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Vulcanization of natural rubber modified with cashew nut shell liquid and its phosphorylated derivative—a comparative study

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The vulcanization characteristics of unfilled natural rubber (NR) compounds was studied in presence and absence of cashew nut shell liquid (CNSL) and its phosphorylated derivative (PCNSL) by using an oscillating disc rheometer at various temperatures. The ease of crosslinking in the presence of PCNSL and the active role of PCNSL in the crosslinking reaction was shown by the comparatively higher values of the cure rate index and lower values of the activation energy of vulcanization. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Modification of elastomers with a variety of resins of natural and synthetic origin has long been practised as means to improve their processability characteristics such as plasticity and tack and vulcanization characteristics such as rate and state of cure[1]. In this respect, cashew nut shell liquid (CNSL)—an abundantly available renewable natural resource of tropical origin—plays a vital role in modifying some of these important properties. CNSL in its raw and chemically modified forms may be used in rubber compounding as a processing aid, adhesion promoter, property modifier, antioxidant and vulcanizing agent, as reported previously[2–6].

A phosphorylated derivative of cashew nut shell liquid (PCNSL) synthesized at the Regional Research Laboratory (CSIR), Thiruvananthapuram, has been found to be capable of acting as a multifunctional additive during compounding of natural rubber (NR)[7]. Preliminary experiments indicated its ability to improve the tensile strength, elongation at break and flame-retardant properties of NR[8]. It was observed that, at concentrations ranging from 10 to 20 phr, PCNSL improves the tensile properties, thermal stability and resistances to fatigue failure, heat ageing and thermo-oxidative decomposition of NR vulcanizates[9,10] as well as improving the self-adhesion strength (tack strength) of unfilled NR formulations[11]. Elucidation of the network structure and chemical crosslink density of the above vulcanizates established the probable involvement of PCNSL in the formation of the network structure[12]. Also, it has been established by the authors that PCNSL in the range of 10 to 20 phr acts as an excellent plasticizer and softening agent for NR[13]. The above findings put PCNSL in the category of a 'vulcanizing plasticizer' for NR. 'Vulcanizing plasticizers' are those compounds which are capable of crosslinking polymeric chains, in addition to imparting a plasticization effect, subsequently leading to a more extensible and softer product having increased tensile strength[14].

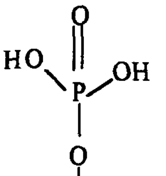
The objective of the present work was to study the vulcanization characteristics of NR modified with 10 phr each of CNSL and PCNSL and to make a comparative evaluation of the kinetic parameters for crosslinking over a range of temperatures from 150 to 180°C, in order to assess the extent of involvement of these resins in the vulcanization reactions of NR.

MATERIALS AND METHODS

Materials

Cashew nut shell liquid (CNSL) of 'technical grade', conforming to Indian Standard IS-841-1987, was obtained from M/s Vijayalakshmi Cashew Factory, Quilon.

Phosphorylated cashew nut shell liquid (PCNSL) was synthesized by phosphorylating the pre-heated CNSL with *o*-phosphoric acid at 175 ± 5°C for 4 h according to a patented process[15]. The triene fraction of the monomer component of PCNSL has the following structure:



Natural rubber (ISNR-5) was supplied by the Rubber Research Institute of India, Kottayam. Other chemicals such as zinc oxide, stearic acid, sulfur, mercapto benzothiazole (MBT) and tetra methyl thiuram disulfide (TMTD) were of the laboratory reagent (LR) grade.

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Table 1 Formulations

Composition (phr)	Mix code		
	U	C	PC
NR	100	100	100
ZnO	10	10	10
Stearic acid	2	2	2
Sulfur	2	2	2
MBT	1.5	1.5	1.5
TMTD	0.5	0.5	0.5
CNSL	—	10	—
PCNSL	—	—	10

Table 2 Vulcanization characteristics[a] of the formulations

	Temperature (°C)			
	150	160	170	180
Mix code U				
t_2 (min)	1.92	1.38	0.97	0.78
t_{90} (min)	3.38	2.38	1.60	1.32
M_L (dN m)	3.25	3.00	3.50	3.50
M_H (dN m)	60	58.5	55	54
Mix code C				
t_2 (min)	2	1.75	1.13	1
t_{90} (min)	3.5	3	1.75	1.5
M_L (dN m)	3.5	4.5	4.5	4.25
M_H (dN m)	47	47.5	45	42.75
Mix code PC				
t_2 (min)	1.82	1.37	1.13	0.88
t_{90} (min)	3.08	2.25	1.75	1.38
M_L (dN m)	4	4.25	4.5	4.5
M_H (dN m)	45.5	46	45.25	43.75

