

# Self Crosslinkable Blends of Polychloroprene and Phosphorylated Cashew Nut Shell Liquid Prepolymer

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**ABSTRACT:** The self crosslinking behavior of polychloroprene rubber (CR) containing phosphorylated cashew nut shell liquid (PCNSL) prepolymer was studied. The cure characteristics and kinetics of crosslinking of blends of CR and PCNSL were determined using an oscillating disk rheometer. The extent of crosslinking was determined from chemical crosslink density index obtained by equilibrium swelling method in a solvent. Evidence for heat induced self crosslinking was obtained from FTIR spectroscopy. It was

found that 5 to 10 phr of PCNSL accelerates the heat induced self crosslinking behavior of CR. The effect of conventional curatives and fillers on the cure characteristics and mechanical properties of CR was also studied and compared. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 1619–1625, 2004

**Key words:** additives; elastomers; mechanical properties; vulcanization

## INTRODUCTION

Various blends of functionally active rubbers are reported to be capable of partial crosslinking at high temperatures in the absence of any curatives.<sup>1–9</sup> Some of these self vulcanizable rubber blends include binary blends of epoxidized natural rubber (ENR), carboxylated nitrile rubber (XNBR),<sup>2–4</sup> ENR–polychloroprene rubber (CR),<sup>5</sup> CR–XNBR,<sup>6</sup> chlorosulphonated polyethylene (*Hypalon*)–XNBR<sup>7</sup> and ENR–*Hypalon*.<sup>8,9</sup> The self crosslinking capability of such rubbers may help in eliminating the use of conventional additives such as curatives, accelerators and activators, thereby making it possible to design simple compositions (having fewer additives) for potential applications, in addition to eliminating the use of conventional curatives such as ethylene thiourea (ETU), which is a potentially carcinogenic compound.<sup>10</sup> The objective of simplifying the composition could be met by the use of a reactive multifunctional additive in a polar elastomer having reactive functionality. It has been found that phosphorylated cashew nut shell liquid prepolymer<sup>11</sup> (PCNSL) can serve as an excellent multifunctional additive in the compounding of natural rubber (NR), improving the processability of mixes and the physicochemical properties of vulcanizates.<sup>12–15</sup>

Previous studies on the multifunctional behavior of PCNSL were carried out in NR, which is nonpolar in nature. It was found that PCNSL can function as a

crosslinkable plasticizer, softener, tackifier, improver of filler dispersion, antioxidant and improver of tensile properties, tear strength, resistance to fatigue failure, thermal stability and resistance to thermo-oxidative decomposition. However, it seems that the properties inherent in the peculiar structural features of PCNSL have not been fully exploited. PCNSL is amphiphilic in nature. It has a polar phosphate group and a nonpolar C<sub>15</sub> unsaturated side chain in an aromatic ring. Thus, the phosphate group can react with the polar groups of polar elastomers and the unsaturated aliphatic side chain is compatible with nonpolar polymers. This can make it an ideal candidate as a compatibilizer between polar and nonpolar polymers. Hence, the present study is focused on its performance and reactions in polychloroprene rubber (CR), particularly on its self crosslinkable behavior. To this end, we have studied the cure characteristics and mechanical properties of CR containing different dosages of PCNSL (0 to 10 phr) in various unfilled and filled mixes with and without conventional curatives. Also, comparisons have been made of the relative efficiency in curing.

## EXPERIMENTAL

### Materials

CR of grade Neoprene W was supplied by Du Pont, Dow Elastomers, LLC. Silica filler (grade Tixosil) was supplied by Rhodia do Brasil S/A. Carbon black (Grade Furnex N-762) was obtained from Columbian Chemicals, Brasil. Curatives, such as ethylene thiourea (NA22), zinc oxide, magnesium oxide, stearic acid and solvent benzene were of laboratory reagent grade.

