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Processability characteristics and physico-mechanical properties of natural rubber modified with cashewnut shell liquid and cashewnut shell liquid–formaldehyde resin

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Abstract

Natural rubber (NR) has been modified with 5–15 phr each of cashewnut shell liquid (CNSL) and cashewnut shell liquid–formaldehyde (CNSLF) resin with a view to studying the processability characteristics of the mixes and physicomechanical properties of their vulcanizates. The plasticizing effect of these additives in NR was shown by the reduction in melt viscosity and power consumption during mixing in a Brabender Plasticorder compared to that of unmodified NR. Despite the reduction in chemical crosslink density, the vulcanizates containing 15 phr of CNSL and 5–10 phr of CNSLF showed higher tensile and tear strengths and elongation at break. The higher values of activation energy for thermal decomposition of the vulcanizates containing 15 phr each of CNSL (301 kJ/mol) and CNSLF (372 kJ/mol) than that of the unmodified NR vulcanizate (177 kJ/mol) indicate improvement in thermal stability of NR vulcanizates in presence of the modifiers.

Keywords: Natural rubber; Cashewnut shell liquid; Processability characteristics; Physicomechanical properties

1. Introduction

Two of the prime requirements of an elastomer formulation for any specific application are good processability of the mixes and a good combination of desired physicomechanical properties of the vulcanizates. Also, it is essential that the composition should be cost effective. In this respect, the concept of a *multifunctional additive* [1–14] holds significance particularly if it is based on a renewable natural resource. Mixing and curing constitute two of the key operations affecting the economy of the process and the physicomechanical properties of the final product. The plasticizing effect of an additive aids the mixing operation and the presence of crosslinkable sites on a plasticizer may enhance the rate of cure. Physicomechanical properties such as tensile strength, tear strength, elongation at break and thermal stability are very often specified as criteria of quality of the vulcanizates. Cashewnut shell liquid (CNSL), a renewable natural resource obtained from the plant *Anacardium occidentale L* and its derivatives have been used widely in rubber compounding [15,16]. It has recently been shown that phosphorylated cashewnut shell liquid (PCNSL) prepolymer can function as a multifunctional additive in natural rubber (NR) which can lead to improvement in processability of mixes and physicomechanical properties of their vulcanizates

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[17–27]. The multifunctional effect of PCNSL in NR has been attributed to the presence of a hydrophobic aliphatic side chain and a hydrophilic phosphate group in the same molecule. CNSL–formaldehyde (CNSLF) resin (which is being used in many applications such as surface coatings, brake linings, etc. [15]) possesses similar functionalities (the hydrophilic hydroxyl group and the hydrophobic aliphatic side chain) and requires a study of its applicability in NR. The mixing behaviour, cure characteristics and physicomechanical properties of NR modified with different concentrations of CNSLF have been studied in comparison with the same dosages of CNSL, the results of which are presented in this paper.

2. Experimental

2.1. Materials

NR conforming to grade ISNR-5 was obtained from the Rubber Research Institute of India, Kottayam. CNSL (technical grade) conforming to Indian Standard Specification IS:840 (1964), was obtained from Cashew Export Promotion Council, Kollam, India.

CNSLF resin was prepared from CNSL using the method for phenolic resins employing sodium hydroxide (NaOH) as catalyst [28]. Thus, 110 g CNSL and 24 ml of 37% formaldehyde (aq.) corresponding to a mole ratio of 1.25:1 and 10 ml of 4 M NaOH (aq.) were reacted in a round bottom flask fitted with a stirrer, reflux condenser and thermometer at 100°C [29]. The reaction mixture was stirred continuously while heating for 4 h. Thereafter, the water of reaction was distilled under vacuum at about 80°C.

Benzene (AR grade) was obtained from E. Merck. Other chemicals such as zinc oxide, stearic acid, sulphur, mercaptobenzothiazole sulphenamide (MBT) and tetramethyl thiuramdisulphide (TMT) were of the commercially available rubber grade.

