Use of rice-bran oil in the compounding of styrene butadiene rubber

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The compounding of rubber involves mixing of activator, co-activator, accelerator, antioxidant, filler, processing aid, vulcanizing agent, etc., to produce the rubber. The replacement of three of the above ingredients by rice-bran oil in the compounding of styrene butadiene rubber has been investigated. The higher fatty acids and phenols present in rice-bran oil act as co-activator and antioxidant, respectively, in the vulcanization process. Addition of this oil together with fillers, also meets the requirement of processing aid. The results obtained were compared with those obtained with reference mixes containing stearic acid, styrenated phenol and aromatic/napthenic oil in carbon-black and silica-filled systems. Evaluation of the cure characteristics of the mixes indicates that substitution of the above ingredients with rice-bran oil did not affect the cure properties. Vulcanizates containing the rice-bran oil also showed physical properties comparable to the reference mixes. Processability studies using a plasticorder also showed similar trends. Considering the fact that rice-bran oil is cheaper than other conventional oils used as processing aids in rubber compounding, this non-toxic natural oil can be advantageously used in rubber product manufacture.

1. Introduction

Rice-bran oil is available in plenty in India in the areas where rice is being processed. The rice bran constitutes about 5%–7% of rice and it is a rich source of various nutrients. Fresh rice bran contains a considerable amount of oil with a free fatty acid (FFA) content as low as 1.4%–1.9% [1]. But the presence of an active lipase enzyme in bran catalyses the hydrolysis of lipids into fatty acids during the storage of bran. As a result, the FFA may reach as high as 30% within 10 days, making the oil unfit for edible purposes [2]. Hence out of about 0.6 million tonnes of rice-bran oil produced in India per annum at least 0.4 million tonnes has FFA of more than 30%.

The general characteristics of the rice-bran oil are given in Table I. Oleic and saturated fatty acids constitute more than 50% of the total acids with a negligible amount of linolenic acid in this oil. The unsaponifiable fraction of this oil, which is rather high in comparison with other edible oils, contains ferulic acid esters of triterpenoid alcohols, tocopherols, squalene and the naphthalene group of hydrocarbons [3]. A mixture of two or more ferulic acid esters of triterpene alcohol is called oryzanol and it is reported to have antioxidant properties [4]. The percentage of unsaponifiable matter in rice-bran oil varies between 3.9% and 6.6% [5, 6]. This oil also contains a considerable amount of wax, ranging from 2%–6% [7]. The presence of chlorophyll often gives the oil a greenish shade. The peculiar odour of rice-bran oil is due to ferulates and squalene and the brown colour is attributed to methyl ferulates. The amount of tocopherol ranges from 0.03%–0.1% [8]. Tocopherols are potent antioxidants and the antioxidant property depends upon the presence of a free phenolic hydroxyl group. Chemically, they are chroman derivatives [9].

Sulphur vulcanization of rubber involves heating the rubber with accelerator, activator, co-activator, antioxidant, filler, processing oil, etc., to obtain products of required properties. Accelerators enable the vulcanization time to be reduced considerably. Synthetic rubbers require a higher proportion of accelerator with a corresponding reduction in the amount of sulphur. Zinc oxide, which is the usual activator in rubber vulcanization, enhances the action of accelerators. Stearic acid is added with zinc oxide and is the usual co-activator. Antioxidants are added to reduce ageing processes in the vulcanizates. Amines or phenols are generally used as antioxidants. Fillers are incorporated to improve the physical properties and/or to reduce the cost of the final product. The function of the processing oil is to provide better processability during the addition of fillers. Aromatic or naphthenic oil is the usual processing oil used in the rubber industry.

