Indian Journal of Natural Rubber Research, **15**(2) : 143-149, 2002.

USE OF RUBBER SEED OIL IN POLYCHLOROPRENE RUBBER COMPOUNDS

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Joseph, R., Alex, R., Premalatha, C.K. and Kuriakose, B. (2002). Use of rubber seed oil in polychloroprene rubber compounds. *Indian Journal of Natural Rubber Research*, **15**(2) : 143-149.

Rubber seed oil has been evaluated as an acid acceptor and plasticizer in gum and carbon black filled polychloroprene compounds replacing magnesium oxide and naphthenic type process oil. The results of the study indicate that use of rubber seed oil helps to achieve better scorch safety, faster cure rate and better ageing resistance in polychloroprene compounds. It can replace magnesium oxide and process oil in carbon black filled polychloroprene compounds. Use of rubber seed oil gives comparable tensile and tear strength and better abrasion resistance for the carbon black filled polychloroprene vulcanisates. Vulcanisates containing rubber seed oil do not develop fungus on their surface.

Key words: Ageing resistance, Epoxidised rubber seed oil, Fungal growth, Plasticizer, Polychloroprene rubber, Rubber seed oil.

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INTRODUCTION

In India, natural rubber is grown mainly in the southern states with Kerala having the largest area. Rubber seed is an important byproduct from the rubber tree. The oil extracted from the seed has many industrial uses. The estimated production potential of rubber seed in India is about 150 kg per ha (Haridasan, 1977). Rubber seed contains oil and a high protein residue (Dayaratne, 1973). The production of rubber seed oil (RSO) in India in 1999-00 was 1600 MT. The oil content in the dried kernel is about 42%. The oil contains 18 to 22% saturated fatty acids and 78-82% unsaturated fatty acids. The properties of oil and the composition of fatty acids present in RSO as reported earlier (Bhushan, 1958) are given in Tables 1 and 2 respectively.

As RSO satisfies certain standard requirements in the manufacture of alkyd resin, soap and paints, it finds application in these industries. RSO can be used as a substitute for linseed oil in the manufacture of paints. RSO / alkyd resin paints are ideally suited for many surface coatings (Dayaratne, 1973; Obioma and Ikpendu, 1995). Even though RSO can be chemically modified to produce epoxidised rubber seed oil (ERSO) (Vijayagopalan and Gopalakrishnan, 1971) and factice (Vijayagopalan, 1971) in India the current industrial use of rubber seed oil is confined to soap manufacture. Use of limited quantities of vegetable oils such as linseed oil is reported to give better ozone resistance for polychloroprene rubber vulcanisates (Murray, 1959). Use of coconut oil in NR compounds as plasticiser for footwear application is also reported (Parab, 1976). Since RSO contains a large proportion of unsaturated fatty acids (Table 2), an attempt is made

Table 1. **Properties of rubber seed oil**

Parameter	Range of values
Acid value	4 - 40
Saponification value	190 - 195
Iodine value	132 - 141
Hydroxyl value	12 - 32
Unsaponifiables (%)	0.5 - 1
Refractive index (40°C)	1.466 -1.469
Specific gravity	0.92 - 0.93
Titre°C	28 - 32

Table 2. **Higher fatty acid profile of rubber seed oil**

Fatty acid	Content (%)
Palmitic acid	11
Stearic acid	12
Arachidic acid	1
Oleic acid	17
Linoleic acid	35
Linolenic acid	24

to use RSO/ERSO as a cure activator cum plasticizer in polychloroprene rubber compounds.

MATERIALS AND METHODS

Polychloroprene rubber used for this study was Neoprene W grade. It contains no staining stabilizer, elemental sulphur, thiuram disulphide or other chemicals capable of decomposing to yield either free sulphur or a vulcanizing accelerator. Rubber seed oil was commercial grade prepared by expulsion process of dry kernel. ERSO was prepared from RSO using hydrogen peroxide and acetic acid at a temperature of 60°C (Vijayagopalan and Gopalakrishnan, 1971). All other chemicals used in the study were of commercial grade.