2.2. Methods

2.2.1. Processability characteristics

2.2.1.1. Melt viscosity and power consumption for mixing. Unmodified NR and NR containing 5, 10 and 15 phr each of CNSL and CNSLF 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 speed (S) of 30, 60 and 90 rpm and at different temperatures viz. 30°C, 100°C and 140°C. The melt viscosity index (η) and power consumption for mixing (P) were calculated from the steady value of torque at the tenth minute (M) using the following relations as reported earlier [30,31]. Thus,

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

and

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

where M is the torque and ω is the angular frequency of the rotor. The melt viscosity of the mixes are given in Tables 1 and 2.

NR was mixed with 5–15 phr each of CNSL and CNSLF in an open two roll mixing mill (150 mm × 300 mm) as per the composition given in Table 3 and as per ASTM D-3182-74.

Table 1
Melt viscosity (η) of unmodified and CNSL modified NR (Pa s)

CNSL (phr)	Temperature (°C)	Shear rate, γ (s^{-1})		
		28.5	57	85.5
–	30	2409	1004	625
	100	1608	768	532
	140	1352	676	424
5	30	2258	937	580
	100	1472	703	491
	140	1205	602	402
10	30	2142	870	491
	100	1339	636	446
	140	1071	534	379
15	30	1941	803	446
	100	1205	569	379
	140	937	469	312

Table 2
Melt viscosity (η) of CNSLF modified NR (Pa s)

CNSLF (phr)	Temperature (°C)	Shear rate, γ (s^{-1})		
		28.5	57	85.5
5	30	2409	937	556
	100	1790	736	488
	140	1406	703	445
10	30	2276	789	446
	100	1663	724	469
	140	1322	671	436
15	30	2046	629	332
	100	1577	703	455
	140	1278	639	426

Table 3
Composition of mixes

	Mix code[a]						
	BM	C_5	C_{10}	C_{15}	CF_5	CF_{10}	CF_{15}
CNSL	–	5	10	15	–	–	–
CNSLF	–	–	–	–	5	10	15

[a] Basic mix – NR 100, ZnO 5, Stearic acid 2, Sulphur 2, MBT 1.5, TMT 0.5.

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

2.2.2. Mechanical properties

Test specimens were moulded in an electrically heated hydraulic press at 150°C and for the optimum cure times as determined from the ODR. Tensile properties of the vulcanizates were measured in an INSTRON tensile testing machine (model-1121) at a crosshead speed of 500 mm/min using dumbell 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.

2.2.3. Chemical crosslink density

The chemical crosslink density (CLD) of the vulcanizates was determined by following the procedure of equilibrium swelling in benzene [32–34]. The volume fraction of the rubber, V_r was calculated from the swollen and deswollen weights [32]. The CLD expressed as $(2M_c\text{chem})^{-1}$ was calculated using the Flory–Rehner equation [35] given as

$$-(\rho V_0)/M_c = [(\ln(1-V_r)+V_r+\xi V_r^2)/(V_r^{1/3}-V_r/2)] - 2\rho V_0/M_n \qquad (3)$$

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

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

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 and ρ_s is the density of the solvent, ξ is the polymer–solvent interaction parameter given as $\xi = 0.44 + 0.18V_r$ and M_n is the number average molecular weight of NR.

2.2.4. Thermal analysis

Thermogravimetric analysis (TGA) of the vulcanizates was carried out in a thermogravimetric analyser (model DuPont 951) coupled with a data processor (Thermal Analyst 2000) over a temperature range of 40–700°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 [36].

