Use of Rice Bran Oil and Epoxidized Rice Bran Oil in Carbon Black–Filled Natural Rubber–Polychloroprene Blends

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ABSTRACT: In the present study we report the results obtained on the use of rice bran oil (RBO), a naturally occurring nontoxic oil, and its epoxidized variety (epoxidized RBO, or ERBO) in the compounding and vulcanization of different natural rubber–chloroprene rubber (NR–CR) blends. The processability, cure characteristics, and physical properties of the blends prepared with these oils were compared with those of control mixes prepared with aromatic oil. The optimum cure time and scorch time values of the different blends prepared with these oils were found to be lower than those of the respective control blends prepared with aromatic oil. Evaluation of physical properties of the different experimental blends showed that replacement of aromatic oil with these oils did not adversely affect their physical properties. Because RBO contains a good amount of free fatty acids it was tried as a coactivator in addition to its role as a processing aid. The level of these oils required for the blend preparation was optimized in a Brabender plasticorder. Physical properties such as tensile strength, elongation at break, tear strength, swelling index, and abrasion loss, for example, were evaluated for both experimental and control mixes. Comparison of cure characteristics and physical properties of the blends prepared with aromatic oil and with these oils showed that these oils could be used in place of aromatic oil in the above blends. It is also to be noted that aromatic oil is of petroleum origin and is reported to be carcinogenic. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 4084–4092, 2003

Key words: rubber; curing of polymers; rice bran oil; epoxidized rice bran oil; vulcanization

INTRODUCTION

The fact that vegetable oils and vulcanized vegetable oils impart better flow properties, processing action, and ozone resistance when included in a rubber-compounding recipe is well established.[1,2] Application of vegetable oils like rice bran oil (RBO) in the compounding of rubbers can be well appreciated by considering the fact that most of the conventional processing aids like aromatic oil are petroleum based and are reported to be carcinogenic.[3] Preparation of epoxidized rice bran oil (ERBO) and its use as plasticizer have also been reported.[4] The use of vegetable oils as processing aids and crosslinking agents in rubber compounds has also been studied.[5,6] It is also reported that RBO has excellent compatibility with fluorocarbon rubbers and the oil gives good extrusion moldability to the compound.[7] This oil was also tried as a multipurpose compounding ingredient in nonpolar and polar rubbers like styrene butadiene (SBR), nitrile (NBR), and polychloroprene (CR) in this laboratory.[8,9]

Rice bran oil is available at very low cost in India. The oil is extracted from rice bran, which in turn is a byproduct of the rice-milling process. The free fatty acid (FFA) content of the fresh bran is 1.4 to 1.9%.[10] On storage the FFA content of the bran may reach up to 30% within 10 days.[11] This may be attributed to the presence of an active enzyme lipase present in the bran. This enzyme catalyzes the hydrolysis of lipids into fatty acids. A salient feature of RBO is that it contains significant amount of fatty acids, unsaponifiable matter, phosphatides, and wax.[12] The unsaponifiable matter that comes from the glyceride portion of the oil consists of phytosterol, tocopherol, squalene, oryzanol, and naphthene group of hydrocarbons.[13] Phosphatides mainly contain lecithin, present in the order of 0.6%. Oryzanol and tocopherol act as natural antioxidants.[14] We have made an attempt to see whether the free fatty acids present in the oil can function as coactivators when used together with zinc oxide in rubber compounding.

Blending of different elastomers is an important technological process for improving the properties of rubber vulcanizates.[15] Blends of elastomers may be broadly classified into miscible and immiscible. Theo-