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**TABLE I**  
**Composition of Mixes**  
**(a). Unfilled Mixes of CR Containing PCNSL**

Composition	Mix Code		
	CRP0	CRP5	CRP10
CR	100	100	100
PCNSL	0	5	10

**(b). Filled Mixes of CR Containing PCNSL**

Composition	Mix Code					
	S10P0	S10P5	S10P10	B10P0	B10P5	B10P10
CR	100	100	100	100	100	100
PCNSL	–	5	10	–	5	10
Silica	10	10	10	–	–	–
Carbon black	–	–	–	10	10	10

**(c). Unfilled Mix of CR Modified with Curatives**

Composition	Mix code CRCB0
CR	100
ZnO	5
Stearic acid	2
MgO	4
ETU	2

**(d). Filled Mix of CR Modified with Curatives**

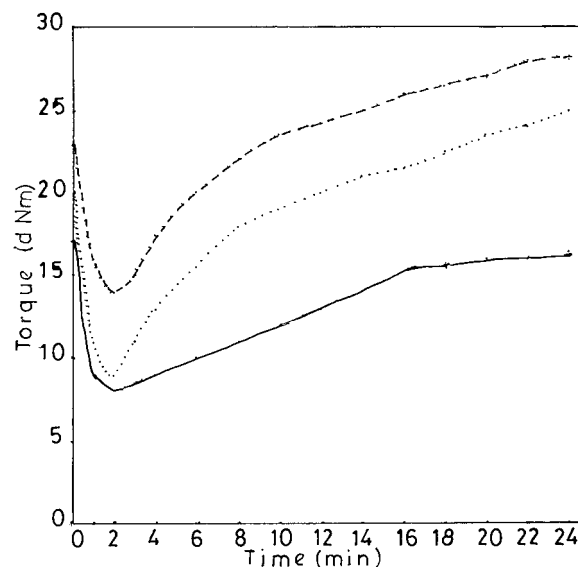
Composition	Mix code CRCB10
CR	100
Carbon black	10
ZnO	5
Stearic acid	2
MgO	4
ETU	2

PCNSL prepolymer (I) was synthesized at Regional Research Laboratory (CSIR), Thiruvananthapuram, according to a patented process.<sup>11</sup>

## Methods

### Mixing and sample preparation

Compositions, as given in Table I(a–d), were mixed on an open, two-roll mixing mill (300 × 150 mm) at a preset roll temperature of 60°C for 10 min as per ASTM D-3182-74. Test specimens were made by compression



**Figure 1** Rheographs at 165°C of CR containing different dosages of PCNSL.

molding the mixes at preset temperatures for the respective optimum cure time ( $t_{90}$ ), as determined using an oscillating disk rheometer.

### Cure characteristics

The cure characteristics of the mixes were determined using an oscillating disk rheometer (ODR, Model-TI-100, Tecnologia Industrial) at preset temperatures of 150, 165 and 180°C as per ASTM D-2084-81.

### Chemical crosslink density index

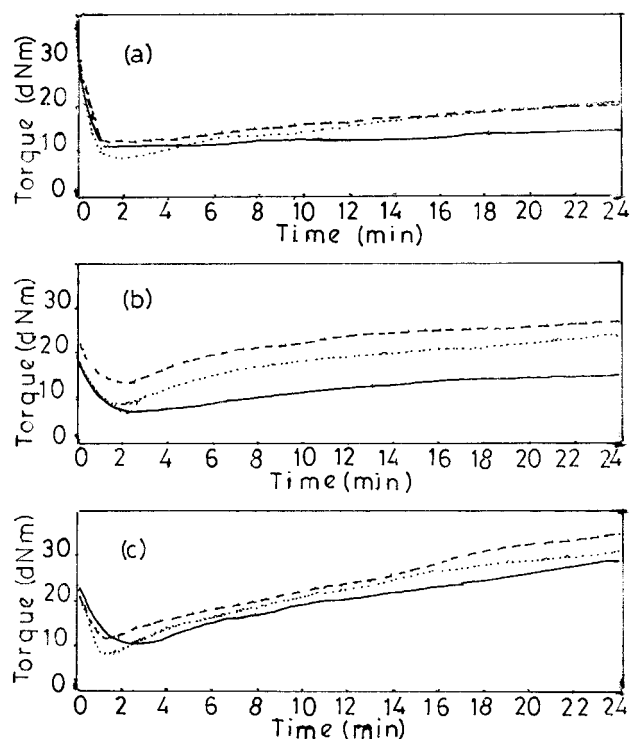
The volume fraction of rubber in a cured sample swollen in benzene under equilibrium conditions ( $V_r$ ) was considered to be an index of chemical crosslink density,<sup>13,16–20</sup> assuming a direct relation between the two as given by the Flory–Rehner equation.<sup>16</sup> The value  $V_r$  was calculated using the relation