Because rice-bran oil contains a good quantity of higher fatty acids and a reasonable amount of natural antioxidants, it was thought worthwhile to try this oil

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TABLE I Characteristics of the crude rice-bran oil [5, 7, 19]

Colour (Y + 5R.1 cm culb)	35–43
Volatile matter (% wt/wt)	0.5–1.0
Flash point (°C)	210
Free fatty acid (% oleic acid)	3–70
Iodine value (wij's) [10]	85–105
Unsaponifiable matter (% wt/wt)	3.9–6.6
Refractive index (40 °C)	1.46–1.47
Phosphatides (% wt/wt)	0.4–3.0
Wax (% wt/wt)	2–6
Hydroxyl value	5–17
Chlorophyll content (p.p.m.)	2

as a substitute for processing oil, co-activator and antioxidant for the compounding of styrene butadiene rubber (SBR). The study becomes all the more important because petroleum oils used as processing aids are becoming prohibitively costly, whereas rice-bran oil (non-edible) is available at much cheaper rates in India. It is also worthwhile to note that many antioxidants used in the rubber industry are reported to have toxic effects, while natural rice-bran oil is devoid of any toxicity.

We used a sulphur-accelerated system for the vulcanization of SBR using rice-bran oil in place of aromatic oil and without stearic acid and antioxidant. The results obtained from these mixes were compared with standard formulations. Because the green strength and tensile properties are poor in SBR gum vulcanizates, experiments were carried out with reinforcing fillers, namely carbon black (HAF) and precipitated silica (Vulkasil). The variation in processing characteristics brought about by the incorporation of rice-bran oil was studied with the help of a Brabender plasticorder. The optimum quantity of rice-bran oil required in the different formulations had also been derived. The mixes obtained from these different formulations were evaluated for their cure characteristics and the vulcanizate samples prepared were evaluated for tensile and other physical properties. In order to evaluate the variation in physical properties of the different vulcanizates, the total chemical cross-link density was also estimated.

2. Experimental procedure

The SBR used in the experiment was Synaprene 1502. Other compounding ingredients, namely zinc oxide, stearic acid, mercaptobenzthiazyldisulphide (MBTS), tetramethylthiuram disulphide (TMTD), sulphur, carbon black (HAF 330) precipitated silica (Vulkasil), aromatic oil, naphthenic oil, silane coupling agent (Si-69) and diethylene glycol (DEG) were of rubber grade. Rice-bran oil (FFA 44%) was obtained from Tamilnadu Agro Industries Corporation, Thanjavur, India.

Free fatty acid in rice-bran oil was determined as follows [10]. Rice-bran oil (2 g) was weighed into a conical flask. Approximately 100 ml alcohol was taken in a beaker and boiled in a water bath for 5 min to remove dissolved gases and then neutralized by adding dilute sodium hydroxide using a few drops of phenolphthalein as indicator. 50 ml of this hot neutralized alcohol was added to the flask and the mixture boiled in a water bath for 5 min. While still hot, the solution was titrated with 0.1 N sodium hydroxide solution until a pale pink colour was obtained. Free fatty acid is expressed as oleic acid because this is the predominant acid in rice-bran oil. Based on the above titre value, this quantity was calculated.

A Brabender plasticorder PL 3S was used for studying the processing characteristics of SBR with rice-bran oil using aromatic/naphthenic oil as a control. SBR was first mixed for 4 min at 30 r.p.m. in the plasticorder with roller mixing heads at room temperature. Activator and accelerator were then added within 2–3 min. Carbon black mixed with rice-bran oil was then added, followed by sulphur. The total mixing time was 16 min. The formulation of the mixes used is given in Table II. The same procedure was repeated by replacing rice-bran oil with aromatic oil. Rice-bran oil and aromatic oil were added at 5, 10 and 15 p.h.r. levels each. A higher torque was obtained in the case of 5 p.h.r. rice-bran oil/aromatic oil. Torque values were lower and somewhat acceptable values were obtained in the 10 and 15 p.h.r. levels of oil. Hence an oil level of 10 p.h.r. has been taken to be optimum for these carbon-black filled systems. The Brabender curves are given in Figs 1 and 2. In the case

TABLE II Formulation of mixes containing carbon black and precipitated silica

	Mix							
	IA	IB	IC	ID	IIA	IIB	IIC	IID
Styrene butadiene rubber	100	100	100	100	100	100	100	100
Zinc oxide	4	4	4	4	4	4	4	4
Stearic acid	1.5	1.5	–	–	1.5	1.5	–	–
Mercaptobenzothiazyl disulphide (MBTS)	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Tetramethyl thiuram disulphide (TMTD)	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Styrenated phenol	–	1.0	–	1.0	–	1.0	–	1.0
Carbon black (HAF. 330)	50	50	50	50	–	–	–	–
Precipitated silica (Vulkasil)	–	–	–	–	50	50	50	50
Aromatic oil	5	5	–	–	–	–	–	–
Naphthenic oil	–	–	–	–	7	7	–	–
Rice-bran oil	–	–	5	5	–	–	7	7
Diethylene glycol	–	–	–	–	2	2	2	2
Silane coupling agent (Si. 69)	–	–	–	–	2	2	2	2
Sulphur	2	2	2	2	2	2	2	2