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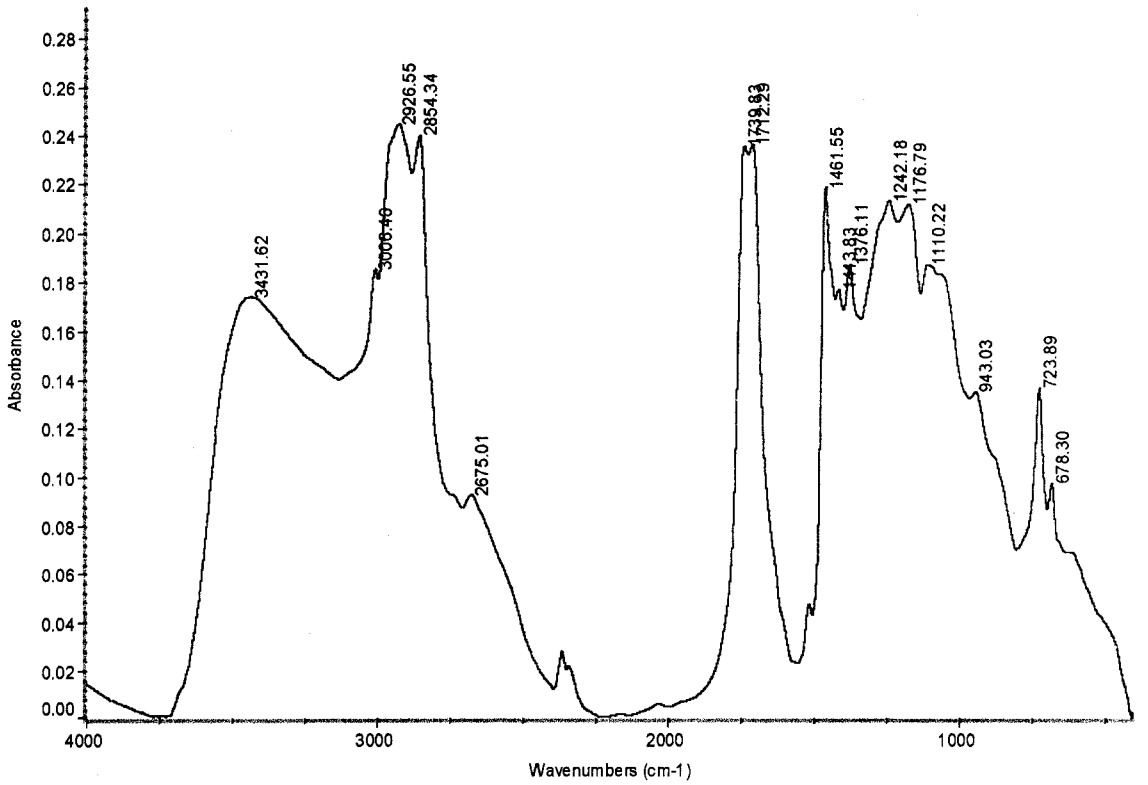

Figure 1 IR spectrum of epoxidized rice bran oil.

retically, blends of chemically dissimilar (immiscible) elastomers can attain a wider variation in properties than blends of miscible and chemically similar elastomers.[16] Incompatible blends of dissimilar polymers like natural rubber (NR) and polychloroprene (CR) are found to have dynamic properties that are characteristic of the component of higher glass-transition temperature (T_g) at ambient temperature, but the lower T_g component appears to dominate at higher temperature.[17] In cases where NR is used for vibration isolation (i.e., under conditions where resonance may occur), a degree of damping is required. Blending of NR with a synthetic rubber of suitable T_g and cure characteristics is one of the techniques for increasing the damping characteristics of NR vulcanizates.

In this study the use of RBO/ERBO as a processing aid for improving the properties of carbon black–filled NR–CR blends was investigated. The blends prepared in different blend ratios were evaluated for their cure characteristics and physical properties. These properties were compared with those of control vulcanizates prepared using aromatic oil as the process aid.

TABLE I
Formulation of Carbon Black–Filled NR–CR Blends

Ingredient (phr)	Blend ratio				
	70/30	60/40	50/50	40/60	30/70
NR	70	60	50	40	30
CR	30	40	50	60	70
ZnO	5	5	5	5	5
MgO	1.8	2.4	3.0	3.6	4.2
Stearic acid	1.55	1.40	1.25	1.10	0.95
Antioxidant	1.0	1.0	1.0	1.0	1.0
Sulfur	1.75	1.50	1.25	1.0	0.75
MOZ	1.12	0.96	0.80	0.64	0.48
TMTD	0.35	0.30	0.25	0.20	0.15
NA-22	0.15	0.20	0.25	0.30	0.35
Aromatic oil/RBO/ERBO	4	4	4	4	4
Carbon black (HAF 330)	40	40	40	40	40

EXPERIMENTAL

Materials

The natural rubber used in this study was ISNR-5 (Mooney viscosity 82) supplied by the Rubber Research Institute of India. Chloroprene rubber was of W-type (Mooney viscosity 47), supplied by DuPont. The rice bran oil, raw grade, was supplied by Tamil Nadu Agro Industries (Thanjavoor, India). Zinc oxide, magnesium oxide, stearic acid, styrenated phenol, tetramethyl thiuram disulfide (TMTD), 2-morpholinothiobenzothiazole (MOZ), ethylene thiourea (NA22), sulfur, carbon black (HAF 330), and aromatic oil were all of rubber grade.

