Cure Characteristics and Physicomechanical Properties of Natural Rubber Modified with Phosphorylated Cashew Nut Shell Liquid Prepolymer—A Comparison with Aromatic Oil

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ABSTRACT: Natural rubber (NR) has been modified with 10 phr each of phosphorylated cashew nut shell liquid (PCNSL) prepolymer and an aromatic oil (spindle oil) in a typical semi-efficient vulcanization (SEV) system. Despite the lower chemical crosslink density, the PCNSL modified NR vulcanizate showed higher tensile strength, elongation at break, thermal stability, and resistances to fatigue failure and thermo-oxidative decomposition, as compared to the vulcanizate containing the same dosage of spindle oil. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 813–818, 1999

Key words: natural rubber; phosphorylated cashew nut shell liquid; cure characteristics; physicomechanical properties

INTRODUCTION

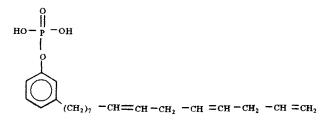
While designing rubber formulations for any application, two of the most important aspects to consider are (1) the ease of processability of the compounds, and (2) the required physicomechanical properties of the vulcanizates. This is quite often achieved by proper designing and "compounding" of the elastomers with such additives as fillers, plasticizers, and curatives. Recently, however, there has been noticeable concern with respect to development of *multifunctional additives* that may help in reduction of cost of the compounds. It has been reported by the authors that phosphorylated cashew nut shell liquid (PCNSL) prepolymer can be used as a "multifunctional additive" in the compounding of NR.¹⁻⁹

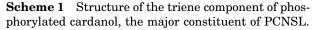
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PCNSL performs various roles as a plasticizer,¹ tackifier,² co-agent for curing,^{3,4} and improver of physicomechanical properties of gum and filled compounds of NR.⁵⁻⁹ It is well known that aromatic oils are widely used in compounding of diene rubbers to improve the processability of compounds and to impart the desired physicomechanical properties to their vulcanizates. Hence, it was considered appropriate to make a comparative study between a commercially available plasticizer (spindle oil) and PCNSL with respect to their effect on the cure characteristics and physicomechanical properties of NR. The study was limited to a semi-efficient vulcanization (SEV) system of NR with 10 phr each of spindle oil and PCNSL. The cure characteristics of the compounds and some of the physicomechanical properties and thermo-oxidative decomposition characteristics of the vulcanizates have been studied, the results of which are reported in this article.





EXPERIMENTAL

Materials

Natural rubber (ISNR 5 grade) was obtained from the Rubber Research Institute of India, Kottayam. Technical grade cashew nut shell liquid (CNSL) of Indian Standard specification IS:840 (1964) was obtained from Kerala State Cashew Development Corporation, Kollam. PCNSL prepolymer (I) was synthesized at the Regional Research Laboratory (CSIR), Trivandrum, by the phosphorylation of CNSL with o-phosphoric acid at $175 \pm 5^{\circ}$ C.¹⁰

Aromatic oil (spindle oil) and such chemicals as ZnO, stearic acid, sulphur, mercaptobenzothiazole (MBT), and tetramethyl thiuram disulphide (TMT) were the commercially available rubber grades obtained from Calcutta.

Methods

Formulations of the mixes are given in Table I. The mixes were prepared on a two-roll open mixing mill (300 mm \times 150 mm) as per ASTM D-3182-74.

Cure characteristics of the compounds were measured at 150°C and 180°C in an oscillating disk rheometer (Monsanto R100) as per ASTM D-2084-79. Test specimens were prepared by compression molding at 150°C for the respective optimum cure time in an electrically heated hydraulic press at a pressure of 5 N/mm². Tensile properties of the vulcanizates were measured in a universal testing machine (Zwick UTM 1435) at a crosshead speed of 500 mm/min, as per ASTM D-412-75 (method A). Hardness was measured using an indentation hardness tester (Durometer Shore A) as per ASTM D-2240-75. Tear strength was measured on the Zwick tensile tester with unnicked tear test specimens (die C) as per ASTM D-624-73. The fatigue resistance of the samples in tensile deformation cycles was measured using a

Monsanto fatigue-to-failure tester, at an extension ratio of 1.61. The dynamic flex fatigue resistance of the vulcanizates was studied using a De Mattia flexing machine as per ASTM D-430-73 (Method B) under a strain of 20%.

