

Processability Characteristics and Physico-mechanical Properties of Natural Rubber Modified with Rubber Seed Oil and Epoxidized Rubber Seed Oil

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Received March 1999; accepted August 1999

ABSTRACT: The processability characteristics and physico-mechanical properties of natural rubber (NR) modified with raw rubber seed oil and epoxidized rubber seed oil have been studied. The modified mixes showed higher scorch time and lower cure rate, crosslink density, and ultimate state of cure compared to an unmodified mix. The thermal stability of the vulcanizates was practically unaffected by the modification. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 1413–1418, 2000

Key words: natural rubber; rubber seed oil; epoxidized rubber seed oil; processability; physico-mechanical properties

INTRODUCTION

Modification of elastomers with plasticizers or process aids is a widely accepted practice to improve the processability of mixes and to impart desired properties to the vulcanizates. Many of such additives presently being used are based on petrochemical sources that are rather expensive. However, there exists quite a few molecules of plant origin with unique structural features that can be used as such or after chemical modification as excellent plasticizers or process aids of low cost. Thus, for example, a variety of compounds have been synthesized from renewable natural resources¹ such as cashew nut shell liquid (CNSL),^{2,3} castor oil,⁴ linseed oil,⁵ rubber seed oil (RSO),⁶ etc., which have shown potential for a variety of applications. Rubber seed oil, which

contains unsaturated triglycerides,⁷ has been found to be suitable for the manufacture of soaps,⁸ surface coatings, etc.⁹ Aigbodion et al.^{10,11} have synthesized a variety of alkyd resins containing a wide range of RSO content. Epoxidation of rubber seed oil has also been reported.^{12,13–15} It was found that epoxidized rubber seed oil (ERSO) markedly enhance the thermal stability of polyvinyl chloride (PVC).¹³ The stabilizing effect of RSO, ERSO, and the barium soaps of RSO and ERSO on the degradation of PVC has also been studied by Okieimen et al.¹⁴ It has been shown that barium, cadmium, and lead soaps of rubber seed oil are relatively effective in suppressing thermal dehydrochlorination of PVC.¹⁵ It has also been reported that dark factice prepared from rubber seed oil has functioned well as a processing aid in rubber goods manufacture with equal result as those obtained from commercial factice.¹⁶

However, the use of either RSO or ERSO as a processing aid or a modifier of vulcanizate properties of NR has not been reported. An attempt has been made in this direction to study the pro-

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Contract grant sponsor: Third World Academy of Science, Italy; Council of Scientific and Industrial Research, New Delhi.

Journal of Applied Polymer Science, Vol. 77, 1413–1418 (2000)
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Table I Major Fatty Acid Components of Rubber Seed Oil

Fatty Acid	%
Saturated	
C _{16:0} palmitic acid	10.2
C _{18:0} stearic acid	8.7
Total	18.9
Unsaturated	
C _{18:1} oleic acid	24.6
C _{18:2} linoleic acid	39.6
C _{18:3} linolenic acid	16.3
Total	80.5
Others	0.6

cessability and physico-mechanical properties of NR modified with RSO and ERSO, the results of which are presented in this article.

EXPERIMENTAL

Materials

NR conforming to grade "ISNR-5" was obtained from the Rubber Research Institute of India, Kottayam. RSO, having the characteristics given in Tables I and II, was obtained from M/s Kathrivel & Bros., Tamil Nadu, India, and used after refining by neutralisation with alkali.¹⁷ Analytical grade reagents for the synthesis and characterization of ERSO were obtained from British Drug House (BDH), Poole, UK. Other chemicals such as zinc oxide, stearic acid, sulphur, mercapto benzothiazole sulphenamide (MBT), and tetramethyl thiuram disulphide (TMT) were of the commercially available rubber grades.

Methods

Analysis of RSO

Properties of RSO such as color, specific gravity, acid value, saponification value, and iodine value were determined according to IUPAC standard methods.¹⁸

Epoxidation of RSO

Epoxidation was carried out with peracetic acid generated *in situ* at 60–70°C in solution of the oil in benzene. Three hundred grams of RSO was weighed into a three-neck round-bottom flask fitted with motorized stirrer, reflux condenser, and

thermometer. Forty-eight grams of glacial acetic acid and 3.36 g conc. sulphuric acid were added and the mixture heated to 60°C. One hundred nineteen grams of 30% hydrogen peroxide was added dropwise over a 2-h period with constant stirring, while maintaining the temperature between 60 and 70°C. The reaction was continued for 8 h. At the end of the reaction, the content of the flask was transferred to a separating funnel where the aqueous phase was separated from the oil phase. The oil phase was washed repeatedly with warm water until free of acid. Benzene was removed under reduced pressure using rotary flash evaporator. The product was dried with magnesium sulphate and analyzed for its properties such as acid value, iodine value, saponification value, color, and oxirane content using IUPAC standard methods.¹⁸