The epoxidized rice bran oil prepared in our laboratory (having an epoxy content of 3.4%) was used for the compounding of the blend. The epoxidization of the oil was achieved with hydrogen peroxide in glacial acetic acid in the presence of sulfuric acid as catalyst. For preparing ERBO, 25 g of crude RBO (iodine value = 92; 0.091 mol of double bond), 6 g of benzene, 2.73 g of acetic acid (0.5 mol/mol of double bond in oil), and 1 : 1 sulfuric acid (4% of total weight of hydrogen peroxide and acetic acid) were mixed under stirring in a three-neck flask provided with a thermometer and a condenser. Hydrogen peroxide (30%; 15.47 g, 1.5 mol/mol of double bond in oil) was added slowly over a period of 2 h and the temperature was maintained at 60–65°C for 14 h. The epoxidized oil was isolated and vacuum dried.

The epoxy content was determined volumetrically.[18] For the determination of epoxy content a known weight of the oil (0.5 g) was added to a measured volume (25 mL) of HCl–dioxan. The reaction mixture was allowed to stand for 15 min, after which 25 mL of neutral ethyl alcohol prepared by using 1 mL cresol red indicator was then added to the reaction mixture. The excess of the acid present in the mixture was titrated with standard 0.1*N* methanolic sodium hydroxide. The color of the indicator changed from pink to yellow just before the end point and from yellow to violet at the end point. A blank titration was also conducted with 25 mL HCl–dioxan reagent only. The free acids in the sample were determined by dissolving a known weight of the sample in 50 mL neutral ethanol and then titrating against standard 0.1*N* methanolic sodium hydroxide. The volume of the standard alkali for the weight of ERBO used in epoxy determination was then calculated. The percentage of oxirane oxygen is thus given by the following equation:

$$\%\text{Oxirane O}_2 = \frac{[V_1 - (V_2 - V_3) \times N_1 \times 16 \times 100]}{W \times 1000}$$

where V_1 is the volume of NaOH used for blank, V_2 is the volume of NaOH used for sample, V_3 is the volume of NaOH used for titration of the free acid in the

TABLE II
Cure Characteristics of the Different NR–CR Blends

Parameter	70/30			60/40			50/50				40/60			30/70		
	Mix with aromatic oil	Mix with RBO	Mix with ERBO	Mix with aromatic oil	Mix with RBO	Mix with ERBO	Mix with aromatic oil	WSA[a]	Mix with RBO	WSA[a]	Mix with ERBO	Mix with aromatic oil	Mix with RBO	Mix with ERBO	Mix with aromatic oil	Mix with RBO
Maximum torque (Nm)	0.54	0.56	0.45	0.50	0.41	0.37	0.29	0.35	0.35	0.37	0.24	0.32	0.32	0.30	0.39	0.36	0.33
Minimum torque (Nm)	0.05	0.04	0.04	0.05	0.04	0.03	0.04	0.04	0.05	0.05	0.03	0.04	0.04	0.04	0.05	0.04	0.04
Optimum cure time t_{90} (min)	2.90	2.50	2.70	3.40	3.20	3.10	5.60	6.40	5.20	5.70	5.30	9.00	8.30	8.80	17.0	15.8	16.0
Scorch time t_{10} (min)	1.40	1.30	1.30	1.60	1.50	1.40	1.60	2.20	1.50	2.00	1.40	1.50	1.40	1.40	1.60	1.50	1.40
Cure rate index	67	83	71	56	59	59	25	23	27	27	26	13	15	14	6.5	7	7

[a] WSA, without stearic acid.

