

The Compounding of Nitrile and Polychloroprene Rubbers with Rice Bran Oil

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ABSTRACT

The use of rice bran oil as a processing aid in styrene butadiene rubber has already been investigated in this laboratory. Based on the encouraging results obtained from this study, we thought also of trying this oil in polar rubbers like nitrile butadiene (NBR) and polychloroprene (CR). In this study an attempt is made to see whether rice bran oil which is a natural product, devoid of any toxic effects, can function as co-activator, antioxidant and as a processing aid in nitrile and as processing aid and antioxidant in polychloroprene rubber. The plasticizer, co-activator and antioxidant properties are compared with DOP, stearic acid and styrenated phenol, respectively, in the NBR vulcanization system and antioxidant, stearic acid and aromatic oil are replaced by the oil in the polychloroprene system. The mixes were evaluated for cure characteristics. Scorch time, cure time and the cure rate index values have shown that this oil can effectively replace plasticizer, co-activator and antioxidant from NBR mixes and processing aid and antioxidant from CR systems. The evaluation of mechanical properties and ageing studies of the vulcanizates also indicate that rice bran oil can be used as a multi-purpose additive in these rubbers.

Key Words: rice bran oil, processing aid, tocopherol, polychloroprene, nitrile rubber

INTRODUCTION

It has already been established that rubber mixes containing vegetable oils and vulcanized vegetable oils give better flow properties, plasticizing action, low temperature flexibility and ozone resistance [1, 2]. Preparation of epoxidized rice bran oil and its use

as a plasticizer has also been reported [3]. Vegetable oils like linseed oil is also reported to be tried as plasticizer in heat resistant neoprene rubber [4], and in some elastomer blends for cold resistance [5]. Rice bran oil extracted from fresh bran, which is a byproduct of rice milling process, contains 1.4% to 1.9% free fatty acid [6]. On storage the free fatty acid

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(FFA) content of the oil may reach up to 30% due to the action of an active lipase enzyme, which catalyzes the hydrolysis of lipids into free fatty acids [7]. Higher FFA rice bran oil is non-edible and hence comparatively cheap. The general characteristics of the rice bran oil (RBO) are given in Table 1. The FFA content of the crude RBO is expressed in terms of oleic acid as it forms the major component in the oil. Oleic acid, the concentrations of which varies between 39 to 44%, together with certain other saturated fatty acids constitute more than 50% of the total acids present in the oil. Besides this, a small percentage linolenic acid is also found in the oil. The unsaponifiable matter in the oil, which varies between 3.9–6.6%, contains ferulic acid esters of triterpenoid alcohols, tocopherols, squalene, and naphthalene groups of hydrocarbons [8–10]. The amount of tocopherol in the oil varies between 0.03–0.1% [11]. Tocopherol is a substituted chroman and can function as a biological antioxidant by inhibiting the oxidation of unsaturated fatty acids. This oil also contains oryzanol, which is also reported to have antioxidant property [12].

Oryzanol is a mixture of two or more ferulic acid esters of triterpene alcohol. The peculiar odour of the oil is due to the ferulates and squalene. The brown colour is due to methyl ferulates. Presence of chlorophyll, imparts a greenish shade to the oil.

In the conventional compounding recipe of NBR, besides rubber, it involves sulphur, activator, co-activator, accelerator, filler, processing aid, etc.

Table 1. Characteristics of the crude rice bran oil.

Characteristics	Values
Colour (Y+5R, 1 cm ³ /lb)	35–43
Volatile matter (% w/wt)	0.5–1.0
Flash point (°C)	210.0
Free fatty acid (% oleic acid)	3–70
Iodine value (Wij's)	85–105
Unsaponifiable matter (% w/wt)	3.9–6.6
Refractive index (40 °C)	1.46–1.47
Phosphatides (% w/wt)	0.4–3.0
Wax (% w/wt)	2–6
Hydroxy value	5–17
Chlorophyll content (ppm)	2.0

Petroleum based process oils namely aromatic, naphthenic and paraffinic oils are generally used in rubber industry as plasticizers and extenders. Petroleum oils, vegetable oils, fatty acids and esters, etc. come under the classification of physical plasticizers (processing aids) as they do not react chemically with the rubbers involved. Their function is to modify the physical properties of either the compounded rubber or the finished vulcanizate.