Processability Characteristics

Melt Viscosity and Power Consumption for Mixing

Unmodified NR and NR containing 10% each of RSO and ERSO were mixed on a Brabender Plasticorder (PLE 651) fitted with a cam-type mixer/measuring head at room temperature and at a rotor speed of 30 rpm. The torque profiles of 40 g each of the samples were measured at preset rotor speeds (*S*) of 30, 45, and 60 rpm. The melt viscosity index (η) and power consumption for mixing (*P*) were calculated from the steady value of torque at the 10th minute (*M*) using the following relations as reported earlier.^{19,20} Thus,

$$\eta = M/S \quad (1)$$

Table II Some Physico-Chemical Properties of Rubber Seed Oil (RSO) and Epoxidized Rubber Seed Oil (ERSO)

Property	RSO	ERSO
Color	Dark	Light brown
Specific gravity at 30°C	0.910	0.919
Acid value (mg KOH/g)	53.09	53.20
Saponification value (mg KOH/g)	206.20	216.34
Iodine value (Wijs) (g I ₂ /100 g)	135.36	81.58
Bulk viscosity (Poise)	0.42	0.54
Oxirane oxygen (%)	—	2.10

Table III Processability Characteristics of the Mixes^a

Parameter	Sample	Rotor Speed (rpm)		
		30	45	60
Melt viscosity index, η (m · g/rpm)	NR	47.6	30.6	22.1
	NR+ 10% RSO	44.2	27.2	18.7
	NR+ 10% ERSO	44.2	27.2	17.9
Power consumption for mixing, P (W)	NR	44	64	82
	NR+ 10% RSO	41	57	69
	NR+ 10% ERSO	41	57	66

^a Obtained from Brabender Plasticorder at room temperature.

$$P = M\omega \quad (2)$$

where M is the torque and ω is the angular frequency of the rotor. The results are given in Table III.

Plasticity

NR was mixed with 10 phr each of RSO and ERSO in an open two-roll mixing mill (150 × 300 mm) as per ASTM D-3182-74 using the recipe given in Table IV. The initial plasticity (P_0) of the mixes at room temperature was measured using a Wallace Rapid Plastimeter as per ASTM D-926-67.

Cure Characteristics

The cure characteristics at 150°C of the mixes were measured using an oscillating disk rheometer (Monsanto ODR-R100) as per ASTM D-2084-81.

Mechanical Properties

Test specimens were molded in an electrically heated hydraulic press at 150°C and for the optimum cure times as determined from the ODR. Hardness of the specimens were measured using an indentation hardness tester (Type Shore-A) as per ASTM D-2240-86. Tensile properties of the

vulcanizates were measured in an INSTRON tensile testing machine (model-1121) at a crosshead speed of 500 mm/min using dumbbell test specimens (Type II) as per ASTM D-412-87 (method A). Tear strength was measured on the same instrument using angle tear test specimens (Die C) at a crosshead speed of 500 mm/min as per ASTM D-624-86.

Chemical Crosslink Density

The chemical crosslink density (CLD) of the vulcanizates was determined by following the procedure of equilibrium swelling in benzene.²²⁻²⁴ The volume fraction of the rubber, V_r , was calculated from the swollen and deswollen weights.²² The chemical crosslink density expressed as $(2M_c\text{-chem})^{-1}$ was calculated using the Flory-Rehner equation²⁴ given as

$$\begin{aligned}
 & -(\rho V_0)/M_c \\
 & = [(\ln(1 - V_r) + V_r + \xi V_r^2)/(V_r^{1/3} - V_r/2)] \\
 & \quad - 2\rho V_0/M_n \quad (3)
 \end{aligned}$$

where ρ is the density of the vulcanizate, V_0 is the molar volume of the solvent, M_c is the molecular weight between crosslinks, V_r is the volume fraction of rubber in the swollen sample given as

$$V_r = [(D - FT)\rho_r^{-1}]/[(D - FT)\rho_r^{-1} + A_0\rho_s^{-1}] \quad (4)$$

where D is the deswollen weight of the vulcanizate, F is the weight fraction of insoluble components of the vulcanizate, T is the initial weight of test specimens, ρ_r is the density of rubber, A_0 is the weight of solvent absorbed under equilibrium condition, ρ_s is the density of the solvent, ξ is the polymer-solvent interaction parameter given as

Table IV Composition of Mixes

Mix Code ^a	BM	R	E
RSO	—	10	—
ERSO	—	—	10

^a Base mix—NR 100, ZnO 5, Stearic acid 2, sulphur 2, MBT 1.5, TMT 0.5.