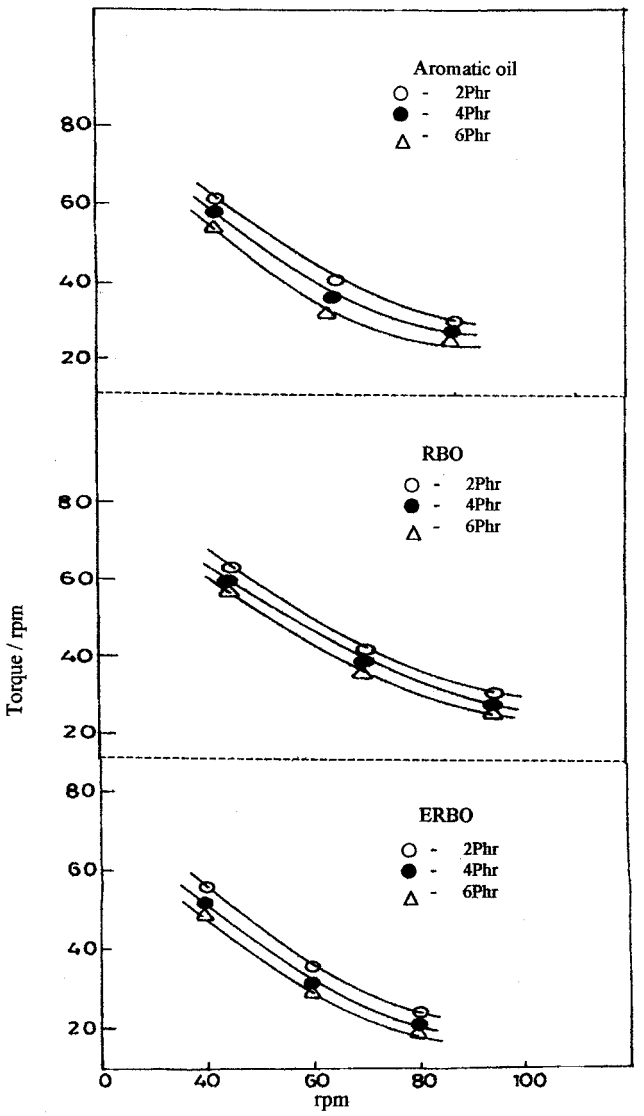

Figure 2 Flow curves of CB-filled 70/30 NR–CR blends with different levels of aromatic oil/RBO/ERBO.

sample, N_1 is the normality of the NaOH, and W is the weight of the sample.

The ERBO was also characterized by taking the IR spectrum of the oil using a Nicolet Avatar 360 ESP FTIR spectrometer (Nicolet Analytical Instruments, Madison, WI) (Fig. 1). A strong band characteristic of the epoxy group ($\approx$ 1250 cm^{-1}) was observed at 1242 cm^{-1}, indicating the presence of symmetric stretching of the epoxy group.

The processing characteristics of the NR–CR blends with aromatic oil/RBO/ERBO were studied in a Brabender (Germany) plasticorder (PL3S) at 27°C. The initial speed of the roller mixing head in the plasticorder was set at 40 rpm. The total weight of the blend including other compounding ingredients was restricted to 40 g. The blend of NR and CR, weighed according to their ratio in the blend, was first passed six times in a two-roll mill at a nip gap of 0.8 mm to obtain a thin sheet. This was then cut into small strips before feeding into the plasticorder. The total mixing time was kept at 16 min with the following breakup. The rubber was first masticated for 4 min followed by adding activator and accelerator within 3 min. Carbon black mixed with oil was then added within 8 min and finally sulfur within 1 min. The formulation of the mix for each blend ratio for the processability study (i.e., 70/30, 50/50, and 30/70 NR–CR) is as given in Table I, except for the variation in the quantity of the process oils used. Different levels, 2, 4, and 6 phr each, of these oils were used in the study. The final torque value is noted in all the cases and the optimum was determined accordingly. The experiment was repeated for 60 and 80 rpm also for all the blend ratios mentioned above. Flow curves were drawn by plotting viscosity against rotor speed.

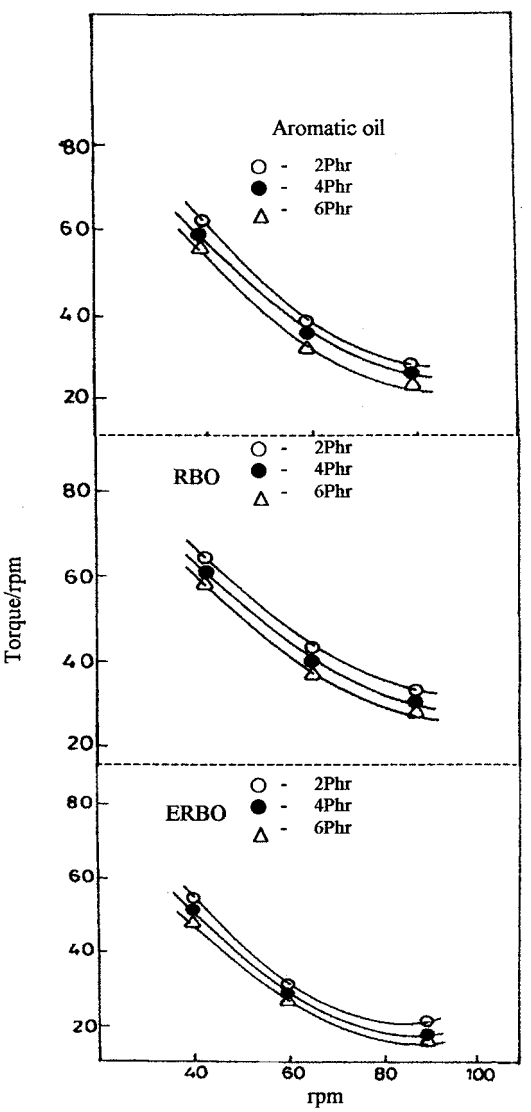

Figure 3 Flow curves of CB-filled 50/50 NR–CR blends with different levels of aromatic oil/RBO/ERBO.