3. Results and discussion

3.1. Processability characteristics

3.1.1. Melt viscosity

The melt viscosity of unmodified NR, CNSL modified NR and CNSLF modified NR at different shear rates and temperatures are given in Tables 1 and 2. The results show progressive decrease in melt viscosity of NR with increase in temperature, shear rate and dosage of the modifiers. However, the decrease at corresponding dosage of the modifier in CNSL modified NR is to a greater extent than that of the CNSLF modified NR. Fig. 1 shows the plots of power consumption for mixing unmodified NR, CNSL modified NR and CNSLF modified NR at room temperature and at rotor speed ranging from 30 to 90 rpm. It shows a distinct reduction in power consumption for mixing NR in presence of the modifiers, particularly with the increase in dosage from 5 to 15 phr.

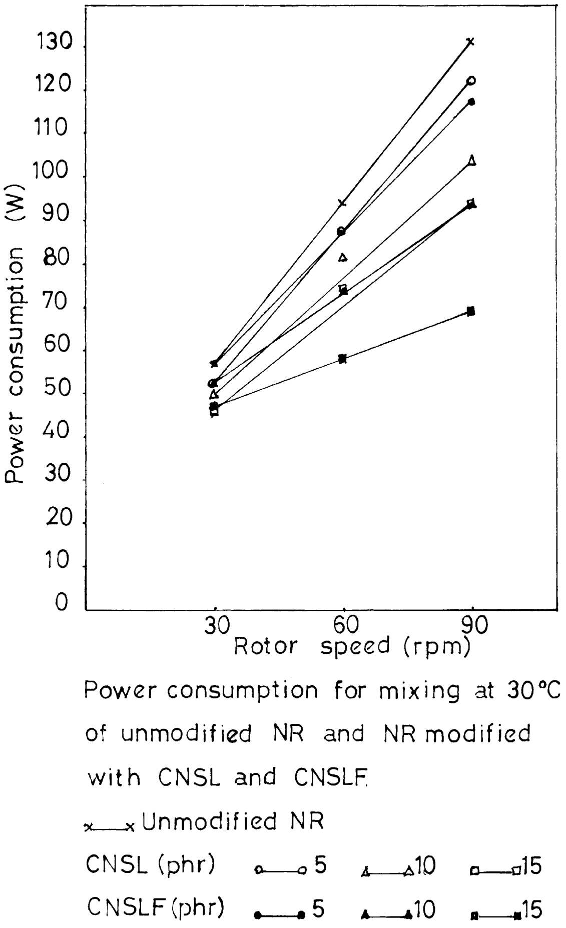

Fig. 1. Power consumption for mixing at 30°C of unmodified NR and NR modified with CNSL and CNSLF.

Table 4
Cure characteristics of the mixes

Parameter	Mix code						
	BM	C_5	C_{10}	C_{15}	CF_5	CF_{10}	CF_{15}
Minimum torque, L_i (dN m)	3.5	4	4.5	4.5	5	7	7
Scorch time, t_2 (s)	150	120	90	75	120	105	105
Optimum cure time, t_{90} (s)	270	240	210	180	225	225	180
Optimum torque (dN m)	52	49	47	42	50	50	46
Maximum torque, L_f (dN m)	57.5	54	52	46	54.5	55	50
Cure rate (s^{-1})	0.83	0.83	0.83	0.95	0.95	0.83	1.33

The reduction in melt viscosity of NR in presence of CNSL and CNSLF indicates the plasticizing effect of these additives on NR. This plasticizing effect may possibly be due to the C_{15} unsaturated side chain of CNSL and CNSLF which may enhance the segmental mobility of NR.

3.1.2. Cure characteristics

The cure characteristics of the mixes obtained using an ODR at 150°C are given in Table 4 and the rheographs in Fig. 2.