As processing aids they cause reduction in viscosity of the compounded rubber, facilitate filler incorporation, reduce power consumption and minimize scorch by reducing internal friction during processing operations like calendaring and extrusion.

Compatibility, staining characteristics, low temperature flexibility, effect on vulcanization and ageing characteristics etc., are the important factors that are to be considered while selecting a plasticizer for a particular rubber. Incompatibility usually leads to poor physical properties of the vulcanizate and the plasticizer will bleed out from the vulcanizate. For polar rubbers like NBR and CR, polar plasticizers are preferred to improve processability and low temperature flexibility. For non-polar rubbers like NR, SBR and BR etc., various grades of mineral oil are usually employed. In rice bran oil, some polarity is expected because of the presence of significant amount of acids together with carbonyl groups. Vulcanization studies of NBR and CR using rice bran oil show that the oil is satisfactorily compatible with both rubbers.

Antioxidants are added to the rubber compound to minimize ageing effects from heat, light oxygen, etc. The common antioxidants used to improve ageing resistance are such organic compounds as aromatic amines, phenols, aminophenols etc. For general purpose application aromatic amines are most suitable where discolouration and possible staining are not problems. In light coloured stocks hindered phenols are often used. Zinc oxide and stearic acid are the usual activator and co-activator used in the NBR curing system. Their function along with the accelerator is to complete the vulcanization reaction in as short a time as possible.

Due to the presence of high amount of fatty acids and reasonable amount of natural antioxidants in

rice bran oil it is expected to function both as co-activator and anti-degradant when used in NBR vulcanization systems. In CR, the double bonds are sufficiently deactivated by electronegative chlorine atom so that direct vulcanization with sulphur is limited. A curing system based on metal oxides (ZnO/MgO) and ethylene thiourea (Na 22) as the accelerator combination is generally used when fast cures are required. Stearic acid of 0.5–1% is also included in the recipe that mainly functions as a lubricant.

Plasticizers based on mineral oil are most often employed to improve processing of the polychloroprene mixes. Naphthenic oil is preferred provided the end product is not subject to hot air exposure. For improved flame resistance phosphoric acid esters or chlorinated hydrocarbons are generally employed.

For higher loading, aromatic mineral oil is used, as it is more compatible with rubber. Aromatic process oils are reported to be carcinogenic because of the presence of higher levels of polycyclic aromatic compounds in these oils [13].

NBR being amorphous in nature needs fillers for reinforcement in order to have optimum physical properties. Both carbon black and non-black fillers are used with NBR rubber. The tensile strength and tear resistance of polychloroprene gum vulcanizate are fairly good because of the strong tendency of the polymer to crystallize. However, to acquire superior physical properties reinforcing or semi-reinforcing carbon blacks are used. Because of the presence of high molecular weight acids present in rice bran oil, it should function as a processing aid as well when used with filler. The antioxidant property of the oil is attributed to the significant amount of phenols present in the oil.

Rice bran oil was tried in this laboratory as a multi-purpose compounding ingredient in non-polar rubbers like natural rubber and styrene butadiene [14,15]. As a continuation of these studies, the present study was undertaken to assess whether the rice bran oil, a natural product and devoid of toxic effects, can replace the conventional process aid co-activator, antioxidant in the vulcanization systems of polychloroprene and nitrile rubbers. The results obtained on the use of rice bran oil as a substitute for processing oil,

co-activator, antioxidant, and lubricant in nitrile and polychloroprene rubber vulcanizates are reported in the following sections.

EXPERIMENTAL

Materials Used

Nitrile rubber: Aparene N854NS with bound ACN content of 42% supplied by Apar Polymers; polychloroprene: W. Type; rice bran oil: raw grade, supplied by Tamil Nadu Agro Industries Limited, Thanjavoor, India; ZnO, MgO, stearic acid, styrenated phenol, MBTS, sulphur, TMTD: all of commercial grade; carbon black (HAF 330), DOP, aromatic oil ethylene thiourea (Na22): supplied by National Physical Oceanographic Laboratory, Cochin, India.

A Brabender plasticorder PL 3S was used for comparing the processability of NBR and CR compounds with RBO/DOP/aromatic oil. Mixes were prepared as per Tables 2 and 3 except for the fact that only optimum quantity of the oil is shown in the table.