Formulations of the gum and black filled polychloroprene compounds used for this study are given in Table 3. The compounds were prepared on a two roll laboratory mixing mill of 150 x 300 mm size. The cure characteristics were determined using Monsanto Rheometer R-100 at 150°C. Test slabs for tensile properties were prepared by compression moulding of the compounds in an electrically heated hydraulic press at 150°C to their respective optimum cure times. Dumb-bell shaped test pieces were punched out from the vulcanized sheets, along the direction of the grain and tested for tensile properties as per ASTM D-412 (1980), using Zwick 1474 Universal Testing Machine. Tests such as hardness (ASTM D-2240, 1997), abrasion loss (DIN 53516, 1977), compression set (ASTM D- 395, 1998), resilience (ASTM D-1054, 1991) etc. were also performed using the test samples prepared from the filled compounds. Ageing resistance of the vulcanizates was determined by measuring tensile properties of the samples after ageing at 100°C for 72 h and 120 h respectively for the gum and black filled vulcanizates. Crosslink density, as measured by Vr values, was determined by swelling the vulcanized test samples in toluene to equilibrium, as per the method reported by Ellis and Welding (1964).

RESULTS AND DISCUSSION

Polychloroprene vulcanizes in a different manner from that of natural rubber, styrene butadiene rubber and nitrile rubber. It is crosslinked by bivalent metallic oxides. The metallic oxide most commonly used as

Table 3. **Formulation of polychloroprene gum compounds**

Ingredient	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11
Polychloroprene (NeopreneW-Type)	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Stearic acid	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Antioxidant TDQ *	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Zinc oxide	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Magnesium oxide	4.0	-	-	4.0	4.0	4.0	4.0	-	-	-	-
Rubber seed oil	-	4.0	-	-	-	-	-	1.0	2.0	3.0	4.0
Epoxidised rubber seed oil (2% epoxy content)	-	-	4.0	-	-	-	-	-	-	-	-
Accelerator NA-22 **	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
GPF black	-	-	-	10.0	20.0	30.0	40.0	10.0	20.0	30.0	40.0
Naphthenic oil	-	-	-	1.0	2.0	3.0	4.0	-	-	-	-

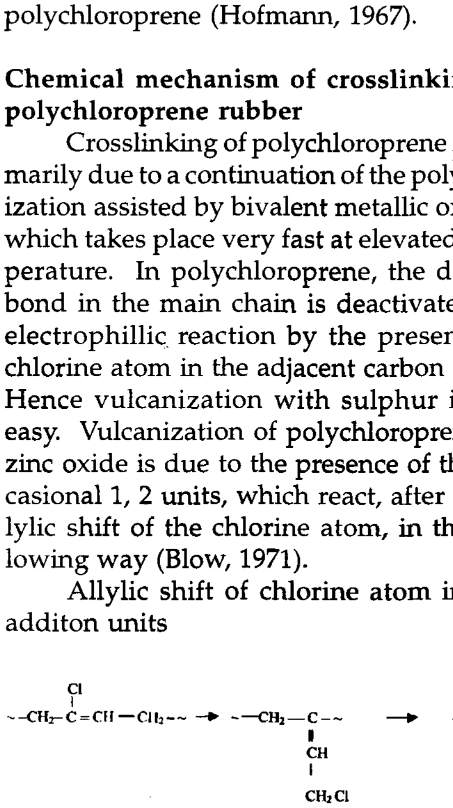
* 2, 2, 4- trimethyl 1, 2- dihydroquinoline " ** Ethylene thiourea

crosslinking agent is zinc oxide. Magnesium oxide serves as an acid acceptor, preventing premature crosslinking and cyclisation of polychloroprene and it also helps to enhance the properties of the vulcanizate. The proportions of magnesium oxide and zinc oxide are 4 and 5 parts by weight respectively for 100 parts by weight of polychloroprene (Hofmann, 1967).

Chemical mechanism of crosslinking of polychloroprene rubber

Crosslinking of polychloroprene is primarily due to a continuation of the polymerization assisted by bivalent metallic oxides, which takes place very fast at elevated temperature. In polychloroprene, the double bond in the main chain is deactivated for electrophillic reaction by the presence of chlorine atom in the adjacent carbon atom. Hence vulcanization with sulphur is not easy. Vulcanization of polychloroprene by zinc oxide is due to the presence of the occasional 1, 2 units, which react, after an allylic shift of the chlorine atom, in the following way (Blow, 1971).