The results given in Table 4 and Fig. 2 show that there is a progressive reduction in the scorch time of the rubber compounds with increase in dosage of both CNSL and CNSLF. This is expected to be due to the increased availability of unsaturation sites of the side chain fragment of CNSL and CNSLF for cure reactions with that of the isoprene chains of NR. The possibility for such a reaction has been reported for a similar system earlier also [23]. Further, the results in Table 4 show that the maximum state of cure decreases progressively with the increase in dosage of CNSL in NR. However, this decrease is comparatively lower in presence of CNSLF. This is further supported by the values of CLD of the vulcanizates given in Table 5. The comparatively higher values of CLD of the vulcanizates containing CNSLF as against that containing CNSL suggest the probable interactions between methylol groups in CNSLF resin in addition to the entanglement between the unsaturated C_{15} side chain and the isoprene main chain of NR. The higher cure rate of the mixes containing 15 phr each of CNSL and CNSLF also indicates the probability for such interactions. The decrease in the maximum state of cure and CLD of the modified NR vulcanizates at lower concentrations may be due to the presence of C_{15} hydrocarbon chain coming in between the crosslink sites of the isoprene main chains. A similar observation has been made recently in PCNSL modified NR vulcanizates which also showed a reduction in CLD with increase in dosage of the modifier [18].

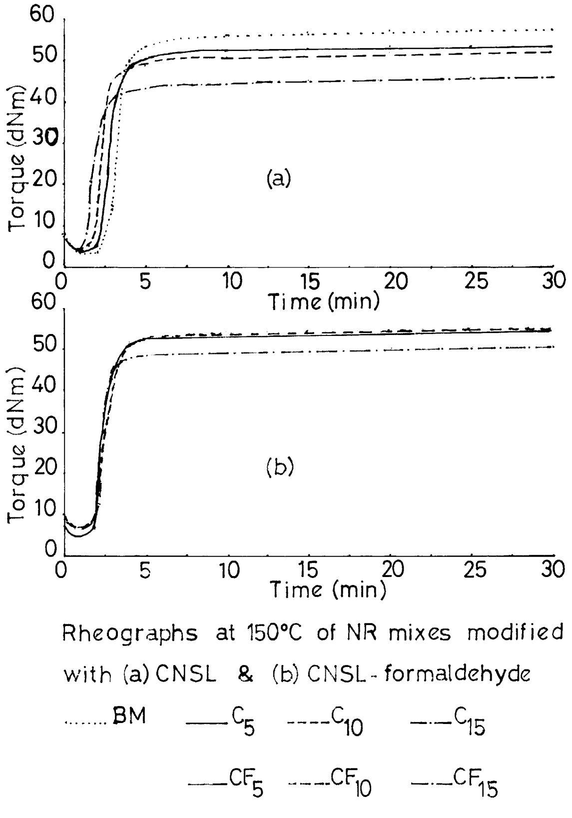

Fig. 2. Rheographs at 150°C of NR mixes modified with (a) CNSL and (b) CNSLF.

3.2. Physicomechanical properties

The tensile properties, tear strength and activation energy for thermal decomposition of the different vulcanizates are given in Table 5. This data shows that both tensile strength and elongation at break of the NR vulcanizate increase progressively with the increase in dosage of the modifiers from 5 to 15 phr. It is also seen that tensile strength of the vulcanizate modified with CNSLF is higher than that containing the same dosage of CNSL which is a reflection of the higher CLD of the former. However, it is to be noted that the tensile strength of the NR vulcanizates containing CNSL and CNSLF are higher than that of the unmodified NR

Table 5
Physicomechanical properties of the vulcanizates

Parameter	Mix code						
	BM	C_5	C_{10}	C_{15}	CF_5	CF_{10}	CF_{15}
Tensile modulus 300% (MPa)	1.9	1.9	1.7	2.3	2.4	2.2	2.5
Tensile strength (MPa)	9	10	9	12	14	13	15
Elongation at break (%)	990	980	1030	950	1000	1060	1130
Tear strength (kN/m)	31	29	27	35	42	34	28
Activation energy for thermal decomposition, E_a (kJ/mol)	177	157	159	301	274	264	372
CLD ($\times 10^4$ mol/g RH)	3.48	–	1.02	1.21	2.05	1.85	3.10

vulcanizate despite the lower CLD of the modified NR vulcanizates. This is expected to be due to the probable participation of the unsaturated side chain segment of CNSL and CNSLF in crosslinking reaction with those of NR. Such a reaction has been reported earlier for similar systems containing PCNSL prepolymer [18,23]. In such systems, it is believed that the lower CLD along with plasticizing and softening effect of the additive permits a higher degree of extension prior to break along with higher strength. The results also show that the tear strength of the vulcanizate increases in presence of 15 phr of CNSL and 5–10 phr of CNSLF.