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

**TABLE II**  
**Effect of dosage of PCNSL and Cure Temperature on Cure Characteristics of Unfilled CR**

Temp. (°C)	150			165			180		
	CRP0	CRP5	CRP10	CRP0	CRP5	CRP10	CRP0	CRP5	CRP10
Max. torque, $M_t$ (dNm)	14.9	19.3	19.8	20.3	22.7	23.5	29.8	35.8	32.3
Scorch time, $t_{s2}$ (min)	13.5	7.1	4.9	6.4	3.8	2.5	4.7	2.8	2.1
OCT, $t_{90}$ (min)	21.9	20.5	20	21.5	20.4	19.9	21.4	20.5	19.7
Cure rate, (dNm/min)	0.192	0.384	0.510	0.444	0.612	0.732	0.834	1.086	1.050

<sup>a</sup> OCT = Optimum cure time

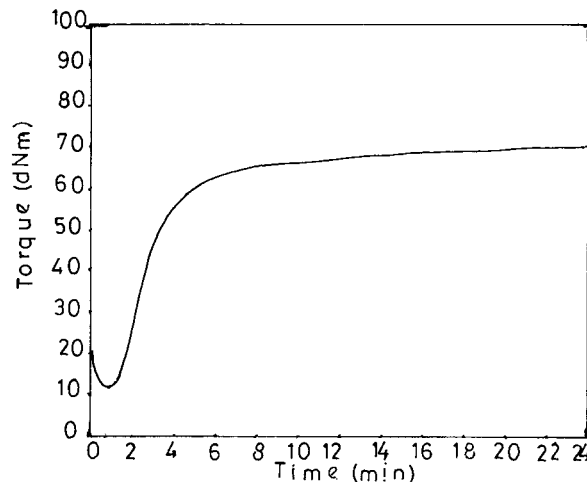


**Figure 2** Rheographs at (a) 150°C, (b) 165°C and (c) 180°C of CR containing different dosages of PCNSL.

where  $D$  is the deswollen weight of the cured sample,  $F$  is the weight fraction of insoluble components in the sample,  $T$  is the initial weight of the test specimen,  $\rho_r$  is the density of the rubber sample,  $A_0$  is the weight of solvent absorbed under equilibrium conditions and  $\rho_s$  is the density of the solvent.

IR spectroscopy

CR was mixed with and without 10 phr of PCNSL in a Brabender Plasticorder at room temperature (measuring mixer W-30) at a rotor speed of 30 rpm for 15 min. Thin films were prepared from each of the mixes by compression molding at 165°C for 20 min. IR spec-



**Figure 3** Rheograph at 165°C of unfilled CR containing curatives.

tra of the films were obtained on a Nicolet FTIR spectrometer (model 400D) over the frequency range from 450 to 4000  $\text{cm}^{-1}$ .

Mechanical properties

Tensile properties of the cured samples were measured on a universal tensile testing machine (model INSTRON 1145) as per ASTM D-416.

RESULTS AND DISCUSSION

Unfilled CR

Cure characteristics

The cure characteristics of CR containing different dosages (0 to 10 phr) of PCNSL were measured using the ODR. The rheographs obtained at 165°C are shown in Figure 1. The cure parameters of CR containing different dosages of PCNSL (0 to 10 phr) are given in Table II. The results show a distinct and steady increase in cure rate and ultimate state of cure