Table V Wallace Plasticity of the Mixes

Mix Code	BM	R	E
Initial Plasticity, P_0	16.5	20	21

$\xi = 0.44 + 0.18 V_r$, and M_n is the number average molecular weight of NR.

Thermal Analysis

Thermogravimetric analysis (TGA) of the vulcanizates was carried out in a thermogravimetric analyzer (model DuPont 951) coupled with a data processor (Thermal Analyst 2000) over the temperature range of 40 to 700°C in air at a heating rate of 20°C/min. The activation energy for decomposition (E_a) of the vulcanizates in the range of 350–390°C was calculated by the Freeman-Carroll method.²⁵

RESULTS AND DISCUSSION

Processability of the Mixes

Melt Viscosity and Power Consumption for Mixing

The melt viscosity and power consumption for mixing of raw NR and NR containing 10 phr each of RSO and ERSO have been studied using the Brabender Plasticorder at room temperature and at different rotor speeds such as 30, 45, and 60 rpm. The results are given in Table III. Thus, at the rotor speed of 30 rpm the melt viscosity index decreases from 47.6 m · g/rpm to 44.2 m · g/rpm in the presence of 10 phr each of RSO and ERSO. At the rotor speed of 45 rpm the corresponding decrease is from 30.6 to 27.2. However, at the rotor speed of 60 rpm, the melt viscosity index decreases from 22.1 for the unmodified NR to 18.7 for the sample containing 10 phr of RSO and 17.9 for the sample containing 10 phr of ERSO. The power consumption for mixing also decreases proportionately in all cases. But at the rotor speed of 60 rpm, power consumption for NR modified with ERSO is slightly lower.

The comparatively lower values of melt viscosity index and power consumption for mixing of NR modified with RSO and ERSO show the softening action and plasticizing effect of RSO and ERSO on NR.

Table VI Cure Characteristics of the Mixes at 150°C

Mix Code	BM	R	E
Scorch time, t_2 (s)	150	195	195
Optimum cure time, t_{90} (s)	270	360	375
Maximum cure, L_f (dNm)	57.5	49.8	52
Cure rate, (s ⁻¹)	0.83	0.61	0.56

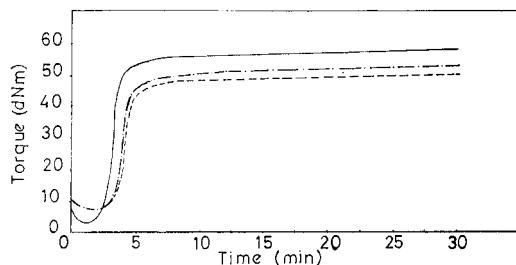
Plasticity

NR was mixed with curatives and 10 phr each of RSO and ERSO as per the composition given in Table IV. The results on the initial plasticity index (P_0) of the mixes are given in Table V. The increase in plasticity index from 16.5 to 20 in the presence of 10 phr of RSO, and the increase from 16.5 to 21 in the presence of 10 phr of ERSO further confirms the plasticizing effect of these oils.

The plasticizing effect may be due to the presence of long chain unsaturated and saturated fatty acids (as given in Table I) present in RSO, which may enhance the segmental mobility of NR.

Cure Characteristics

The cure characteristics of the mixes as obtained from the ODR at 150°C are given in Table VI and the rheographs in Figure 1. The results given in Table VI and the rheographs show an increase in scorch time from 150 to 195 s, and a considerable decrease in the rate of cure and maximum state of cure. The lower state of cure of the mixes containing 10 phr each of RSO and ERSO has been further confirmed by the comparatively lower chemical crosslink density (CLD) of their vulcanizates as given in Table VII. A similar reduction in the rate of cure and chemical crosslink density have been reported for NR modified with 10 phr of

**Figure 1** Rheographs at 150°C of the NR mixes.

phosphorylated cashew nut shell liquid prepolymer (PCNSL),³ wherein the long chain aliphatic unsaturated segment of the prepolymer is understood to take part in the cure reaction with NR, preventing the crosslinking between NR at nearby unsaturation sites. It is presumed that a similar mechanism may be operating in the present systems containing RSO and ERSO, because they contain C₁₈ unsaturated hydrocarbon moieties.