The rubber was first mixed for 4 min at 40 rpm in the plasticorder with roller mixing heads at 27 °C. Sulphur, zinc oxide and stearic acid for NBR and MgO, ZnO and stearic acid for CR were then added within 2–3 min. This was followed by carbon black mixed with DOP/RBO and accelerator for NBR. For CR carbon black was mixed with aromatic oil/RBO along with accelerator. Total mixing time was about 16 min. The experiment was repeated using 3, 5 and 7 phr each of DOP/rice bran oil for NBR. For CR the experiment was done using 2, 4 and 6 phr aromatic/rice bran oil. In each case a Brabender torque-time curve was plotted for varying amounts of DOP/aromatic oil (Figures 1 and 3) and rice bran oil (Figures 2 and 4).

After the mixing studies on the Brabender plasticorder the experimental mixes were prepared in a two roll mixing mill (6" X 12") as per ASTM D 3185-88 using the formulation given in Tables 2 and 3. In each case a reference mix was prepared with DOP for NBR and aromatic oil for CR. Mixes D₀, D₁, D₂, D₃ are based on NBR and DOP and C₀, C₁, C₂, C₃ are based on CR and aromatic oil. Apart from rubber,

Table 2. Formulation of NBR mixes.

Ingredient	Mixes number							
	D ₀	D ₁	D ₂	D ₃	R ₀	R ₁	R ₂	R ₃
NBR	100	100	100	100	100	100	100	100
ZnO	5	5	5	5	5	5	5	5
Stearic acid	2	2	0	0	2	2	0	0
Styrenated phenol	1.0	0	1.0	0	1.0	0	1.0	0
HAF black	40	40	40	40	40	40	40	40
DOP	5	5	5	5	0	0	0	0
RBO	0	0	0	0	5	5	5	5
TMTD	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
MBTS	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5

Table 3. Formulation of CR mixes.

Ingredient	Mixes number							
	C ₀	C ₁	C ₂	C ₃	RC ₀	RC ₁	RC ₂	RC ₃
CR	100	100	100	100	100	100	100	100
MgO	4	4	4	4	4	4	4	4
ZnO	5	5	5	5	5	5	5	5
Stearic acid	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Styrenated phenol	1.0	0	1.0	0	1.0	0	1.0	0
HAF black	40	40	40	40	40	40	40	40
Aromatic oil	4	4	4	4	0	0	0	0
RBO	0	0	0	0	4	4	4	4
Na22	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5

Table 4. Cure characteristics of NBR mixes.

Properties	Mixes number							
	D ₀	D ₁	D ₂	D ₃	R ₀	R ₁	R ₂	R ₃
Maximum torque (Nm)	0.51	0.48	0.62	0.67	0.41	0.30	0.37	0.27
Minimum torque (Nm)	0.05	0.05	0.05	0.05	0.04	0.04	0.04	0.04
Optimum cure time t_{90} (min)	3.32	3.10	3.40	3.40	3.20	2.70	2.80	2.30
Elastographic scorch time t_{10} (min)	1.90	1.90	1.90	1.90	1.80	1.70	1.80	1.60
Cure rate index	70.40	83.30	67.0	67.0	71.0	100.0	100.0	143.0

filler and curing agent, mixes D₀ and C₀ contain both antioxidant and stearic acid. Mixes D₁ and C₁ contain no antioxidant, D₂ and C₂ contain no stearic acid and in D₃ and C₃ both stearic acid and antioxidant are replaced. R₀, R₁, R₂, R₃ and RC₀, RC₁, RC₂, RC₃ are the corresponding mixes prepared with rice bran oil.

The cure characteristics of the NBR and CR

mixes were determined at 160 °C and 150 °C, respectively, using a Goettfert Elastograph Model 67.85. The cure properties obtained are given in Tables 4 and 5. The t_{90} is the optimum cure time (time to reach 90% of the maximum torque) and t_{10} is the scorch time (time to reach 10% of the maximum torque). The cure rate index is calculated as $100/t_{90}$. The compounds are

Table 5. Cure characteristics of CR mixes.