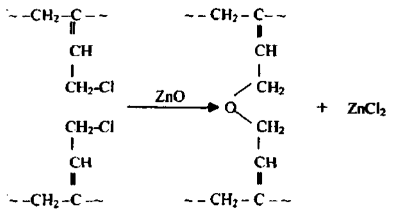
Allylic shift of chlorine atom in 1, 2 additon units



$$\sim CH_2-C(Cl)=CH-CH_2\sim \rightarrow \sim CH_2-C(=CH-CH_2Cl)\sim \rightarrow$$

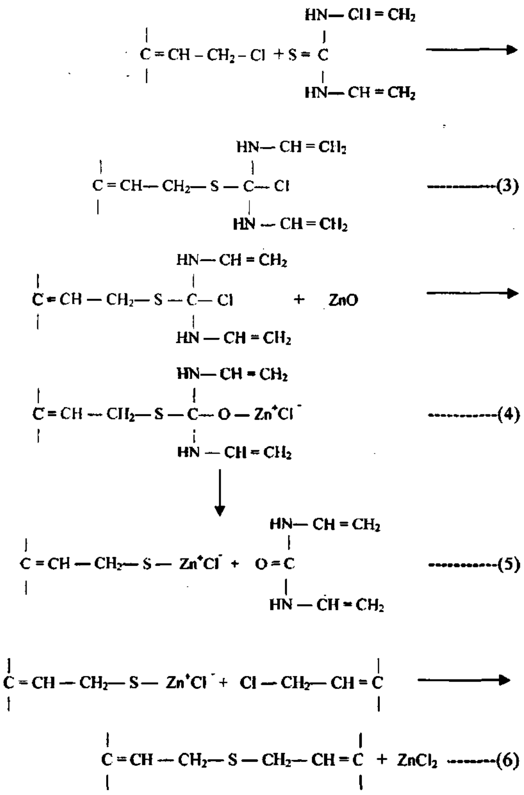
——(1)

Crosslinking in the presence of zinc oxide

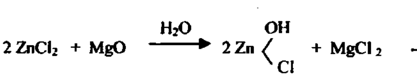


——(2)

In the presence of organic accelerators such as ethylene thiourea, the following reactions also lead to crosslinking of the polychloroprene rubber (Johnson, 1976).



The zinc chloride formed in Equations 2 and 6 is an active catalyst of vulcanization and unless it can be scavenged, its presence during processing operation can cause scorching. Magnesium oxide reacts with zinc chloride thereby enhancing scorch safety and physical properties of the vulcanizate.



$$2\,ZnCl_2 + MgO \xrightarrow{H_2O} 2\,Zn(OH)Cl + MgCl_2$$

——(7)

In the present work magnesium oxide is replaced by rubber seed oil and epoxidised rubber seed oil. The gum compounds were prepared by using the formulations given in Table 3. Compounds prepared are designated as C1, C2 and C3. In compound C1, ZnO / MgO combination is used as vulcanizing system along with ethylene thiourea as accelerator. In compounds C2 and C3 ethylene thiourea (NA-22) is used as accelerator, but magnesium oxide is replaced with RSO and ERSO respectively. The cure characteristics of the mixes are given in Table 4 and physical properties in Table 5.

Table 4. **Cure characteristics of gum compounds**

Properties	C1	C2	C3
Maximum rheometric torque (dNm)	61.00	47.00	47.00
T max - Tmin (ΔTq)	51.00	38.50	38.00
Optimum cure time t_{90} at 150° C (min)	13.00	8.80	9.40
Cure rate index	9.25	15.90	14.50
Scorch time(ts_2) at 150°C (min)	2.20	2.50	2.50

Table 5. **Physical properties of gum vulcanizates**

Properties	C1	C2	C3
Before ageing			
Tensile strength (MPa)	12.3	8.9	7.6
Modulus 300 % (MPa)	1.9	1.2	1.2
Elongation at break (%)	782.0	789.0	781.0
Tear strength (N / mm)	26.1	17.8	19.5
After ageing at 100°C for 72 h			
Tensile strength (MPa)	10.3	8.9	7.9
Modulus 300 % (MPa)	2.3	1.4	1.5
Elongation at break (%)	682.0	763.0	697.0
Retention of tensile strength (%)	83.7	100.0	103.9
Retention of 300% modulus (%)	121.0	116.6	125.0
Retention of elongation at break (%)	87.2	96.7	89.2