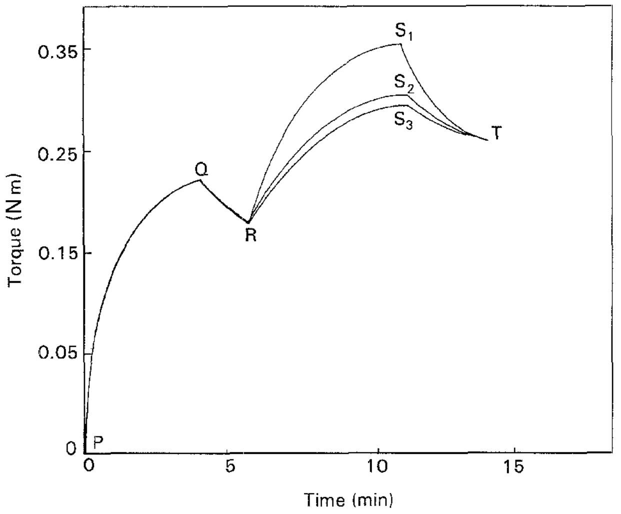

Figure 1 Variation of Brabender torque with varying amounts of rice-bran oil in the carbon-black filled system. PQ, styrene butadiene rubber; QR, activator and accelerator; RSI, carbon black and rice-bran oil (5 p.h.r.); RS2, carbon black and rice-bran oil (10 p.h.r.) RS3, carbon black and rice-bran oil (15 p.h.r.); S_1T, S_2T, S_3T, sulphur.

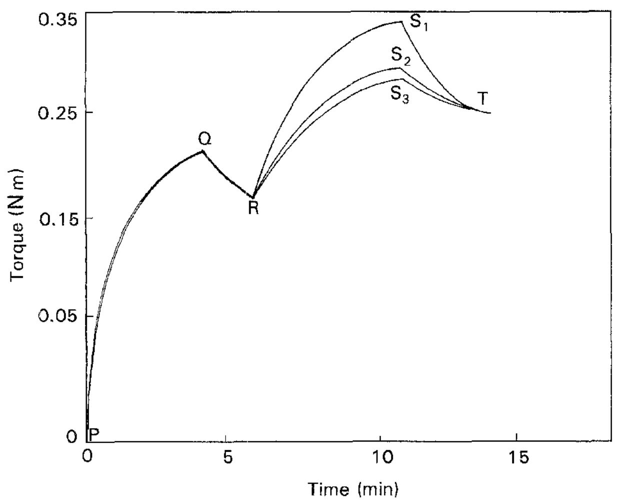

Figure 2 Variation of Brabender torque with varying amounts of aromatic oil in the carbon-black filled system. For key, see Fig. 1, but for aromatic oil, not rice-bran oil.

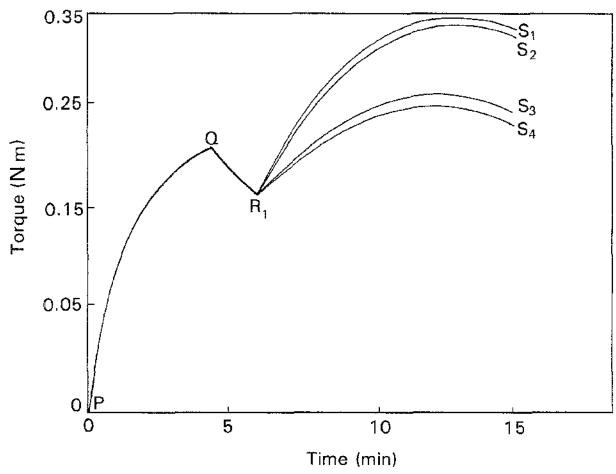

Figure 3 Variation of Brabender torque with varying amounts of rice-bran oil in the silica-filled system. PQ, styrene butadiene rubber; QR_1, activator and accelerator; R_1S_1, silica, rice-bran oil (5 p.h.r.) and sulphur; R_1S_2, silica, rice-bran oil (10 p.h.r.) and sulphur; R_1S_3, silica, rice-bran oil (15 p.h.r.) and sulphur; R_1S_4, silica, rice-bran oil (20 p.h.r.) and sulphur.