After the processability study on the plasticorder the actual experimental mixes for vulcanization were prepared on a two-roll mill (6 × 12 in.) according to ASTM D 3182-89 using the formulation given in Table I. For all the blend preparations an optimum of 4 phr of aromatic oil/RBO/ERBO was found to be optimum for the proper mixing of the ingredients. For the preparation of the mix in the mill, NR was first masticated for 2 min; CR was then added and again masticated for 2 min to obtain a smooth band. MgO was then added followed by stearic acid and ZnO after a hiatus of 1 min. This was then followed by addition of an antioxidant. Carbon black mixed with the processing aid was then added within 5 min. Finally, sulfur and accelerators were added within 1 min. In view of the fact that RBO contains a significant quantity of higher fatty acids, the experiment was also carried out without the use of stearic acid as coactivator in a 50/50 blend. Physical properties and cure characteristics were evaluated and compared with those of control blends based on aromatic oil.

The swelling index, an indirect way of measuring total crosslink density, which in turn is correlated to the physical properties of the various vulcanizates, was determined by swelling 0.2 g of the sample in benzene for 24 h at room temperature. It was calculated using the following equation:

$$\text{Swelling index} = \frac{\text{Swollen weight} - \text{deswollen weight}}{\text{Original weight of sample}}$$

The cure characteristics of the various mixes were evaluated at 150°C using a Goettfert elastograph (Model 67.85). The different cure properties of the mixes evaluated are given in Table II. Cure rate index, optimum cure time, scorch time, minimum torque, maximum torque, and the like are reported therein. The optimum cure time t_{90} is the time to reach 90% of the maximum torque and scorch time t_{10} is the time to reach 10% of the maximum torque. The cure rate index was calculated as $100/(t_{90} - t_{10})$. Vulcanization was carried out in an electrically heated press (18 × 18 in.) maintained at 150°C and at a pressure of 11.764 MPa. Tensile strength and elongation break were determined according to ASTM D 412-87 using a Zwick universal testing machine at a pulling rate of 500 mm/min at 27°C. Dumbbell-shape specimens for the test were punched out of the molded sheets along the mill grain direction. Tear resistance was determined according to ASTM D 624-86 using unnicked 90° test pieces. Ageing studies on the vulcanizates was carried out (ASTM D 573-88) at 100 ± 1°C for 24 h in an air oven. Hardness was measured according to ASTM D 2240-86 and compression set according to ASTM D 395-89 (method B).

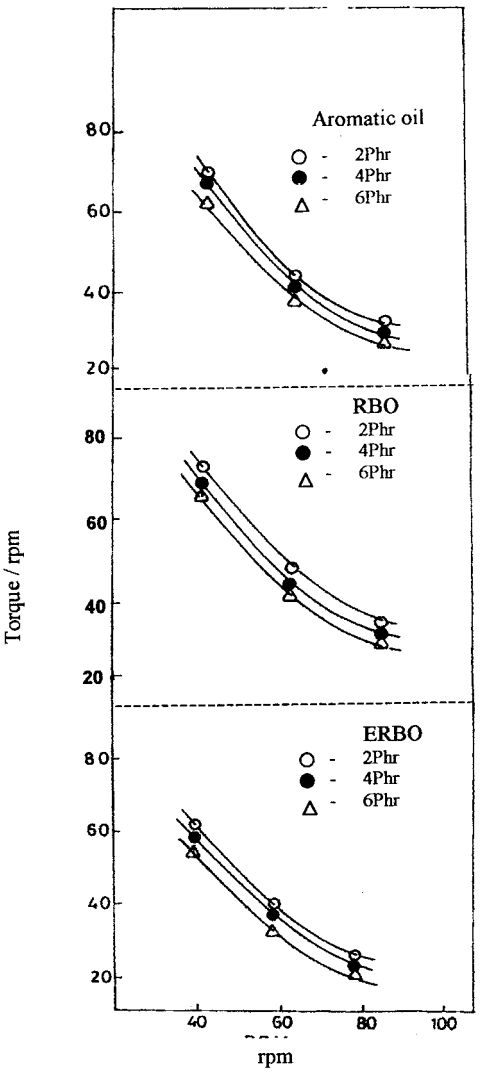

Figure 4 Flow curves of CB-filled 30/70 NR–CR blends with different levels of aromatic oil/RBO/ERBO.