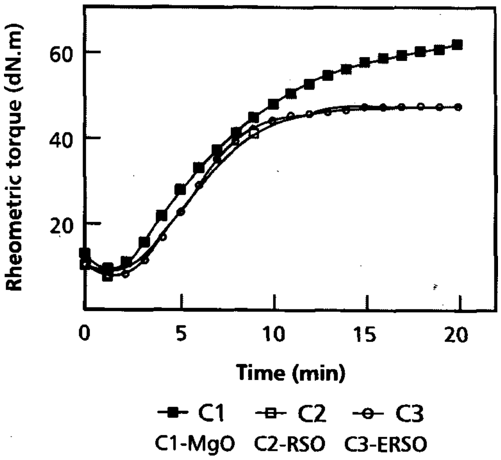
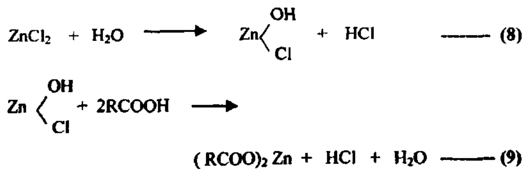


Fig. 1. Rheographs of gum compounds

Properties of the gum compounds

The rheographs in Fig.1 and the cure characteristics given in Table 4 indicate that the gum compounds containing rubber seed oil or epoxidised rubber seed oil have better scorch safety, lower cure time and faster cure rate compared with the compound containing magnesium oxide. The above combination of cure parameters is very much desirable in rubber compounds for better process safety and faster production. The lower values of maximum rheometric torque (Fig.1) for the compounds containing RSO and ERSO is due to the plasticizing effect of these materials or that of the higher fatty acids / their zinc soaps. The vulcanizates from these compounds have lower tensile and tear strength compared with that containing magnesium oxide (Table 5). However these vulcanizates show much better retention of tensile properties after ageing at 100°C for 72 h. Rubber seed oil is an ester of higher fatty acids (Table 2), which may undergo acidic hydrolysis to form higher fatty acids. These can react with zinc hydroxy chloride formed by reaction of zinc chloride with water, to form the corresponding zinc soap, thereby nullifying the effect of zinc chloride on premature vulcanization.



$$ZnCl_2 + H_2O \longrightarrow Zn\langle^{OH}_{Cl} + HCl \quad (8)$$

$$Zn\langle^{OH}_{Cl} + 2RCOOH \longrightarrow (RCOO)_2Zn + HCl + H_2O \quad (9)$$

The HCl produced by reactions involved in Equations 8 and 9 above, can react with the unsaturated higher fatty acids formed by the acid hydrolysis of the rubber seed oil (Finar,1971;Gerhortz, 1987), according to the general equation given below.

$$R-CH=CH-CH_2-COOH + HCl \rightarrow R-CH_2-CHCl-CH_2-COOH \text{ ---- } (10)$$

Reduction in tensile properties is expected to be due to the plasticizing effect of rubber seed oil, which may cause a reduction in the extent of crystallization of the polymer. This effect is further evident from the other physical properties of the filled compounds given in Table 6. Better ageing resistance of the vulcanizates containing a higher dosage of higher fatty acids in NR compounds is already reported (Barnard et al, 1985). Since the properties of the gum compounds containing rubber seed oil and epoxidised rubber seed oil are almost similar, the epoxy group does not seem to have any specific role in neutralising the effect of zinc chloride or HCl and hence in the carbon black filled compounds only rubber seed oil was evaluated.

Properties of black filled compounds

The cure characteristics of the GPF black filled compounds C4 to C11 and physical properties of their vulcanizates are given in Table 6. As in the case of gum compounds, the compounds containing rubber seed oil have better scorch safety, lower cure time and faster cure rates as indicated by higher Mooney scorch time, lower optimum cure time and higher cure rate index values compared with the corresponding values of the compound containing naphthenic oil. Lower values of maximum rheometric