The chemical crosslink density (CLD) of the vulcanizates were determined by following the procedure of "equilibrium swelling" in benzene at room temperature (33°C), using circular test specimens (diameter 10 mm) in duplicate. The volume fraction of the rubber was calculated from the swollen and de-swollen weights, using the relation, $V_r = (D - FT)/\rho_r/[(D - FT)/\rho_r) + (A_0/\rho_s)]$, where T is the weight of the specimen, D is the de-swollen weight, F is the weight-fraction of the insoluble components, A_0 is the weight of the absorbed solvent, and ρ_r and ρ_s are the densities of the rubber and the solvent, respectively. The CLD expressed as $(2 \text{ M}_{c.chem})^{-1}$ was calculated using the Flory–Rehner equation.¹¹

The thermogravimetric analysis of the vulcanizates in air was carried out on a thermal analyzer (Du Pont-951) coupled with a data processor (Thermal Analyst-2000), at heating rates of 10°C/ min, 20°C/min, and 40°C/min and at temperatures ranging from 40 to 700°C, and the kinetic parameters for degradation were determined by the method of Freeman and Carroll.¹²

RESULTS AND DISCUSSION

Modification of the base mix with 10 phr of PCNSL resulted in a decrease in Mooney viscosity $[ML(1 + 4)100^{\circ}C]$ from 35.5 to 23.25. However, the Mooney viscosity of the NR mix containing the same dosage of spindle oil was 14.5, which indicates a higher degree of plasticization in the latter.

Ta	abl	le	Ι	C	ompo	sitio	n of	the	Mixes
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Mix Code	SN_0	SNP_{10}	SNO_{10}
NR	100	100	mix 100
ZnO	10	10	10
Stearic acid	2	2	2
Sulphur	1.6	1.6	1.6
MBT	1.5	1.5	1.5
TMT	0.3	0.3	0.3
PCNSL		10	
Spindle oil			10

	Mix Code ^a			SNO ₁₀
Temp. (°C)	Parameters	SN_0	SNP_{10}	
150	Scorch time, t_2 (s)	100	120	135
	Optimum cure time, t_{90} (s)	165	203	195
	Maximum cure, L_f (dNm)	51	38.25	41
	Cure rate (s^{-1})	1.54	1.20	1.67
180	Scorch time, t_2 (s)	68	68	64
	Optimum cure time, t_{90} (s)	90	120	89
	Maximum cure, L_f (dNm)	27.5	23.3	22
	Cure rate (s^{-1})	4.55	1.92	4
	Reversion time (s)	210	338	143

Table II Cure Characteristics of the NR Mixes Containing PCNSL and Spindle Oil

^a Subscript indicates the dosage of the plasticizer.

Cure Characteristics

The cure characteristics of the mixes at 150 and 180°C are given in Table II and the corresponding rheographs in Figure 1 (a,b). The results given in Table II and Figure 1 (a,b) show a lower rate of cure and state of cure (maximum torque) for the PCNSL modified NR compound, as compared to the unmodified NR compound. At 150°C, the scorch time of the NR compound containing PCNSL (120 s) and spindle oil (135 s) are higher

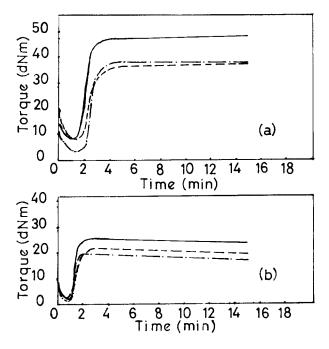


Figure 1 Rheographs of unmodified NR, PCNSLmodified NR, and oil-modified NR; (a) 150°C, (b) 180°C.