RESULTS AND DISCUSSION

The flow curves of the 70/30, 50/50, and 30/70 NR–CR blends based on the maximum torque generated and rpm used in the processability study are given in Figures 2, 3, and 4, respectively. In the figures the (torque/rpm) represents viscosity calculated from the shear rate. The flow behavior of the compounds containing aromatic oil is more or less similar to that of the compounds containing RBO, showing a similar pseudoplastic nature for both. However, when 4 phr ERBO was used the torque developed was slightly less compared to the mix containing an equal quantity of aromatic oil. Nearly similar behavior was noted with all blend ratios under investigation. From the results it is evident that the viscosity at 40 rpm is reasonable when 2 phr of these oils were used as processing aids irrespective of blend ratio. During the actual compounding of the blend in a two-roll mill, however, it

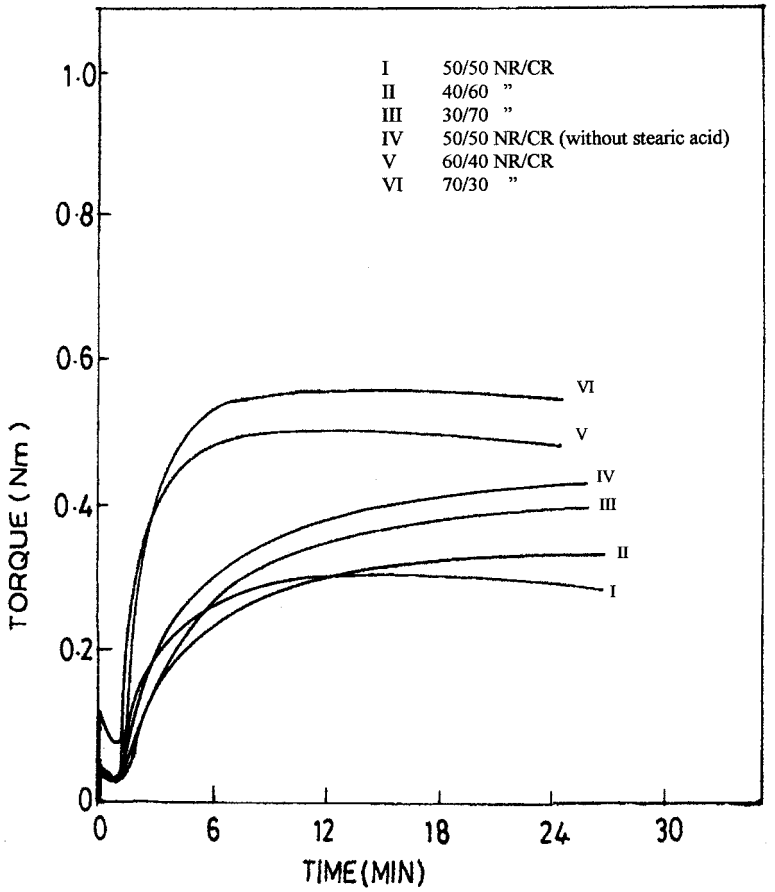

Figure 5 Cure curves of NR–CR blends prepared with aromatic oil.

was found that a minimum of 4 phr was necessary for proper mixing of the ingredients and for the control of temperature.

Figures 5, 6, and 7 show the cure curves and Table II reports the cure characteristics of the mixes prepared using the different process aids. From the figures it is noted that the maximum torque developed is about the same when aromatic oil/RBO is used. The minimum torque value, which is a measure of compound viscosity, is also nearly the same for the blends prepared with these two oils. However, when ERBO was used the torque values obtained were slightly less compared to those of the control mixes prepared with aromatic oil. This observation points to a better plasticizing effect of ERBO over that of either aromatic oil or RBO. From the cure curves of the blends it may also be observed that none of the blends shows any reversion characteristics, irrespective of the processing aids used. The cure rate values for the blends prepared with RBO are higher than those of blends prepared with aromatic oil. This points to a cure-accelerating effect of RBO, in addition to its role as a processing aid. The cure-accelerating effect of RBO, in addition to its role as a processing aid. The cure-accelerating property of RBO can be attributed to the presence of different free fatty acids in the oil, which has a positive influence in the curing reactions. The scorch time values are slightly lower for the blends prepared with RBO/ERBO compared with those of the control mixes prepared with aromatic oil. From Table II it may also be seen that for a 50/50 RBO-based blend the cure characteristics like optimum cure time, scorch time, and maximum torque are less affected compared to those of the control blend when stearic acid was replaced in the blend formulation. This indicates that the higher fatty acids present in the oil can act as a coactivator in the vulcanization step.

