

Surface Modification of Carbon Black by Vegetable Oil—Its Effect on the Rheometric, Hardness, Abrasion, Rebound Resilience, Tensile, Tear, and Adhesion Properties

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ABSTRACT: Plasticizer (vegetable or parafinic oil) pretreated carbon black is mixed with rubber for its compounding. It is observed that the extent of cure obtained from rheometric torque decreases linearly with an increase in vegetable oil content. The presence of a coupling action and a monolayer (microplasticization) of vegetable oil at carbon black–rubber interfaces causes a decrease in $\tan \delta$ (from rheometric studies), elongation at break, and tensile strength, and increase in abrasion loss, hardness, and 300% modulus up to 3 phr, beyond which all the properties show just the opposite trend with an increase in the content of vegetable oil. Both tear strength and rebound resilience increases with increasing doses of vegetable oil; the rate of increase is slow up to 3 phr due to the coupling action and microplasticization, and it is faster beyond 3 phr due to the presence of both coupling and plasticising action. Upon the addition of a plasticizer, adhesive strength increases up to 1 phr in the case of vegetable oil, and remains almost constant in the case of parafinic oil; beyond 1 phr, adhesive strength decreases due to the presence of a multiple layer of plasticizer between rubber–metal interfaces. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 256–260, 2002; DOI 10.1002/app.10320

Key words: mechanical properties; adhesion; interfaces; modification; reinforcement

INTRODUCTION

Carbon black is used in rubber compounding as a reinforcing filler. It is generally accepted that surface characteristics of reinforcing fillers are the most important factors influencing the reinforcing effect in rubber. It has already been proven that the surface energies of fillers play a dominant role in the processability as well as in the

end use of rubber products.^{1–3} The surface activity of carbon black depends on the dispersive and specific (polar) component of surface energy.⁴ An earlier report by Donnet et al.⁵ showed that surface modification of carbon black by a silane coupling agent reduces its reinforcement properties, thus deteriorating ultimate properties, whereas the author of this article has recently reported⁶ an improvement of filler–rubber interaction by the surface modification of carbon black by vegetable oil, leading to the enhancement of ultimate properties. The objective of the present work is to study the effect of total replacement of petroleum oils by vegetable oil for rubber compounding on the ultimate properties.

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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.; Stearic acid: melting point 62°C, acid value 192–204; Vegetable oil (proprietary chemical): aniline point 22°C, more unsaturated compared to the reported one.⁶ Brass (70% Cu and 30% Zn) coated mild steel was used as substrate for testing adhesive strength between metal–rubber interfaces.

Sample Preparation

The compounds are formulated as NR (RMA-1X): 70, PBR: 30, Carbon black, HAF (reinforcing agent): 50, Plasticizer (Vegetable or parafinic oil): varying amount, ZnO: 4.5, Stearic acid: 1.5, 6 PPD: 1, H. S. Beads (Antioxidant): 1.5, Paraffin wax: 2, Cyclohexyl Benzsulphenamide, CBS (accelerator): 1, Sulphur: 1.5. Eight compounds are formulated by using 0, 0.2, 1, 2, 3, 4, 5, and 5.8 phr of vegetable oil. Parafinic oil is used only for comparison of adhesion properties with compounds containing vegetable oil. The formulated compounds were mixed on a two-roll mill according to a standard procedure. In a standard procedure, a mixing sequence was followed such as first mastication of rubber and its band formation on the front roll of mixing mill; addition of the carbon black and plasticizer (if any), accelerator activator (ZnO and stearic acid), antidegradants (6 PPD and H.S. Beads), plasticising aids (paraffin wax), and finally, addition of an accelerator and vulcanizing agents (CBS and Sulphur). After addition of each compounding ingredients some time was allowed to mix it properly with the rubber. The total mixing time for all compounds was maintained at 17 min such that the dispersion levels of the ingredients were similar. The mixing temperature was kept at 70°C. The plasticizers (vegetable oil or parafinic oil) were not added separately. These were first mixed with carbon black for its pretreatment and then they were added to rubber on the mixing mill. The procedure for pretreatment of carbon black with vegetable or parafinic

oil was described elsewhere.⁶ The above-formulated compounds were used for sample preparation for testing of rheometric, hardness, abrasion, tear, and tensile strength properties.