than that of the unmodified NR compound (100 s). The maximum state of cure of the PCNSL modified NR compound (38.25 dNm) is lower than that of the oil-modified NR compound (41 dNm). Also, the cure rate of the former (1.20 s^{-1}) is lower than that of the latter (1.67 s^{-1}) . The lower state of cure of the PCNSL-modified NR compound at 150°C is further evidenced by the comparatively lower values of tensile modulus at 300% extension and chemical crosslink density (CLD) of its vulcanizate, as shown in Table III. This may be attributable to the steric hindrance caused by the phosphate group and aliphatic side chain segment of PCNSL, which prevents the attainment of a higher degree of crosslinking.³ However, at 180°C, the cure rate of the PCNSL-modified NR compound increases, resulting in the attainment of a higher state of cure (23.3 dNm) as against that of the spindle oil-modified NR compound (22 dNm). Also, the scorch time at 180°C is higher for the former as compared to the latter. The results given in Table II show a distinct improvement in the reversion resistance of the PCNSL-modified NR mix at 180°C, as compared to that of the unmodified and oil modified mixes. The improved cure-reversion resistance of the PCNSL-modified mixes may be caused by the formation of crosslinks between the unsaturation sites in the aliphatic side chain segment of PCNSL and that of NR in addition to the rubber-rubber crosslinks.

Physicomechanical Properties of Vulcanizates

The results on the physicomechanical properties of the different vulcanizates are given in Table

Mix Code ^b	SN_0	SNP_{10}	SNO_{10}
Tensile strength (MPa)	18	17	16
Elongation at break (%)	1060	1120	1080
Modulus—100% (MPa)	0.56	0.44	0.54
Modulus—200% (MPa)	1.17	0.86	0.97
Modulus—300% (MPa)	1.83	1.37	1.49
Hardness (Shore A)	36.5	26	31
Tear strength (kN/m)	30.6	23.9	23.9
Monsanto fatigue-to-failure freq (kC)	42	> 72.7	$>\!50.3$
De Mattia fatigue-to-failure			
Length of crack (mm/30 kC)	23.5	9.5	25
$CLD \times 10^4 \text{ (mol/g RH)}$	0.74	0.54	0.69

Table III Physicomechanical Properties of the NR Vulcanizates Containing PCNSL and Spindle Oila

^a Samples cured at 150°C.

^b Subscript indicates the dosage of the plasticizer.

III. These results show that, despite the lower chemical crosslink density, the PCNSL-modified NR vulcanizate shows improvement in tensile properties and tensile fatigue failure, as compared to that of the vulcanizates containing an equal dosage of spindle oil. The lower tensile modulus and hardness of the PCNSL-modified NR vulcanizate as against that of the oil-modified NR vulcanizate indicate a higher degree of softening effect in the case of the former. Probably the higher flexibility of the NR matrix in presence of PCNSL hinders the propagation of cracks in the tensile and fatigue failure tests to a greater extent than that of the vulcanizate containing spindle oil, resulting in the observed improvements in tensile strength and resistance to fatigue failure. Also, the improved resistance to fatigue failure of the PCNSL-modified NR mix is evident from the lower extent of crack propagation in the De Mattia fatigue-to-failure test. This has been supported by the results given in Table III. It is expected that the lower CLD and the resultant higher flexibility of the PCNSL-modified NR permit a greater number of flexing cycles before the initiation of cracks.

Retention in Mechanical Properties after Aging

The results given in Table IV show the retention in tensile properties of the vulcanizates after accelerated aging in an air oven at 70°C for 24 and 48 hours. These results show improved retention in tensile strength, elongation at break, and tensile modulus of the PCNSL-modified NR vulcanizate after aging at 70°C for 24 and 48 hours, as compared to those of unmodified and oil-modified NR vulcanizates. This may be attributable to the postcuring reactions taking place in the PCNSLmodified NR vulcanizate during the aging period, resulting in additional crosslinks and leading to an increase in crosslink density, as reported earlier.^{3,5}

Period of Aging (h)	Mix Code	SN_0	SNP_{10}	SNO_{10}
24	Tensile strength	105	113	109
	Elongation at break	89	95	94
	Modulus—100%	114	125	109
48	Tensile strength	108	110	124
	Elongation at break	84	91	92
	Modulus—100%	129	125	109

 Table IV
 Retention in Tensile Properties after Aging at 70°C (%)

^a Subscript indicates the dosage of the plasticizer.