Properties	Mixes number							
	C ₀	C ₁	C ₂	C ₃	RC ₀	RC ₁	RC ₂	RC ₃
Maximum torque (Nm)	0.59	0.53	0.49	0.53	0.57	0.59	0.54	0.51
Minimum torque (Nm)	0.06	0.05	0.05	0.05	0.04	0.04	0.05	0.04
Optimum cure time t ₉₀ (min)	18.70	19.0	19.2	19.3	17.3	17.5	17.4	17.6
Elastographic scorch time t ₁₀ (min)	1.40	1.40	1.60	1.50	1.30	1.40	1.30	1.30
Cure rate index	5.78	5.68	5.68	5.61	6.25	6.09	6.21	6.13

vulcanized up to the optimum cure time in an electrically heated hydraulic press. Tensile properties were determined as per ASTM D412-87 using a Zwick universal testing machine at a pulling rate of 500 mm/min at 27 °C. Tear resistance was determined as per ASTM method D624-86 using unnicked 90 °C test pieces. Hardness was measured according to ASTM D 2240-86 and compression set according to ASTM D395-89 (method B). Ageing studies were carried out as per ASTM D 573 at 100±1 °C for 72 and 96 h for NBR and CR vulcanizates, respectively, in an air oven.

In order to understand the variation in physical properties of the different vulcanizates the density of cross-links was also estimated. The cross-link density

of NBR vulcanizate was determined by equilibrium swelling in chloroform for 48 h at 27 °C, and calculated using Flory-Rehner equation [16]. For CR, the above experiment was carried out using benzene as the solvent.

RESULTS AND DISCUSSION

Figures 1 and 2 show the variation of Brabender torque with time of NBR compounds having 5 phr DOP/RBO. Figures 3 and 4 show the torque values for CR compounds having 4 phr aromatic/rice bran oil.

From the figures it is clear that as the level of

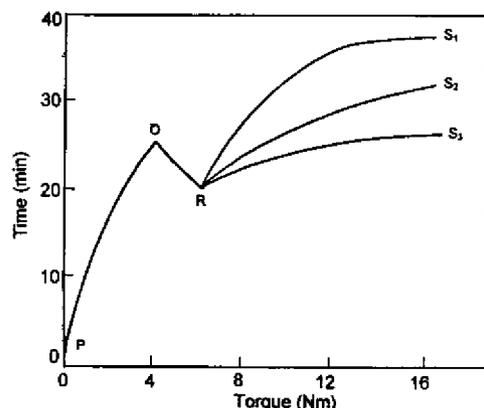


Figure 1. Variation of Brabender torque with varying amounts of DOP in black filled NBR PQ, rubber; QR, activator; RS₁, carbon black, DOP (3 phr), sulphur and accelerator; RS₂, carbon black, DOP (5 phr), sulphur and accelerator; RS₃, carbon black, DOP (7 phr), sulphur and accelerator.

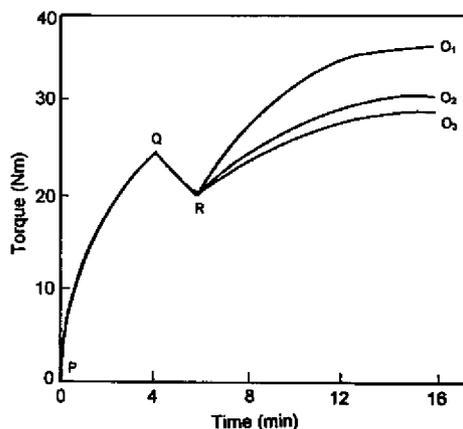


Figure 2. Variation of Brabender torque with varying amounts of rice bran oil in black filled NBR PQ, rubber; QR, activator; RO₁, carbon black, RBO (3 phr) sulphur and accelerator; RO₂, carbon black, RBO (5 phr), sulphur and accelerator; RO₃, carbon black, RBO (7 phr), sulphur and accelerator.

rice bran oil, DOP or aromatic oil increases the torque developed decreases correspondingly. The Brabender torque developed is reasonable for NBR mixes prepared using 5 phr levels of DOP/rice bran oil (Figures 1 and 2). Hence 5 phr levels of each of these oils can be taken as the optimum level. For CR mixes also the torque developed is reasonable when 4 phr levels each of aromatic oil/rice bran oil were used (Figures 3 and 4). Hence 4 phr levels of each of these oils can be taken as the optimum level. In each case the torque generated is more or less similar when RBO replaces DOW aromatic oil indicating that RBO can be used as a processing aid for nitrile butadiene and polychloroprene rubbers used in this study.