Preparation of Metal Surface for Adhesion

Brass-coated mild steel (MS) surfaces were cleaned by rubbing with an emery paper. It was treated with concentrated hydrochloric acid followed by phosphate solution. The surface of MS was then dried and kept in a dirt-free atmosphere. After proper surface treatment, it was coated with a primer (Chemlok 202, a cyno based adhesive). Finally, an adhesive (Chemlok 215) was applied on the surface.

Curing Test

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

Molding

Molding of rubber sheets and adhesion test samples were done on a hydraulic press at 150°C temperature and 15 MPa pressure for 15 min. The set molding time (15 min) was higher than that for 90% cure, t_{90} (from rheometric torque) such that the rubber samples were fully cured.

Testing

Hardness

Hardness was tested on a Shore-A durometer according to ASTM-D-2240.

Tensile Properties

Dumbbell-shaped test samples were punched out from the molded sheets. The thickness was measured with a bench thickness gauge. These were measured on a Universal Tensile Testing Machine (UTM) according to ASTM-D-412-51 at 25°C and at a crosshead speed of 500 mm/min.

Adhesive Strength

Adhesive strength was measured by strip test on a UTM according to ASTM-D-4393.

Tear Strength

Tear strength was measured on a UTM according to ASTM-D-624.

RESULTS AND DISCUSSION

The maximum extent of cure, which is equivalent to the difference of maximum and minimum torque ($D_{\max} - D_{\min}$) and $\tan \delta$ at maximum torque ($\text{kg}\cdot\text{m}$) obtained from the torque-time curve of the MDR-2000 are plotted against the content of vegetable oil in phr in the rubber compounds in Figure 1. The maximum extent of cure decreases linearly with increasing the content of vegetable oil in rubber compounds due to plasticization effect of vegetable oil. The $\tan \delta$ at maximum torque also decreases with increasing the content of vegetable oil up to 3 phr, beyond which it decreases. The decreasing trend of $\tan \delta$ up to 3 phr of vegetable oil is nonlinear and concave upward. Vegetable oil is an unsaturated long chain fatty ester. The polar ester as well as an unsaturation group can interact properly with the carbon black surfaces, whereas its saturated block can be blended with rubbers, leading to its coupling action between vegetable oil and carbon black.⁶ The initial decrease in $\tan \delta$ up to 3 phr may be explained as the formation of physico-chemical crosslinks between carbon black and rubber via the coupling action of vegetable oil. These crosslinks are facile in nature, as they break down in attaining a certain amount of energy at higher temperatures. Thus, these bonds contribute nothing towards the torque in MDR-2000, and causes linear decrease in the maximum extent of cure with increase in the content of

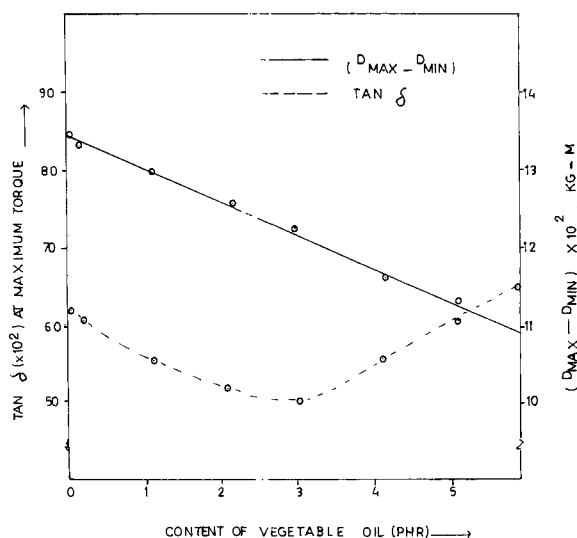


Figure 1 Variation of $\tan \delta$ at maximum torque and $(D_{\max} - D_{\min})$ in $\text{kg}\cdot\text{m}$ with content of vegetable oil.