Table 6. **Properties of GPF black filled polychloroprene compounds**

Properties	C4	C5	C6	C7	C8	C 9	C10	C11
Max. rheometric torque (dNm)	73.0	78.0	85.0	87.0	61.0	70.0	75.0	81.0
Tmax - Tmin (Δt_q)	61.0	65.0	73.0	74.0	50.0	57.0	62.0	67.0
Optimum cure time, (t_{90}) at 150°C (min)	14.2	14.4	14.0	14.5	9.3	8.4	8.8	8.5
Cure rate index	8.2	8.1	8.3	7.9	13.3	15.8	14.7	14.7
Mooney scorch time (ts_2)at 120°C (min)	6.3	6.2	5.4	5.0	7.3	7.4	6.2	6.4
Vr of swollen sample	0.223	0.242	0.255	0.264	0.222	0.221	0.24	0.255
Before ageing								
Tensile strength (MPa)	19.6	20.6	21.5	20.9	21.1	22.1	22.2	20.9
Modulus 300% (MPa)	4.1	7.1	11.4	14.5	3.2	6.2	9.7	13.1
Elongation at break (%)	750.0	700.0	594.0	482.0	780.0	775.0	650.0	511.0
Tear strength (N/mm)	40.3	48.7	53.8	52.4	41.9	51.5	59.0	58.0
Hardness (Shore A)	47.0	49.0	55.0	59.0	46.0	50.0	54.0	60.0
Rebound resilience (%)	61.0	60.0	57.0	55.0	57.0	56.0	55.0	53.0
DIN abrasion loss (mm3)	130.0	109.0	103.0	103.0	135	81.0	68.0	65.0
Compression set (%)	5.3	5.9	7.2	7.5	7.9	7.7	8.7	8.9
After ageing at 100°C, 120 h								
Tensile strength (MPa)	14.1	17.3	18.7	19.9	15.9	20.6	19.6	20.6
Modulus 300% (MPa)	4.7	8.4	13.2	16.6	3.9	7.0	11.6	15.6
Elongation at break(%)	544.0	474.0	415.0	360.0	655.0	644.0	484	397.0
Retention of tensile strength (%)	71.9	84.0	87.0	95.2	75.4	93.2	88.3	98.5
Retention of 300% modulus (%)	114.6	118.3	115.8	114.5	121.9	112.9	119.6	119.1
Retention of elongation at break(%)	72.5	67.7	69.9	74.7	84.0	83.0	74.5	77.7

torque indicate the better plasticizing effect of the rubber seed oil than naphthenic oil. Even though the Vr values of the vulcanizates C8 to C11 are slightly lower than those of the vulcanizates C4 to C7, they show comparable tensile and tear strength values probably due to enhanced dispersion of filler in the presence of RSO. The higher plasticizing effect of rubber seed oil over naphthenic oil is indicated by lower hardness, modulus and resilience and higher elongation at break and compression set of the vulcanizates containing rubber seed oil compared with those containing naphthenic oil. This effect may be due to the better lubricating action between the polymer chains caused by the zinc soap of the fatty acid formed during the vulcanization reaction, as described in the previous section. The vulcanizates containing RSO as plasticizer show excellent resistance to abrasion as compared to naphthenic oil. Improvement in DIN abrasion loss of NR and SBR vulcanizates by incorporation of RSO, as compared with aromatic oil, has been noted earlier (Nandanan *et al.*, 1999). RSO being a better plasticizer gives more uniform distribution of filler and hence imparts better abrasion resistance to the vulcanizates. The higher fatty acid soaps formed from RSO during the vulcanization reaction also may be contributing to the higher abrasion resistance. This reasoning is supported by appreciably lower DIN abrasion values reported for the vulcanizates containing higher dosage of higher fatty acids (Gelling, 1992).

The ageing resistance of the GPF black filled vulcanizates containing rubber seed oil is much better than those containing naphthenic oil, as indicated by both better aged mechanical properties and higher retention of tensile properties after ageing at 100°C for 120 h. Other vegetable oils such as linseed oil are also reported to enhance the oxidative ageing / ozone resistance of polychloroprene vulcanizates (Murray and Thompson, 1963). Even though the exact reason for this behaviour is yet to be known it is possible that these oils act as carriers for the antioxidants added to the compound, helping them to be transported to the surface of the vulcanizate, where the action of the degrading agents is more severe.

Most of the unsaturated vegetable oils are very compatible with polychloroprene. A disadvantage of unsaturated oil is that fungus may grow on the surface of vulcanizates. Sheets moulded from compounds C8, C9, C10 and C11 were inoculated and incubated at high humidity for a week. These sheets did not show any fungal growth on the surface, which indicated that rubber seed oil can be used in polychloroprene compounds without any fear of fungal attack.

CONCLUSION

The results of the present study indicated that rubber seed oil could be used as an acid acceptor and plasticizer in polychloroprene compounds. Use of rubber seed oil helps to achieve better scorch safety, faster cure rate and better ageing resistance in polychloroprene compounds. It can replace magnesium oxide and process oil together in carbon black filled polychloroprene compounds. Use of rubber seed oil gives comparable tensile and tear strength and better abrasion resistance for the carbon black filled polychloroprene vulcanizates. There was no fungal growth on the surface of the vulcanizates containing rubber seed oil.

ACKNOWLEDGEMENT

The authors wish to acknowledge the help rendered by Dr. Annakutty Joseph, Scientist, Plant Pathology Division, RRII in analysis of fungus growth on rubber test pieces.

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