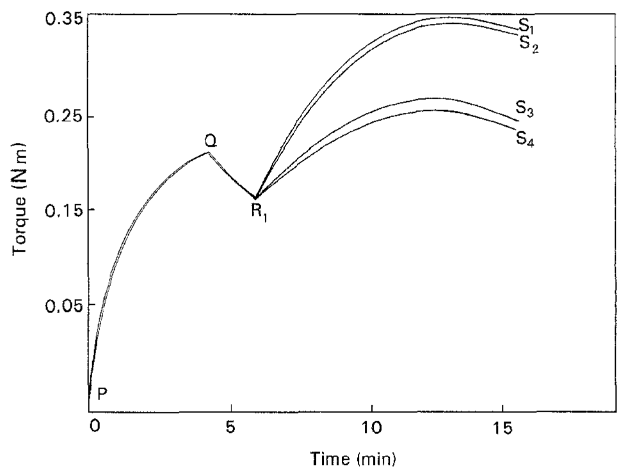

Figure 4 Variation of Brabender torque with varying amounts of naphthenic oil in the silica-filled system. For key, see Fig. 3. but for naphthenic oil, not rice-bran oil.

of silica, the same procedure in sequence and time was followed. Both rice-bran oil and naphthenic oil were added at 5, 10, 15 and 20 p.h.r. levels. DEG was mixed with silica while feeding into the plasticorder. A higher torque was obtained in the plasticorder when 5 and 10 p.h.r. rice-bran oil/naphthenic oil were used, whereas acceptable torque values were obtained in the case of 15 and 20 p.h.r. levels of oil. Hence 15 p.h.r. can be taken to be the optimum level of oil in silica-filled compounds. The torque curves obtained are given in Figs 3 and 4.

The formulation of the mixes was designed in the present study with the following objectives: (1) to study the effect of rice-bran oil as a processing aid, and (2) to evaluate the fatty acids and phenols present in the oil as co-activator and antioxidant, respectively. The conventional system of rubber vulcanization was followed. Compounding was done in a laboratory-size two-roll mixing mill at a friction ratio of 1:1.25 as per ASTM D 3185-88. Owing to the higher shearing force in the mill compared to the plasticorder, the lower dosage of oil was sufficient for mill mixing. Just 5 p.h.r. rice-bran oil/aromatic oil in carbon-black filled compounds and 7 p.h.r. rice-bran oil/naphthenic oil in silica-filled compounds were found to be sufficient. The composition of different mixes is given in Table II. The fillers (carbon black and precipitated silica) were each incorporated at the 50 p.h.r. level. Reference mixes contained stearic acid as coactivator and styrenated phenol as antioxidant. Mix I contained carbon black and mix II contained precipitated silica. Mixes IA and IB contained aromatic oil while IIA and IIB contained naphthenic oil. Mixes IC, ID, IIC and IID contained rice-bran oil. IA and IIA contained no antioxidant but other compounding ingredients were added as usual. IB and IIB each contained 1 p.h.r. of styrenated phenol as antioxidant. Mixes IC and IIC contained no stearic acid and antioxidant, and ID and IID contained antioxidant but no stearic acid.