[a] t_2—Scorch time; t_{90}—optimum cure time; M_L—minumum torque; M_H—maximum torque

Table 3 Mechanical properties of the vulcanizates

	Mix code		
	U	C	PC
Modulus at 200% extension (MPa)	1.77	1.24	1.37
Tensile strength (MPa)	2.54	12.27	25.28
Elongation at break (%)	270	910	1090

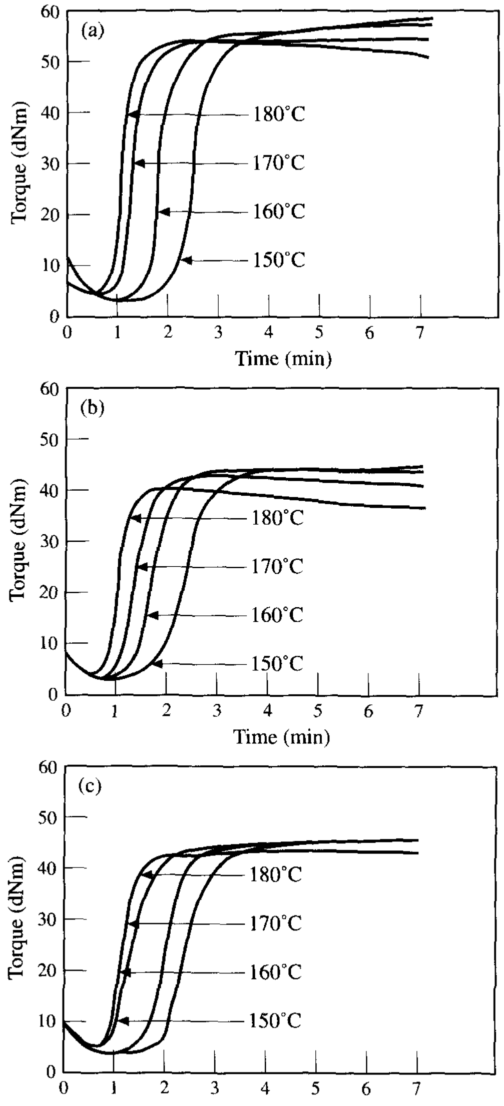

Figure 1 Rheographs of the NR formulations. (a) Unmodified, (b) PCNSL modified and (c) CNSL modified

Methods

The mixes were prepared on an open two-roll mixing mill of size 300 mm×150 mm as per the formulations given in *Table 1*. The vulcanization characteristics of the mixes were measured on an oscillating disc rheometer (Monsanto R-100) at temperatures ranging from 150 to 180°C, as per ASTM D-2084-79.

The kinetic parameters of the vulcanization reactions, such as the cure rate index (*CRI*) and the rate constant (*k*), were estimated according to the method reported by Yehia and Stoll[16].

$$CRI = 100/(t_{90} - t_2)$$

where t_{90} is the optimum cure time and t_2 is the scorch time;

$$k = (dM/dt)/(M_H - M)$$

where M is obtained as $(M_H + M_L)/2$ from the rheometer curve, corresponding to the time t for 50% of the cure, M_H is the maximum modulus and M_L is the minimum modulus obtained directly from the rheograph.

The activation energy of cure, E, was determined by assuming the dependence of the optimum cure time t_{90} on cure temperature T to follow an Arrhenius relationship:

$$t_{90} = A\,e^{-(E/RT)}$$

where A is the pre-exponential factor, R is the universal gas constant and T is the temperature in Kelvin. E was obtained from the slope of Arrhenius plots of log t_{90} *versus* $1/T$ over the temperature range from 150 to 180°C.

RESULTS AND DISCUSSION

Vulcanization characteristics

The rheographs for the mixes at different temperatures ranging from 150 to 180°C are given in *Figure 1*. *Table 2* gives some of the vulcanization parameters of the mixes. It is evident from *Figure 1* and *Table 2* that modification of NR with 10 phr each of CNSL and PCNSL results in a considerable reduction in the ultimate 'state of cure' as shown by the lower values of equilibrium modulus, M_H. Also, the modulus at 200% extension of the vulcanizate decreased in the presence of CNSL and PCNSL as shown in *Table 3*. This is a clear indication of the reduction in the state of cure. However, the scorch time and optimum cure time of the compounds did not change significantly. The