Physico-mechanical Properties of the Vulcanizates

Mechanical Properties

Results on the physico-mechanical properties of the vulcanizates are given in Table VII. It shows a reduction in hardness and tensile modulus at 300% elongation of NR upon modification with 10 phr each of RSO and ERSO, commensurate with the reduction in chemical crosslink density. Thus, RSO and ERSO are found to act as softening agents in NR.

Despite lower CLD, the vulcanizates containing RSO and ERSO are found to have comparatively higher tensile strength and elongation at break. This again is very similar to that of NR modified with 10 phr of PCNSL.^{3,25} This is probable because RSO and ERSO may form an entangled network structure with NR, permitting a higher degree of extensibility and, consequently, a higher strength. The tear strength of the vulcanizate also shows an improvement in presence of RSO and ERSO. It is expected that the softening effect of RSO and ERSO on NR along with higher tensile strength and elongation may lead to deviations in the propagation of major crack path,

Table VII Physico-Mechanical Properties of the Vulcanizates

Mix Code Parameter	BM	R	E
Hardness (Shore A)	28	24.5	27
CLD × 10 ⁴ (mol/g RH)	3.481	1.364	1.371
Tensile modulus—300% (MPa)	1.9	1.8	1.8
Tensile strength (MPa)	9.4	13.9	14.5
Elongation at break (%)	990	1160	1150
Tear strength (kN/m)	30.98	31.18	34.12
Thermal stability index, <i>T</i> ₅₀ (°C)	384	382	381
Activation energy, <i>E</i> _a (kCal/mol)	42.5	45.8	45.8

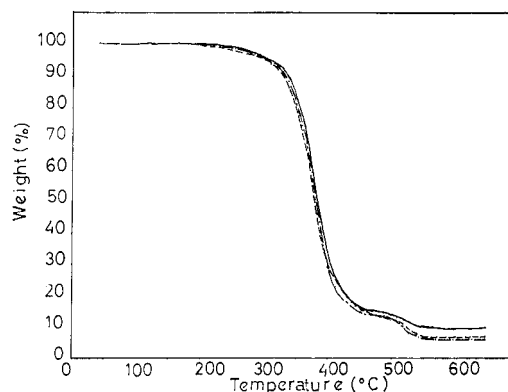


Figure 2 Thermograms of the NR vulcanizates.

resulting in the observed improvement in tear strength. A widening of crack tip diameter has been reported for vulcanizates having a lower CLD and modulus, which in turn, results in an enhancement of tear strength.^{27,28} This mechanism has been found to be operating in PCNSL modified NR also.²⁹

Thermal Stability

The thermograms obtained from decomposition of the vulcanizates in air at a heating rate of 20°C/min are given in Figure 2. The parameters of thermal stability calculated from it are given in Table VII. The closeness of the values of thermal stability index (*T*₅₀) and activation energy for thermal decomposition (*E*_a) indicates that the thermal stability of the NR vulcanizate is practically unaffected by the modification with either RSO or ERSO. It was reported in the case of blends of PVC with ERSO that the blend exhibited a higher thermal stability.^{13–15} This was explained as due to polar–polar interactions between the epoxide group and the PVC. It can, therefore, be noted that such interactions are not possible with NR.

CONCLUSION

The results of the present study show that both RSO and ERSO can act as multifunctional additives in compounding of NR as plasticizers, softening agents, and improvers of scorch safety of the mixes and mechanical properties of the vulcanizates such as tensile strength, elongation at break, and tear strength. The reduction in the rate of cure of the modified mixes and chemical

crosslink densities of their vulcanizates indicates the involvement of these additives in the cure reaction with NR. The marginal improvement in processability characteristics and vulcanizate quality of NR modified with ERSO over that modified with RSO is attributed to the presence of an epoxide group. It seems from these findings that ERSO with a higher epoxide content will be more promising as a multifunctional additive for NR. Furthermore, it appears that the improvement in properties such as tensile and tear strength of the NR formulations modified with RSO and ERSO may be of use in the design of formulations for specific applications such as side walls of automobile tires or molded products.

The authors would like to express their sincere thanks to Dr. G. Vijay Nair, Director, RRL, Thiruvananthapuram, for support and encouragement, and to Dr. N. M. Mathew and Dr. K. T. Thomas of the Rubber Research Institute of India, Kottayam, for extending their processing and testing facilities. Our thanks are also due to Dr. S. Someswara Rao and Dr. S. S. Bhagawan of the Vikram Sarabhai Space Centre, Thiruvananthapuram, for mechanical property measurements. The financial support extended to AIA by the Third World Academy of Sciences, Italy, and the Council of Scientific and Industrial Research, New Delhi, is gratefully acknowledged.

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