The cure characteristics of the various mixes at 160 °C were evaluated using a Goettfert elastograph

(Model 67.85) as per ASTM D 1646 (1981). The cure properties are given in Table III. The cure rate index was calculated from the elastographic curves of the respective mixes as $100/t_{90}-t_{10}$, where t_{90} and t_{10} are times corresponding to the optimum cure and 10% vulcanization, respectively. Induction time (t_1) is the time taken for one unit (0.1 N m) rise above the minimum torque (about 5% vulcanization). Optimum cure time (t_{90}) is the time taken for attaining 90% of the maximum torque. Elastographic scorch is calculated as the time for 10% vulcanization. The vulcanization was carried out in an electrically heated press of 18 in × 18 in (~ 45.7 cm × 45.7 cm) platens maintained at 160 °C and at a pressure of 120 kg cm^{-2}. Tensile properties were determined using ASTM designation D 412-87 with dumb-bell specimens in a Zwick universal testing machine at a pulling rate of 500 mm min^{-1} at room temperature (30 °C). Tear resistance was determined by ASTM method D 624-86 using unnicked 90° test pieces. Hardness was measured according to ASTM D 2240-86 and compression set according to ASTM D 395-89 (method B). A Dunlop tripsometer (BS-903 Pt-22, 1950) was used for rebound resilience at a temperature of 35 °C. Ageing studies were carried out (ASTM D 573) at 100 ± 1 °C for 72 h in an air oven.

The concentration of chemical cross-links (cross-link density) of the vulcanizates was determined from the equilibrium swelling data as follows. Samples of approximately 0.3 g were cut from the central portion of the vulcanizates and allowed to swell in solvent (toluene). After 24 h, the swelling was stopped and the outer portion of the swollen samples was dried using a filter paper and then weighed. These swollen samples were then placed inside an air oven at 60 °C for 24 h to remove toluene. The unswollen weight was then determined.

The volume fraction of rubber in the swollen network was then calculated by the method reported by Ellis and Welding [11] from the following equation

$$V_r = \frac{(D - FT)\rho_r^{-1}}{(D - FT)\rho_r^{-1} + A_0\rho_s^{-1}} \qquad (1)$$

where T is the weight of the test specimen, D the unswollen weight of the test specimen, F the weight fraction of insoluble component, A the weight of the absorbed solvent corrected for the swelling increment, ρ_r the density of the test specimen, and ρ_s the density of solvent. The values of ρ_r and ρ_s taken were ρ_r (SBR) = 0.94 g cm^{-3} and ρ_s(toluene) = 0.886 g cm^{-3}.

For filled vulcanizates, the value of V_r obtained as above were converted into V_{r^0} (the value of V_r is the volume fraction of rubber without the filler) by means of the equation derived by Porter [12]

$$\frac{V_{r^0}}{V_r} = 0.56\,e^{-Z} + 0.44 \qquad (2)$$

where Z is the weight of the filler divided by the total weight of all ingredients. V_{r^0} was then substituted in the Flory–Rehner [13, 14] equation in place of V_r to obtain the cross-link density of the vulcanizates containing filler.

3. Results and discussion

The quantity of rice-bran oil/aromatic oil/naphthenic oil required for the different mixes was optimized by studying the processability in the Brabender plasticorder. However, in practice, the compounds were prepared in a two-roll mill and it was found that a lower dosage of oils was sufficient for mixing in the two-roll mill owing to the higher shearing force of the mill compared to the plasticorder. Just 5 p.h.r. each of rice-bran oil/aromatic oil in carbon-black filled compounds and 7 p.h.r. each of rice-bran oil/naphthenic oil in silica-filled compounds were found to be sufficient for processing in the mill. Based on the processing characteristics both in the Brabender plasticorder and in the mixing mill, it is seen that rice-bran oil can be used for processing the above mixes, similar to the conventional oils such as aromatic or naphthenic oils. Estimation of cure characteristics and physical properties also indicates that rice-bran oil does not have any adverse effect.

The cure curves of SBR–carbon black and SBR–silica systems are given in Figs 5 and 6, respectively. Cure characteristics are given in Table III. The maximum torque developed is greater in the mixes containing rice-bran oil compared to those containing aromatic oil/naphthenic oil. There is no appreciable variation in the induction time, scorch time and optimum cure time of the mixes when rice-bran oil is used in place of other processing oils, both in carbon-black and silica-filled compounds. On substitution of fatty acid and antioxidant with rice-bran oil (Mix IC & IIC) there is also little variation in the cure characteristics of the mixes under review. Thus it can be inferred that

TABLE III Cure characteristics of mixes containing carbon black and precipitated silica (160 °C)