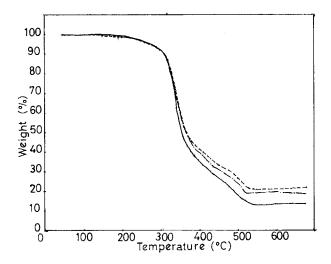


Figure 2 Thermogravitograms of unmodified NR, PCNSL-modified NR, and spindle oil-modified NR at a heating rate of 10°C/min.

Resistance to Thermo-Oxidative Decomposition (Dynamic Thermogravimetry)

The thermogravitograms of the vulcanizates obtained at the heating rates of 10°C/min, 20°C/min and 40°C/min in air are given in Figures 2, 3, and 4, respectively. The decomposition characteristics of the NR vulcanizates are given in Table V. The results show progressive increases in the thermal stability index T_{50} of all the vulcanizates with the increase in rate of heating from 10 to 40°C/min. However, at each heating rate, the T_{50} value of PCNSL-modified NR is higher than that of the

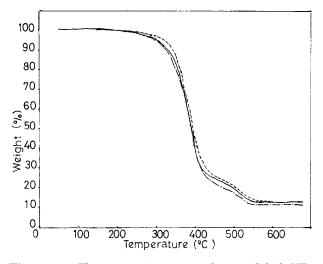


Figure 3 Thermogravitograms of unmodified NR, PCNSL-modified NR, and spindle oil-modified NR at a heating rate of 20°C/min.

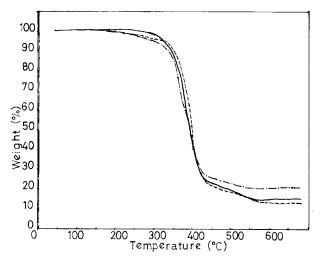


Figure 4 Thermogravitograms of unmodified NR, PCNSL-modified NR, and spindle oil-modified NR at a heating rate of 40°C/min.

unmodified and spindle oil-modified NR vulcanizates. This increase in thermal stability is clear from the thermogravitograms (Figures 2, 3, 4), as evidenced by the greater shift in the curve toward higher temperature for the PCNSL-modified NR vulcanizate, particularly above 300°C. Also, at the heating rates of 20°C/min and at 40°C/min the activation energy of thermal decomposition (in the 350-410°C range) for the PCNSL-modified NR vulcanizate is higher than that of the unmodified and spindle oil-modified NR vulcanizates. This is a clear indication of the improved resistance to thermo-oxidative decomposition of the PCNSL-modified NR vulcanizate. Also, the results from TGA show that at a heating rate of 10°C/min there is an increase in the residue obtained at 600°C for the PCNSL-modified NR vulcanizate, as compared to the unmodified NR vulcanizate and oil-modified NR vulcanizate. This indicates a probable change in the decomposition pathway from a free radical type for the unmodified and oil modified-NR vulcanizates to one involving more of condensed phase reactions in the PCNSL-modified NR vulcanizates, leading to intermediate thermally stable structures, more residue, and improved resistance to thermo-oxidative decomposition.

CONCLUSION

The results of the present study show significant improvements in the resistance to fatigue failure

Heating	Mix Code			SNO ₁₀
Rate (°C/min)	Parameters	SN_0	SNP_{10}	
10	Thermal stability index, T_{50} (°C)	358	366	370
	Activation energy, E_{α} (kCal/mol)	24.8	34.8	36.4
	Residue at 600°C (%)	14	20	19
20	Thermal stability index, T_{50} (°C)	392	396	392
	Activation energy, E_{α} (kCal/mol)	14.5	26.5	23.2
	Residue at 600°C (%)	13	13	11
40	Thermal stability index, T_{50} (°C)	391	397	392
	Activation energy, E_{α} (kCal/mol)	28.7	35.8	21.1
	Residue at 600°C (%)	15	13	20

Table V Thermo-oxidative Decomposition Characteristics from Dynamic Thermogravimetry^a

^a Medium-air.

and thermal stability of PCNSL-modified NR vulcanizate in a semi-efficient vulcanization system, as compared to an unmodified NR vulcanizate and that containing the same dosage of an aromatic oil.

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