castor oil acted only as a plasticizer, causing a steep decrease in both the tear strength and modulus.

The adhesive strength ( $\text{kg}/\text{cm}$ ) for rubber strips between MS and GI substrates is compared with the content of castor oil (phr) in Figure 4. For both substrates, no distinctive variance in the adhesive strength was observed for a small concentration of castor oil (up to 1 phr); the adhesive strength increased up to 3 phr and then abruptly decreased. The initial small variance up to 1 phr castor oil may be explained as a cou-



**Figure 4** Variations of the adhesive strength ( $\text{kg}/\text{cm}$ ) at the MS and GI interfaces with the content of castor oil (phr) in the rubber compounds.

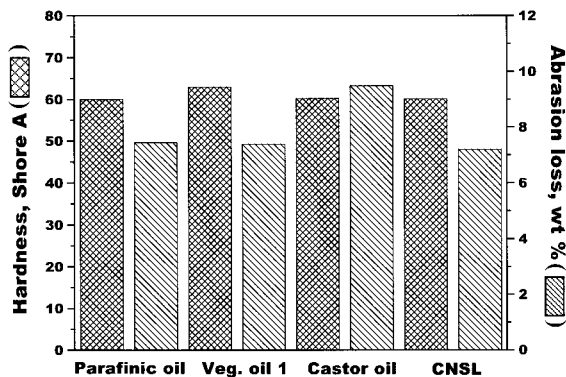


Figure 5 Bar diagram of the hardness (shore A) and abrasion loss (wt %) for the rubber compounds with 1 phr of various oils.

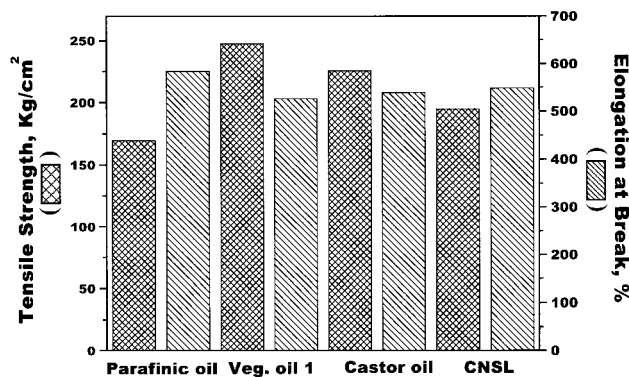


Figure 6 Bar diagram of the tensile strength (kg/cm<sup>2</sup>) and elongation at break (%) for the rubber compounds with 1 phr of various oils.

pling action and participation in curing. The cyano-based primer (Chemlok 202) might have supported the bond formation between the substrate and the rubber, and so improved adhesion strength was observed. The coupling action of castor oil might have reinforced adhesion, but participation in curing through the double bonds might have induced heterogeneity in the crosslink density and, therefore, no discernable improvement in adhesion up to 1 phr. Beyond 1 phr, the plasticizing effect, along with the coupling action and participation in curing, might have reduced the crosslink heterogeneity, and improved adhesion was observed up to 3 phr. Beyond 3 phr castor oil, it penetrated the cyano-based adhesive layer and formed its own layers on the active surfaces of the substrates. These flexible plasticizing layers on the substrate had ability to reduce the adhesive strength.

A comparative bar diagram of the hardness (shore A) and abrasion loss (wt %) for rubber compounds containing 1 phr paraffin oil, vegetable oil 1, castor oil, and CNSL is drawn in Figure 5. Vegetable oil 1 exhibited the highest hardness and lowest abrasion loss, whereas CNSL showed properties comparable to those of paraffin oil. Vegetable oil 1 was a highly unsaturated polyester, whereas castor oil was a comparatively less unsaturated one. CNSL consisted of long-chain substituted styrenic phenols and a limited portion of unsaturated ester linkages. The highest hardness and lowest abrasion loss of vegetable oil 1 in the rubber compounds may be attributed to the high unsaturation participation in crosslinking. The crosslink density was low for both castor oil- and CNSL-containing compounds because of the low amount of unsaturation. These oils took part in dual interactions: one part of the chain end, which was polar in nature, could interact with the carbon black surface, whereas the nonpolar paraffin chain end could interact with the rubber molecules. Therefore, all the oils used for this study could act as coupling agents between the carbon black and rubber matrix, leading to an enhancement in hardness and a lowering

of abrasion loss with respect to a paraffin oil-based compound.

A comparative bar diagram of the elongation at break (%) and tensile strength (kg/cm<sup>2</sup>) for the rubber compounds containing 1 phr paraffin oil, vegetable oil 1, castor oil, and CNSL is drawn in Figure 6. The tensile strength was the maximum and the elongation at break was the minimum for vegetable oil 1. This was due to the presence of large amounts of unsaturated polyester inducing high coupling action at the interface of carbon black and rubber. The castor oil-containing compounds showed higher tensile strength and lower elongation at break than compounds with paraffin oil and CNSL. This might be due to the presence of a high content of unsaturated polyester in castor oil. CNSL-based rubber compounds showed higher tensile strength and lower elongation at break than paraffin oil. This was due to the presence of polarity in the form of styrenated phenols and unsaturation in CNSL in comparison with paraffin oil.