	Mix							
	IA	IB	IC	ID	IIA	IIB	IIC	IID
Maximum torque (Nm)	0.73	0.75	0.78	0.79	0.90	0.93	0.96	0.98
Minimum torque (Nm)	0.08	0.08	0.08	0.08	0.09	0.09	0.09	0.09
Optimum cure time, t_{90} (min)	7.5	7.7	7.7	7.7	7.4	7.4	7.3	7.3
Elastographic scorch time, t_{10} (min)	2.6	2.6	2.6	2.6	1.8	1.8	1.8	1.8
Cure rate index	20.4	19.6	19.6	19.6	17.8	17.8	18.1	18.1
Induction time (min)	1.5	1.5	1.5	1.5	1.0	1.0	1.0	1.0

rice-bran oil can be advantageously used as a processing aid in place of the other conventional processing oils without affecting the cure characteristics of the system. The higher torque value observed with rice-bran oil when used with antioxidant will indicate better mechanical properties of the vulcanizates. It is also observed that the higher free fatty acids and phenols present in rice-bran oil can act as co-activator and antioxidant, respectively. This is further evinced by the evaluation of physical properties reported below.

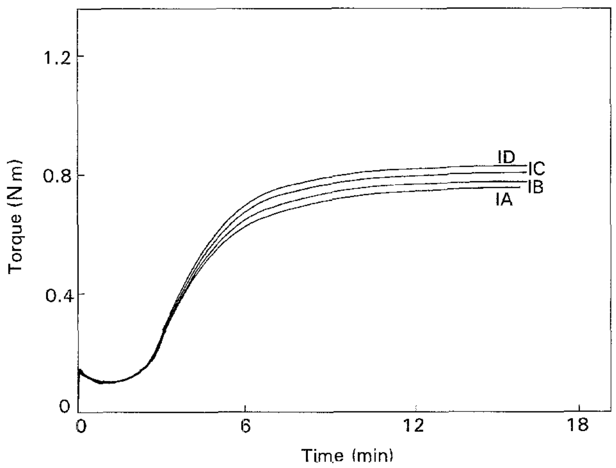

Figure 5 Cure curves for the mixes containing carbon black in rice-bran oil/aromatic oil systems.

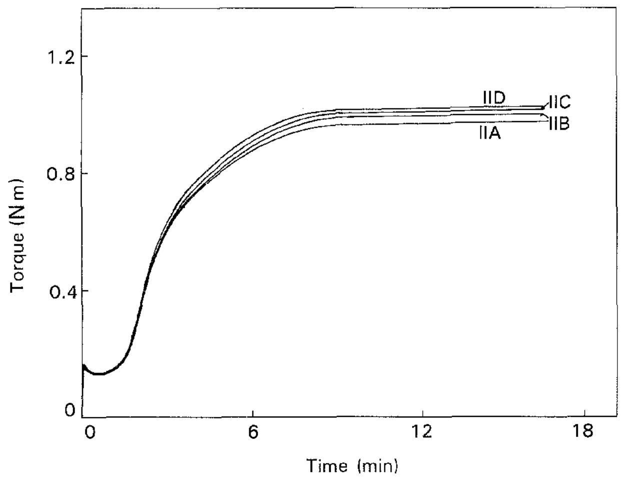

Figure 6 Cure curves for the mixes containing silica in rice-bran oil/naphthenic oil systems.

Tensile and other physical properties of the vulcanizates are given in Table IV. From the results it is seen that the initial tensile strength is slightly higher for the mixes containing rice-bran oil compared to those containing aromatic oil in the carbon-black filled systems. Elongation to break is more or less the same for the mixes containing rice-bran oil and aromatic oil. Modulus values do not show much variation among the mixes containing rice-bran oil, but slightly lower modulus values are observed for the mixes containing aromatic oil. The mixes containing rice-bran oil with and without antioxidant and that containing aromatic oil with antioxidant, retained more or less the same level of tensile properties after ageing. Compared to this, poor retention of tensile properties is noticed in the mix containing aromatic oil without antioxidant. It is inferred that the phenols present in the rice-bran oil impart antioxidant properties to the vulcanizates in the systems under review. In the case of silica-filled compounds, higher tensile strength is also noticed (before ageing) for the mixes containing rice-bran oil compared to the aromatic oil systems. Elongation at break is lower for the mixes containing rice-bran oil. The lower tensile strength values obtained for silica-filled compounds compared to the carbon-black systems can be attributed to the weak bonding and low interaction of silica with rubber [15, 16]. As in the case of carbon-black systems, in silica-filled compounds also the percentage retention of tensile properties is higher for the mixes containing rice-bran oil with and without antioxidant and also for the mix containing naphthenic oil with antioxidant. In contrast, poor retention of tensile properties is noticed for the mix containing naphthenic oil without antioxidant.