The cure curves of NBR mixes using DOP are given in Figure 5 and those with RBO are given in Figure 6. The maximum torque developed is higher in the mixes containing DOP compared to ones containing rice bran oil. The lower torque values in mixes containing RBO might be attributed to the presence of the long paraffin chains of the acids present in the oil which has an effect as an internal lubricant. The optimum cure time of these mixes is

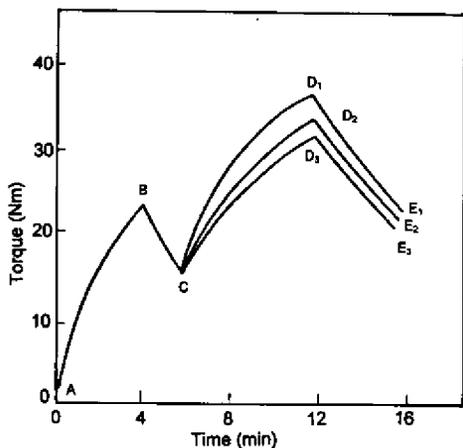


Figure 3. Variation of Brabender torque with varying amounts of aromatic oil in black filled CR. AB, rubber; BC, MgO, ZnO and stearic acid; CD₂, carbon black, aromatic oil (2 phr), CD₂, carbon black, aromatic oil (4 phr); CD₃, carbon black, aromatic oil (6 phr), D₁E₁, D₂E₂-D₃E₃, Na 22.

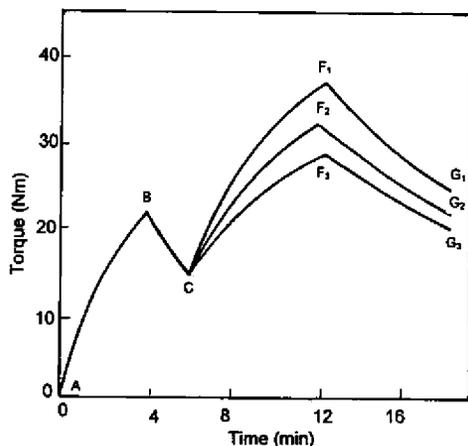


Figure 4. Variation of Brabender torque with varying amounts of rice bran oil in black filled CR. AB, rubber-, BC, MgO, ZnO and stearic acid; CF₁, carbon black, RBO(2 phr); CF₂, carbon black, RBO (4 phr); CF₃, carbon black RBO (6 phr); F₁G₁, F₂G₂, F₃G₃, Na 22.

also appreciably less compared to those with DOP. This can also be considered as an added advantage with RBO. Cure curves of CR mixes with aromatic oil

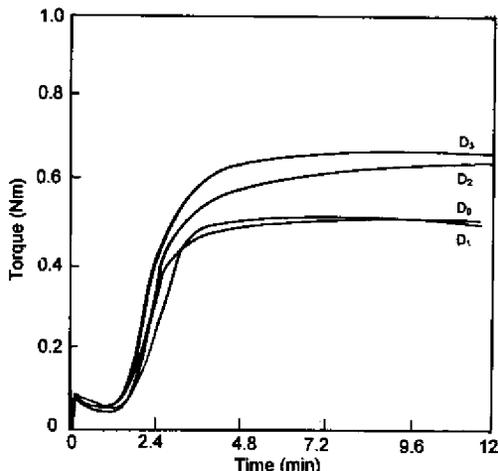


Figure 5. Cure curves of NBR mixes containing DOP.

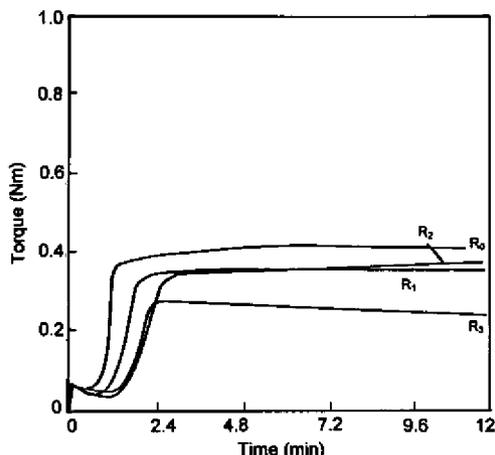


Figure 6. Cure curves of NBR mixes containing RBO.

are given in Figure 7 and those with RBO in Figure 8.