A comparative bar diagram of the modulus at 300% elongation (kg/cm<sup>2</sup>) and tear strength (kg/cm) for the rubber compounds containing 1 phr paraffin oil, vegetable oil 1, castor oil, and CNSL is shown in Figure 7. Both the modulus at 300% elongation and the tear

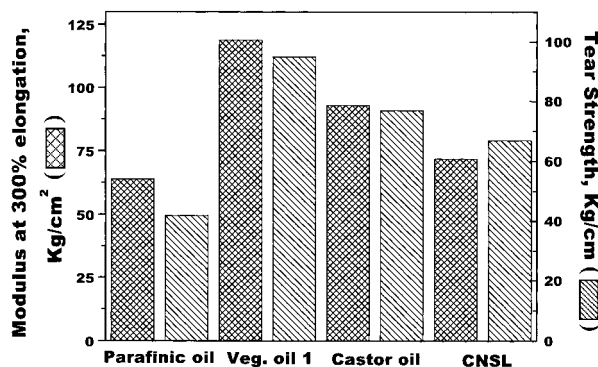
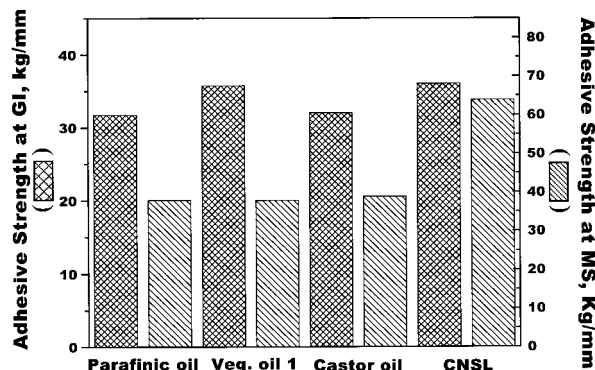


Figure 7 Bar diagram of the tear strength (kg/cm) and modulus at 300% elongation (kg/cm<sup>2</sup>) for the rubber compounds with 1 phr of various oils.



**Figure 8** Bar diagram for the adhesive strength (kg/cm) at the MS and GI interfaces for the rubber compounds with 1 phr of various oils.

strength were the maximum in the vegetable oil 1-based compounds, whereas the poorest values were observed in paraffin oil 1-containing compounds. Vegetable oil 1 contained the highest degree of unsaturation among all the oils used in this study. The unsaturated fatty acid actively participated in curing and coupling at carbon black/rubber interfaces. This might have induced high values of the tear strength and modulus with vegetable oil 1. Because paraffin oil was nonpolar and had a low degree of unsaturation, low values for the tear strength and modulus might have resulted. Vegetable oils seemed to act as coupling agents in the rubber compounds because of their unique capacity for interactions with both rubber and carbon black at the interface, thereby improving the physical and mechanical properties of the rubber compounds.<sup>9</sup> However, the degree and extent of coupling action might have been dependent on the amount of unsaturation and the contents of esters present in the vegetable oils. For castor oil and CNSL, compounds containing castor oil showed improved tear strength and modulus at 300% elongation. This was due to the fact that castor oil had more unsaturated fatty acids, thereby facilitating its active participation as a coupling agent in comparison with CNSL. However, the chain structure of CNSL was dominated by the presence of long-chain substituted styrenic phenols with very limited unsaturated ester linkages. Therefore, the extent of coupling action by CNSL was far less than that of castor oil and vegetable oil 1. The tear strength and modulus at 300% elongation for the CNSL-based compounds were still low but comparable to paraffin oil.

A comparative bar diagram of the adhesive strength (kg/cm) at GI and MS interfaces with 1 phr paraffin oil, vegetable oil 1, castor oil, and CNSL is drawn in Figure 8. The adhesive strength at the interface between the MS and rubber compounds with vegetable oil 1 was higher than that with paraffin and castor oil, but no comparative variation was observed for CNSL. CNSL-containing rubber compounds exhibited the highest adhesion at the GI interface, whereas the rubber compounds with the rest of the oils showed similar strengths. This might have

been due to the presence of polar styrenic phenols and saturated polyester in CNSL, which supported the formation of adhesion layers around the metal surfaces, thereby improving adhesion.

## CONCLUSIONS

The effects of additives with various oils on the physical, mechanical, and adhesion properties of carbon black/rubber compounds were studied. Various doses (0–5 phr) of castor oil and some other oils such as paraffin oil, vegetable oil 1, and CNSL at a fixed dose (1 phr) were used. As a result, with an increase in the content of castor oil, the modulus, tear strength, and tensile strength showed an increase, whereas the hardness and adhesive strength exhibited little variation up to 1 phr. Beyond 1 phr castor oil, the modulus, tear strength, and hardness decreased, whereas the adhesive and tensile strength exhibited an increase up to 2.5–3 phr, followed by a decrease. Therefore, castor oil seemed to behave as a coupling agent up to 1 phr and as a coupling agent and a plasticizer in the range of 1–3 phr; beyond that, plasticization was the main role of castor oil. Various oils such as paraffin oil, vegetable oil 1, castor oil, and CNSL at a fixed dose (1 phr) were compared in terms of hardness, abrasion loss, tensile strength, elongation at break, modulus at 300% elongation, tear strength, and adhesive strength. All the vegetable oils exhibited enhanced properties with respect to those of paraffin oil, which is a normal additive used as a plasticizer for regular carbon black/rubber compounds. In addition, both castor oil and vegetable oil 1 showed improved physical and mechanical properties in comparison with CNSL and paraffin oil. This might have been due to the high unsaturation present in castor oil and vegetable oil 1. CNSL exhibited the best adhesive strength against MS and GI substrates.

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