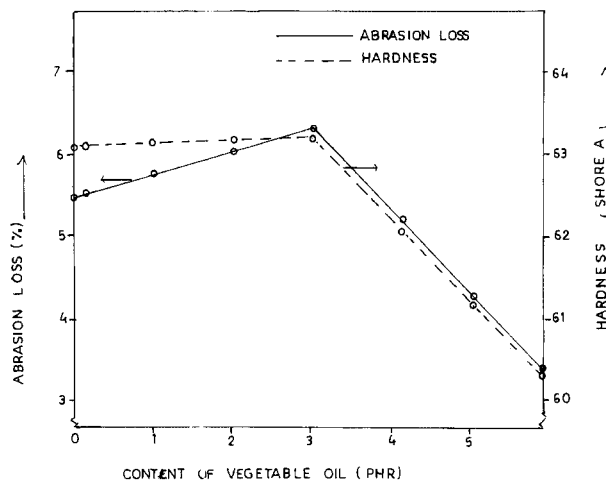


Figure 2 Variation of abrasion loss in % and hardness in Shore A with content of vegetable oil.

vegetable oil. At lower doses (below 3 phr), the monolayers of vegetable oil are present at rubber-carbon black interfaces, leading to its microplasticization. The decreasing trend of $\tan \delta$ up to 3 phr of vegetable oil is due to its coupling action as well as microplasticization between the carbon black and rubber interfaces. Beyond 3 phr of vegetable oil, plasticization effect predominates, leading to the increase of $\tan \delta$ with increase in the content of vegetable oil.

The plots for hardness (Shore A) and abrasion loss (%) against content of vegetable oil (phr) are shown in Figure 2. Abrasion loss increases, whereas hardness shows almost constant value (very small increase) with an increase in vegetable oil up to 3 phr, beyond which both of them decrease. The low content of vegetable oil may microplasticise as well as form loose bonds, leading to its coupling action at carbon black-rubber interfaces. This may explain the increase in abrasion loss and almost unchanging behavior in hardness with an increase in vegetable oil content (below 3 phr). At higher content of vegetable oil (beyond 3 phr), the presence of a multi-layer of vegetable oil at the rubber-carbon black interfaces leads to its only plasticization effect. This explains the decrease in abrasion loss and hardness with the increase in vegetable oil content beyond 3 phr.

The modulus at 300% elongation, tensile strength (kg/cm^2), and elongation at break (%) are plotted against the content of vegetable oil (phr) in Figure 3. Both tensile strength and elongation at break decreases, whereas 300% modulus in-

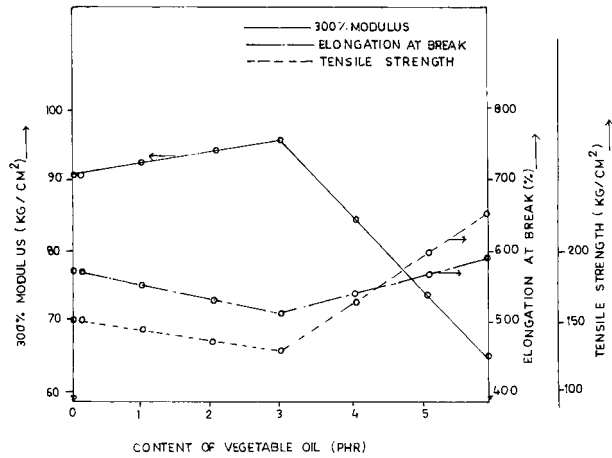


Figure 3 Variation of 300% modulus in kg/cm², elongation at break in %, and tensile strength in kg/cm² with content of vegetable oil.

creases with the increase in content of vegetable oil up to 3 phr, beyond which all these properties show just the opposite trend. The possible coupling action of vegetable oil (up to 3 phr) induces the facile physico-chemical bond formation between rubber and carbon black interfaces. There is a possibility that a part of the vegetable oil may get cocured along with rubber at the curing temperature. Thus, the coupling action as well as cocuring of the vegetable oil contributes for the enhancement of total crosslink density. This leads to the enhancement of 300% modulus and a decrease in elongation at break, which causes lowering of the ultimate tensile strength with an increase in vegetable oil content (up to 3 phr). Beyond 3 phr doses of vegetable oil, the presence of its multi-layer between the carbon black and rubber interfaces leads to macroplasticization, which predominates over microplasticization and coupling. Thus, higher doses of vegetable oil increase elongation at break and tensile strength and reduce the 300% modulus.