The torque development is more or less similar in these mixes. However, the optimum cure time of mixes with RBO are lower than that with aromatic oil. These observations are a clear indication of the cure accelerating effect of rice bran oil in both NBR and CR vulcanization systems. It is also noted that in all the mixes of NBR and CR; replacement of the

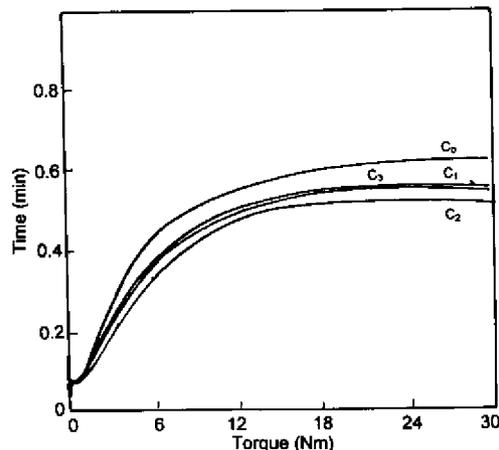


Figure 7. Cure curves of CR mixes containing aromatic oil.

conventional process oils with rice bran oil does not affect the scorch characteristics.

Replacing stearic acid from the NBR mix containing DOP (D_2) causes reduction in cure rate compared to control mix (D_0), whereas, similar change in the mix containing RBO (R_2) causes decrease of cure time value and corresponding increase in cure rate compared with the control mix (R_0). Replacing stearic acid in the polychloroprene rubber mix (C_2) containing aromatic oil results in the decrease of cure rate but similar changes in the mix containing RBO (RC_2) causes decrease in cure time value compared to the control mix (C_0). This indicates that rice bran oil can effectively function as a processing aid even in the absence of stearic acid in both NBR and CR systems. This also suggests that the higher fatty acids present in rice bran oil can act as co-activator in the vulcanization under review.

The tensile and other physical properties of the NBR vulcaizates evaluated are given in Table 6 and those of CR in Table 7, From the results it is clear that in both NBR and CR systems initial tensile strength, and tear strength are slightly higher for mixes containing DOP/aromatic oil. This is also reflected to be in the cross-link density values. Hence it can be inferred that DOP/aromatic oil is more comparable with NBR/CR, respectively, than rice bran oil. This may be

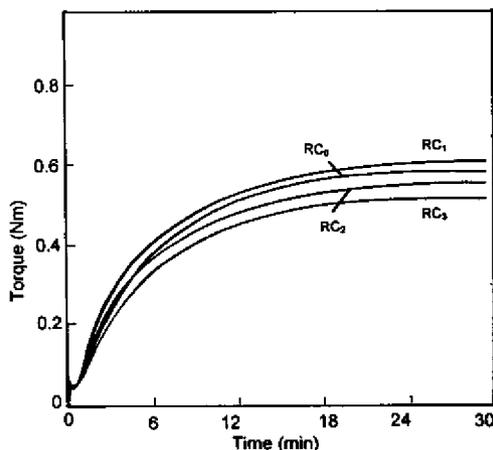


Figure 8. Cure curves of CR mixes containing RBO.

Table 6. Physical properties of NBR vulcanizates.

Properties	Mixes number							
	D ₀	D ₁	D ₂	D ₃	R ₀	R ₁	R ₂	R ₃
Tensile strength (MPa) BA*	23.16	23.89	26.45	26.76	22.61	24.41	25.66	25.81
Tensile strength (MPa) AA*	16.38	15.48	17.51	16.46	17.76	16.48	17.25	17.81
Retention (%)	70.72	64.79	66.20	61.00	78.55	67.51	67.20	69.00
Elongation at break (%) BA*	397.0	535.0	390.0	345.0	393.0	354.0	415.0	439.0
Elongation at break (%) AA*	164.0	158.0	174.0	141.0	162.0	142.0	163.0	171.0
Modulus at 200 % (MPa)	9.48	11.14	9.87	12.51	8.61	11.42	8.86	8.34
Tear strength (Nmm ⁻¹)	74.0	72.0	72.0	76.0	70.0	69.0	71.0	73.0
Compression set (%)	19.0	20.0	20.0	21.0	19.0	19.0	20.0	18.0
Hardness (shore A)	65.0	66.0	67.0	65.0	64.0	65.0	65.0	66.0
Abrasion loss (cm ³ h ⁻¹)	3.33	3.31	3.30	3.32	2.86	2.84	2.88	2.84
Cross-link density (g.mol/g)×10 ⁻⁵	5.98	6.08	5.86	6.29	5.48	5.82	5.32	5.29

*BA-before ageing

*AA-after ageing

attributed to the less polar character of RBO compared to the other oils.