Table 4 Kinetic parameters[a] of vulcanization

	Temperature (°C)			
	150	160	170	180
Mix code U				
100*k* (min^{-1})	78.9	85.6	92.2	100
CRI (min^{-1})	68.4	100.2	157.8	187.8
Mix code C				
100*k* (min^{-1})	80.5	83.7	90.1	96.1
CRI (min^{-1})	66.6	79.8	162	199.8
Mix code PC				
100*k* (min^{-1})	88	88	89	86
CRI (min^{-1})	79.2	113.4	162	199.8

[a] *k*—rate constant; *CRI*—cure rate index

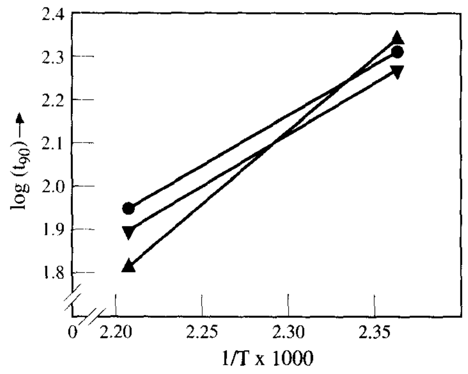

Figure 2 Arrhenius plots. (a) Unmodified, (b) PCNSL modified and (c) CNSL modified

Table 5 Activation energy of vulcanization[a]

Mix code	Activation energy, *E* (kJ mol^{-1})
U	27.579
C	20.088
PC	19.737

[a] Temperature range—150 to 180°C

tendency for 'reversion' starts gradually above 170°C for all the mixes.

The lower state of cure of the PCNSL-modified NR vulcanizate is evident from its lower crosslink density[12]. This is quite reasonable when considering the possibility for the formation of an entangled network structure between the side chains of PCNSL and the main chains of NR, which would lower the crosslink density[12].

Kinetic parameters of vulcanization

Cure rate index. It is widely known that acidic materials in general retard the cure of elastomers[17]. It has also been shown earlier that PCNSL retards the cure of NR at high concentrations (above 20 phr) and at normal dosage of zinc oxide (ZnO)[8,9]. But an increase in ZnO/PCNSL ratio to 1:1 results in cure restoration. The results in *Table 4* show relatively higher values of cure rate index at lower concentrations of PCNSL (10 phr) compared with that of the unmodified formulation. This may be due to enhanced mobility of isoprene chains in the presence of PCNSL and/or to the immediate access to sufficient unsaturation sites of the side chains of PCNSL, for crosslink formation with the isoprene main chains[12].

Rate constant of vulcanization. It has been shown by Gee and Morrell that the rate constant *k* for the cure of gum NR compound may be determined from measurement of the equilibrium modulus and that 1/*k* is a valuable measure of the vulcanization time required[18].

Assuming that the crosslinking reactions are of first-order, the rate constants were calculated as per the method reported earlier[16]. The results are also given in *Table 4*. An increase in temperature results in a progressive increase in the rate constant in all cases; but the increase is at a lower rate for the samples modified with CNSL and PCNSL. However, the PCNSL-modified NR shows comparatively higher values of the rate constant at 150°C and 160°C. The lower value of chemical crosslink density of PCNSL-modified NR vulcanizates compared with that of the unmodified sample[12] indicates the comparatively lower extent of cure of the former. Also, the possibility of crosslink formation between the unsaturation sites of PCNSL and NR has been proposed. It is possible that the initial formation of such crosslinks may hinder the mobility of the unsaturated segments of CNSL/PCNSL and NR, accounting for the lower rate constants at the higher temperatures.

Activation energy of vulcanization. The values for the activation energy of crosslinking, *E*, estimated for the different mixes from the Arrhenius plots (*Figure 2*), are given in *Table 5*. The results show a decrease in activation energy by 7.491 kJ mol^{-1} for the CNSL-modified NR mix and 7.842 kJ mol^{-1} for the PCNSL-modified NR mix. This clearly shows the ease of crosslinking of NR in the presence of CNSL or PCNSL. This is in contrast to the passive role of additives such as lignin in the overall vulcanization reactions of NR, as reported by Kumaran and De on the basis of results from activation energy measurements[19].

CONCLUSIONS

The above results show that modification of a gum NR compound with 10 phr of CNSL or PCNSL results in a decrease in the state of cure and increases in the cure rate index and rate constant of vulcanization. This is expected to be due to the enhanced mobility of the unsaturated side chains of CNSL/PCNSL which can participate in the crosslinking reactions. Also, the ease of crosslinking of NR in the presence of PCNSL was shown by the comparatively lower values of activation energy of crosslinking.

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