The tear strength (kg/cm) and rebound resilience (%) are plotted against the content of vegetable oil in Figure 4. It is evident from the plots that both of them increases with an increase in vegetable oil content. The rate of increase in both properties is slower up to 3 phr, beyond which the rate is higher. At lower doses of vegetable oil, the coupling action is predominant, whereas all of the macroplasticization as well as the microplasticization and coupling action are active at higher doses of vegetable oil. All of these facts can explain the slower and faster increasing trend of

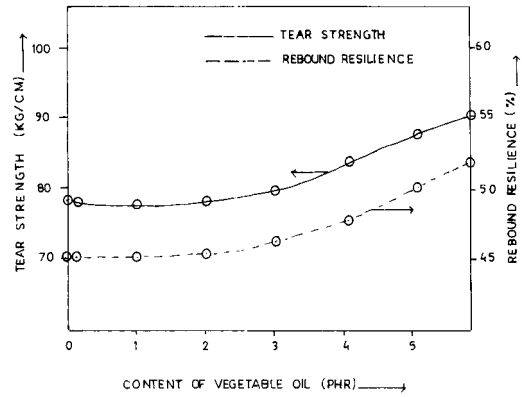


Figure 4 Variation of tear strength in kg/cm and rebound resilience in % with content of vegetable oil.

these properties at lower (below 3 phr) and higher (beyond 3 phr) doses of vegetable oil.

Variation in adhesive strength (kg/mm) at mild steel-rubber interface against the content of plasticizer (phr) using both vegetable oil and hydrocarbon oil (parafinic) is shown in Figure 5. It is evident from the plot that there is sharp rise in adhesive strength upon the increase in vegetable oil content up to 1 phr, beyond which it decreases. This may be explained due to the presence of high unsaturation, which not only helps in curing but also enhances the coupling action between the rubber-carbon black and rubber-metal inter-

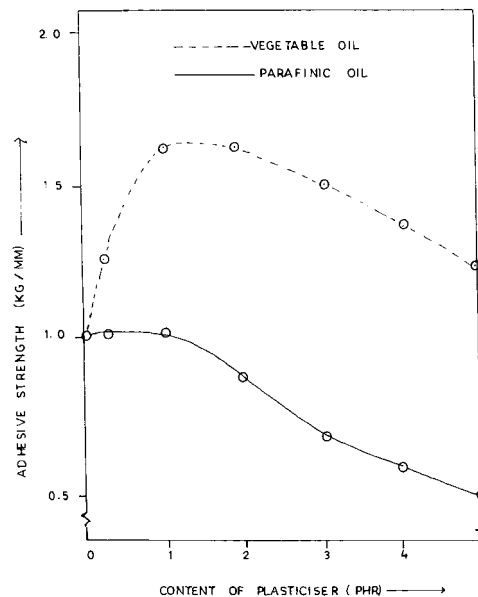


Figure 5 Variation of adhesive strength in kg/mm at mild steel-rubber interfaces with content of vegetable oil and parafinic oil.

faces. In the case of parafinic oil, adhesive strength remains almost constant up to 1 phr, beyond which it decreases rapidly with an increase in parafinic oil content. At higher doses of oil, the presence of an oil multi-layer greatly reduces the adhesive strength. The decreasing trend observed beyond 1 phr may be explained by this macroplasticizing action of oil (which is evident from the lowering of hardness).

CONCLUSION

It can be concluded that pretreated carbon black with vegetable oil when mixed with rubber greatly improves the physical as well as mechanical properties. The extent of cure obtained from rheometric torque decreases linearly with an increase in vegetable oil content. The decrease in $\tan \delta$ (from rheometric studies), elongation at break, and tensile strength, and increase in abrasion loss, hardness, and 300% modulus up to 3 phr is due to the presence of coupling action and monolayer (microplasticization) of vegetable oil at carbon black–rubber interfaces. Whereas beyond 3 phr of vegetable oil, all these properties show just the opposite trend, with an increase in content of vegetable oil due to the predominantly plasticising action of vegetable oil. Both tear strength and rebound resilience increases with increasing the content of vegetable oil. The rate of increase is slow up to 3 phr due to the coupling

action and microplasticization, and is faster beyond 3 phr due to the presence of both coupling and plasticizing action. Upon the addition of a plasticizer, adhesive strength increases up to 1 phr in the case of vegetable oil, and remains almost constant in the case of parafinic oil; beyond 1 phr, adhesive strength decreases due to the presence of a multiple layer of plasticizer between the rubber–metal interfaces. Although adhesive strength decreases with an increase in vegetable oil, still the highly vegetable oil-loaded compound shows higher adhesion compared to the unplasticized one.

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