Table III shows the variation in physical properties of the vulcanizates obtained from the above blends using different processing aids. It is noted that tensile strength values increase when the weight of NR in the blend increases. Blends prepared with different processing aids under investigation show more or less the same tensile strength values. After-ageing properties were also found to be better for the vulcanizate prepared with ERBO. This may be attributed to the ageing resistance offered by ERBO because of the presence of epoxy groups in the oil and corresponding reduction in unsaturation. The elongation at break values are higher for the blends prepared with ERBO

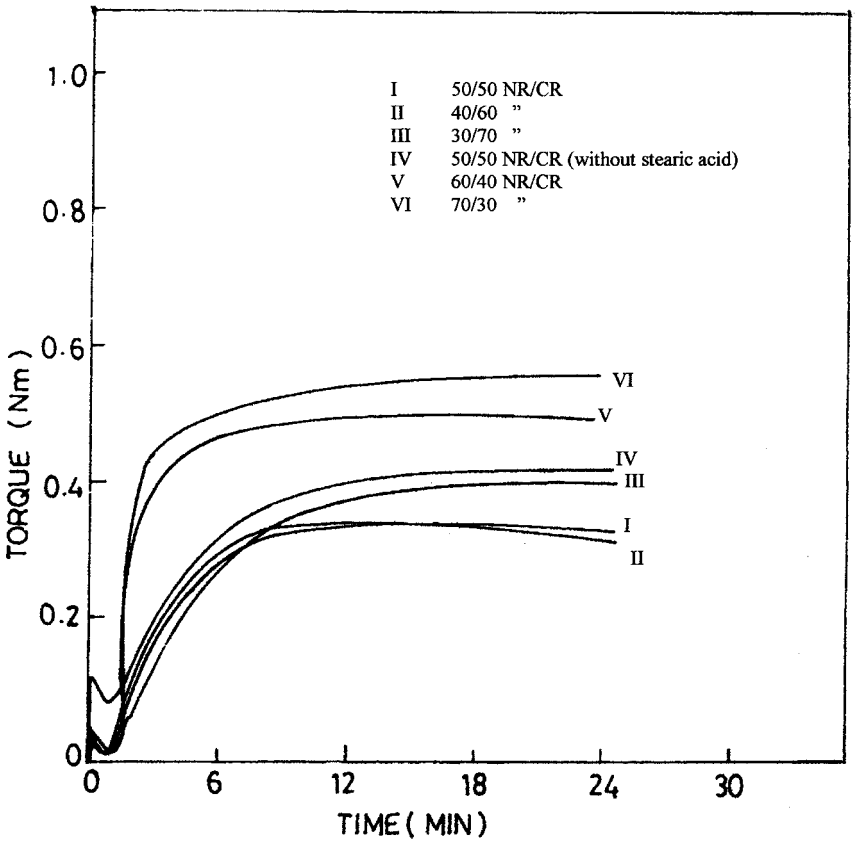

Figure 6 Cure curves of NR–CR blends prepared with RBO.

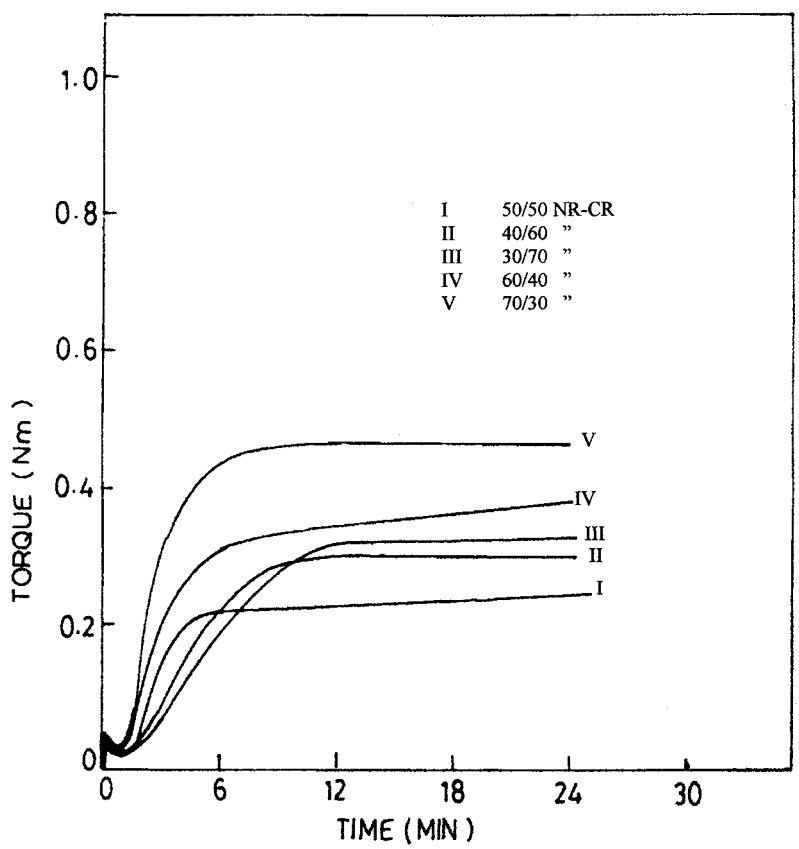

Figure 7 Cure curves of NR–CR blends prepared with ERBO.