The presence of rice-bran oil in carbon-black and silica-filled systems of styrene butadiene rubber provides ageing resistance comparable to that of styrenated phenol. As suggested earlier, the antioxidant property of rice-bran oil may be attributed to

TABLE IV Physical properties of vulcanizates

		Mix							
		IA	IB	IC	ID	IIA	IIB	IIC	IID
Tensile strength (MPa)	BA[a]	24.19	24.32	24.60	24.68	21.62	21.70	21.86	21.98
	AA[b]	10.45	14.15	14.55	14.55	10.04	14.70	14.71	14.90
Elongation at break (%)	BA[a]	386	388	384	385	521	530	524	526
	AA[b]	98	122	120	132	103	205	216	218
Modulus at 200% (MPa)		9.17	9.20	9.27	9.28	6.40	6.42	6.45	6.45
Tear strength ($N mm^{-1}$)		58	59	58	58	60	60	60	61
Compression set (%)		23.16	22.47	22.94	22.51	37.72	37.64	38.09	37.63
Hardness (Shore A)		64	64	64	64	67	67	67	67
Abrasion loss ($cm^3 h^{-1}$)		6.149	6.250	6.199	6.161	7.094	7.088	6.906	7.094
Resilience (%)		53.14	53.14	52.49	52.49	51.87	51.56	51.26	51.56
Crosslink density ($Mmol kg^{-1}$)		79.80	80.62	81.34	82.23	80.10	80.27	81.66	82.65

[a] BA, Before ageing.
[b] AA, After ageing.

the presence of tocopherol and oryzanol in this oil [17]. The effect of vulcanized vegetable oils on the ageing resistance of rubber was reported earlier [18].

Hardness, compression set, resilience, tear strength and abrasion resistance were also evaluated for the different vulcanizates. In carbon-black systems tear strength, compression set, hardness and abrasion loss were found to be more or less the same for the mixes containing aromatic oil and rice-bran oil. A similar trend is also observed for silica-filled systems. Resilience is slightly higher for the mixes containing aromatic oil compared to those containing rice-bran oil.

The total chemical cross-link density was evaluated for both carbon-black and silica-filled systems. The results are given in Table IV. In the carbon-black filled compounds, mixes containing rice bran oil showed higher cross-link density compared to the aromatic oil system. Slightly higher tensile strength values for the vulcanizates from the former systems can be attributed to this. In the case of silica-filled system also, there is a marginal increase in cross-link density for the rice-bran oil-containing mixes. The higher cross-link density obtained in the filled vulcanizates can be attributed to better interaction between rubber and filler [14, 15]. Rice-bran oil seems to have a positive effect on this interaction.

4. Conclusion

From the results obtained in this study it is evident that raw rice-bran oil can be advantageously used in the sulphur vulcanization of styrene butadiene rubber. This oil can very well replace the conventional processing oils, fatty acid and antioxidant in an SBR compound. Evaluation of cure characteristics of the mixes containing rice-bran oil and those containing conventional processing aids such as aromatic oil in carbon-black filled systems, indicate that rice-bran oil does not have any adverse effect on the cure properties of the mixes. A similar trend is also seen in silica systems where rice-bran oil was used in place of naphthenic oil. A study of the physical properties of the vulcanizates (before and after ageing) also points to the above conclusions. Apart from the non-toxic nature of the rice-bran oil, it is comparatively cheaper than the aromatic/naphthenic oils used in rubber compounding. Studies of the processing characteristics also suggest that SBR compounds can be processed with rice-bran oil, similar to other conventional processing aids. The results also indicate that this nonedible oil exhibits co-activator and antioxidant properties by virtue of the presence in it of higher fatty acids and phenols.

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