Table 5 also shows that addition of CNSLF improved the properties to a higher level than that of CNSL itself. This can be understood from the fact that CNSLF is a polymeric resin and CNSL is monomeric in nature. It is reported that in many similar cases the contribution of polymeric additives is much more pronounced than that of the monomeric additives [37,38].

Fig. 3 shows the thermograms of unmodified NR vulcanizate and NR vulcanizates containing 5–15 phr each of CNSL and CNSLF. The results given in Table 5 show that the activation energy for thermooxidative decomposition of the NR vulcanizate increases significantly with the increase in dosage of CNSLF from 5 to 15 phr. This again is analogous to similar results obtained for PCNSL modified NR vulcanizates [16,17,20]. The improved resistance to thermooxidative decomposition of the vulcanizates containing CNSL and CNSLF may possibly be due to the participation of the aromatic groups of CNSL and CNSLF in the decomposition reaction.

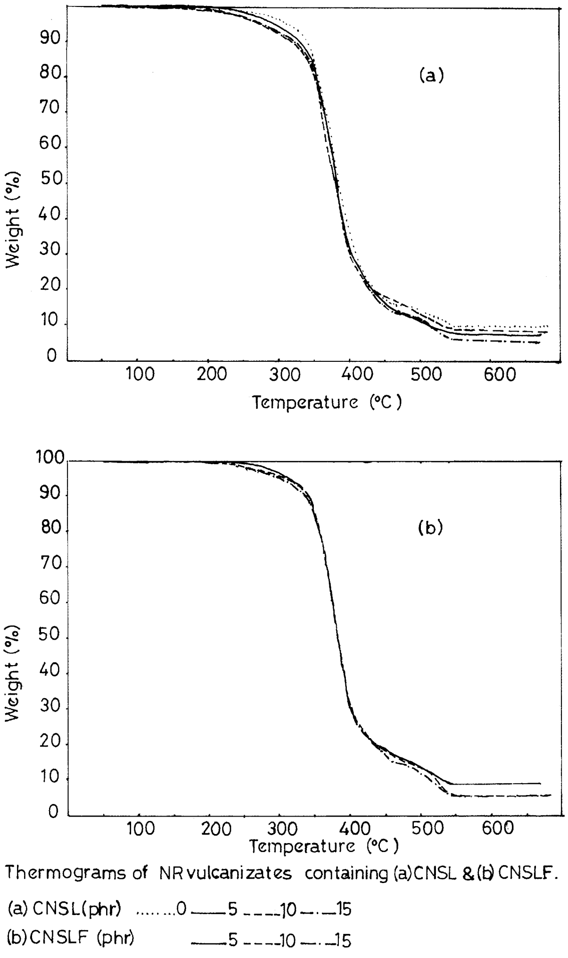

Fig. 3. Thermograms of unmodified NR vulcanizate and NR vulcanizates containing 5–15 phr each of CNSL and CNSLF.

4. Conclusion

The results of the present study show that modification of NR with 5–15 phr each of CNSL and CNSLF can lead to improvement in processability of the mixes due to plasticization effect along with increase in some of the physicomechanical properties, despite a reduction in CLD. The results further indicate that the effect of CNSLF (a polymeric resin) on the physicomechanical properties of NR is more pronounced than that of CNSL alone. This study thus gives an indication of the roles of CNSL and CNSLF as potential multifunctional additives in compounding of NR.

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