TABLE III
Physical Properties of the Different NR–CR Blends

	70/30			60/40			50/50					40/60			30/70		
Property[a]	ARO[b]	RBO[b]	ERBO[b]	ARO	RBO	ERBO	ARO	WSA[c]	RBO	WSA	ERBO	ARO	RBO	ERBO	ARO	RBO	ERBO
Tensile strength (MPa) BA	22.7	22.25	23.14	22.87	22.69	22.76	19.69	20.8	20.84	21.5	20.86	15.61	16.6	20.4	14.5	16.12	16.52
Tensile strength (MPa) AA	13.59	13.36	15	14.62	14.53	19.6	10.18	13.5	9.8	14.2	19.22	10.5	10.6	14.8	11.2	11.7	13.3
Retention (%) of tensile strength	60	60	65	64	64	86	52	65	47	66	92	67	64	73	77	73	83
Elongation at break (%) BA	347	350	387	427	450	475	430	374	380	370	430	285	317	364	264	280	312
Elongation at break (%) AA	260	214	290	330	343	358	251	224	233	229	340	201	205	305	201	203	265
Retention (%) of elongation at break	75	61	75	77	76	75	59	60	61	62	79	71	65	84	78	73	85
200% modulus (MPa)	9.6	11.2	7.8	7.4	7.8	6.8	7.4	10	9.2	10.1	6.2	9.8	9.4	8.4	11.4	10.6	9.6
Tear strength (N/mm)	60	56	77	71	66	71	55	60	57	62	67	60	64	62	53	52	53
Compression set (%)	22	23	25	23	23	28	31	33	28	29	35	28	24	30	19	18	31
Abrasion loss (cm^3/h)	4.1	3.78	3.57	4.14	3.61	3.46	4.39	4.44	3.94	3.96	3.92	4.59	4.41	4.24	4.86	4.76	4.38
Swelling index	1.63	1.68	1.44	1.8	1.84	1.54	1.88	1.82	1.86	1.8	1.52	1.92	1.9	1.7	1.94	1.88	1.79

[a] BA, before ageing; AA, after ageing.
[b] ARO, aromatic oil; RBO, rice bran oil; ERBO, epoxidized rice bran oil.
[c] WSA, without stearic acid.

than those for blends prepared with aromatic oil. Modulus values are more or less the same for the blends prepared with RBO and aromatic oil, whereas slightly lower modulus values were observed for the mixes containing ERBO. The percentage retention of elongation at break was also found to be better for the blends prepared with ERBO over the respective control mixes. From Table III it is also evident that removal of stearic acid from a 50/50 RBO-based blend formulation did not adversely affect the curing characteristics or physical properties. Because of the higher content of fatty acids, RBO can act effectively as a coactivator.

Compression set, tear strength, and abrasion resistance of the vulcanizates were also evaluated according to relevant ASTM procedures. Results from these tests indicate that the values of tear strength and compression set are more or less the same for the mixes containing RBO/aromatic oil. Tear values are higher for the blends richer in the NR phase irrespective of the nature of the processing aids used. Tear values of the vulcanizates prepared with ERBO, however, were found to be higher than values of those prepared with aromatic oil. The abrasion loss values of the vulcanizate prepared with RBO/ERBO were found to be lower (i.e., higher abrasion resistance) than values of the control formulations. This may be attributed to the better rubber–filler interaction in the presence of RBO/ERBO. Vulcanizates prepared with ERBO showed a lower swelling index value and hence higher crosslink density (swelling index being inversely proportional to the crosslink density). In general this is seen reflected in the physical properties of the vulcanizates.

CONCLUSIONS

Studies on the use of rice bran oil and epoxidized rice bran oil in the compounding of NR–CR blends at different blend ratios using carbon black as filler show that these oils can advantageously be used as processing aids in place of aromatic oil in such blends. The cure characteristics of the blends prepared with RBO/ERBO showed that optimum cure time values are lower than those of blends prepared with aromatic oil, indicating a cure-accelerating effect of these oils. The scorch time values are scarcely affected when aromatic oil is replaced with RBO/ERBO. The torque and compound viscosity values are less when ERBO is used in place of aromatic oil. A study of the mechanical properties of the blends based on RBO/ERBO also suggests that these oils do not have an adverse effect on the above properties. The cure characteristics and mechanical properties of the blends based on RBO also suggest that this oil could be used even in the absence of stearic acid for the blend preparation. It may also be noted that nonedible RBO is appreciably cheaper than aromatic oil. Rice bran oil is a natural product, nontoxic, and environmentally friendly. Some of the mineral oils conventionally used for rubber compounding applications are also reported to be toxic.

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