For NBR vulcanizates the elongation at break is higher for mixes with RBO (R₂, R₃) than the corresponding mixes with DOP (D₂, D₃), which might be due to the higher internal lubrication afforded by the rice bran oil. This will impart more chain flexibility to the NBR mixes prepared with RBO. The rice bran oil based NBR mixes with R₀, R₂ and without antioxidant R₁ showed better ageing resistance (high

value of percentage retention) compared to corresponding mixes containing DOP.

Similar trend is observed in the CR mixes too, which indicates the antioxidant properties of the phenols present in rice bran oil. Mix R₃ where rice bran oil substitutes both stearic acid and antioxidant showed good tensile values and satisfactory ageing resistance was observed in comparison to control mix containing DOP. Hardness, compression set and tear strength values of NBR mixes containing RBO/DOP

Table 7. Physical properties of CR vulcanizates.

Properties	Mixes number							
	C ₀	C ₁	C ₂	C ₃	RC ₀	RC ₁	RC ₂	RC ₃
Tensile strength (MPa) BA*	18.20	19.53	20.53	20.04	17.09	17.28	18.86	18.15
Tensile strength (MPa) AA*	16.38	15.57	16.37	16.38	16.29	15.52	18.14	16.80
Retention (%)	92.20	80.80	89.47	83.90	95.30	89.80	96.18	92.50
Elongation at break (%) BA*	257.0	268.0	261.0	266.0	225.0	227.0	261.0	254.0
Elongation at break (%) AA*	223.0	207.0	215.0	200.0	221.0	195.0	218.0	188.0
Modulus at 200 % (Mpa)	5.03	5.00	5.04	4.96	5.50	5.38	5.10	5.17
Tear strength (Nmm ⁻¹)	71	69	73	64	64	62	63	61
Compression set (%)	14	14	14	14	15	15	15	15
Hardness (shore A)	61	62	63	63	64	64	64	64
Abrasion loss (cm ³ h ⁻¹)	2.90	2.94	2.98	2.98	2.48	2.52	2.57	2.56
Cross-link density (g.mol/g)×10 ⁻⁴	1.51	1.56	1.48	1.58	1.44	1.54	1.46	1.53

*BA-before ageing

*AA-after ageing

are more or less similar. This is true in CR mixes containing RBO/aromatic oil too. Abrasion loss values of NBR and CR vulcanizates with RBO are smaller (better abrasion resistance) compared to the control mixes. The better abrasion resistance may be attributed to lower stiffness of vulcanizate and better interaction of the filler with rubber in presence of rice bran oil.

Based on these results it is reasonable to conclude that rice bran oil can be used in place of other conventional process aids in both NBR and CR systems without any adverse effect on processing parameters, cure characteristics and vulcanizate properties. Also noted is the fact that the higher fatty acids present in RBO can act as a co-activator and the natural phenols in the oils has satisfactory antioxidant properties in these rubber mixes.

CONCLUSION

From the processability studies using Brabender plasticorder, it is clear that rice bran oil can be effectively used in compounding both NBR and CR rubbers in place of conventional processing aids. The cure time values of the NBR and CR mixes prepared with RBO are found to be lower than that of the mixes prepared with DOP/aromatic oil indicating that this oil exhibits cure acceleration in both the vulcanization studies under review. A study of the physical properties of the vulcanizate (before and after ageing) points to the fact that rice bran oil can very well replace conventional processing aids, fatty acid and antioxidant in NBR and CR compounds. Rice bran oil which is a natural product and it is non-toxic and cheaper (Price of rice bran oil is about 1\$/5 kg

whereas, that of DOP/aromatic oil is about 10 and 4\$/5 kg, respectively) than the conventional plasticizers like DOP or aromatic oil can be advantageously used in the compounding of nitrile butadiene and polychloroprene rubbers.

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