**TABLE III**  
Effect of Dosage of PCNSL and Temperature on Kinetic Parameters for Crosslinking of Unfilled CR

Temp (°C)	Mix Code	CRP0	CRP5	CRP10
150-180	Activation energy for crosslinking, $E_a$ (J/mol)	24.3	3.8	14.0
150	Modulus, $M^a$ (dNm)	12.8	15.2	14.1
	Cure rate, $dM/dt$ (dNm/min)	0.234	0.288	0.390
	$(M_H - M_L)$ , (dNm)	4.2	8.3	11.4
165	Modulus, $M^a$ (dNm)	15.5	15.8	14.9
	Cure rate, $dM/dt$ (dNm/min)	0.360	0.462	0.504
	$(M_H - M_L)$ , (dNm)	9.7	13.8	17.2
180	Modulus, $M^a$ (dNm)	20.7	23.5	20
	Cure rate, $dM/dt$ (dNm/min)	0.720	0.948	0.702
	$(M_H - M_L)$ , (dNm)	18.3	24.6	24.6

<sup>a</sup>  $M = (M_H + M_L)/2$

TABLE IV  
Cure Parameters of Unfilled CR Containing Curatives

Parameter	Mix Code CRCB0
Min. torque, $M_1$ (dNm)	10.7
Max. torque, $M_H$ (dNm)	71.7
Scorch time, $t_{s2}$ (min)	1.2
OCT*, $t_{90}$ (min)	6.1
Cure rate, (dNm/min)	3.258

(maximum torque) with an increase in dosage of PCNSL in CR. This is a clear indication of the acceleration effect of PCNSL on the heat-induced, self crosslinking reaction of CR.

*Effect of Dosage of PCNSL and Temperature on Cure Characteristics.* Figure 2 shows the rheographs at 150, 165 and 180°C of CR containing different dosages of PCNSL. The cure parameters obtained from them are given in Table II. It can be seen that progressive increases in the cure rate and the ultimate state of cure of CR are obtained with an increase of PCNSL from 0 to 10 phr and of temperature from 150 to 180°C. However, at 180°C, the highest cure rate and maximum torque were obtained for the mix containing 5 phr PCNSL. The steady decrease in scorch time and optimum cure time with increase in dosage of PCNSL and temperature also show the acceleration effect of PCNSL on the self crosslinking of CR.

*Effect of Dosage of PCNSL and Temperature on Kinetic Parameters of Crosslinking.* Table III gives the kinetic parameters for the crosslinking of CR in the presence of 0 to 10 phr PCNSL over a temperature range from 150 to 180°C. The activation energy for crosslinking,  $E_{ar}$  over the temperature range 150–180°C was calculated from the Arrhenius relation, given as

$$t_{90} = A e^{E_a/RT}$$

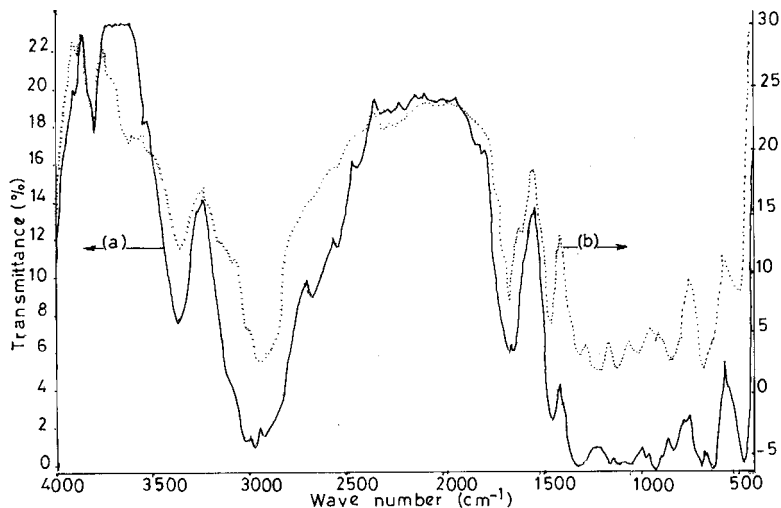


Figure 4 FTIR spectra of (a) CR and (b) CR containing PCNSL (10 phr). Cure: 165°C/20 min.

TABLE V  
Chemical Crosslink Density Index ( $V_r$ ) of Unfilled CR Containing Different Dosages of PCNSL

Mix Code	Dosage of PCNSL (phr)	$V_r$
CRP0	0	0.096
CRP5	5	0.1266
CRP10	10	0.1679

where  $t_{90}$  is the optimum cure time obtained from ODR. The lower values of activation energy for the samples containing 5 phr PCNSL (3.8 J/mol) and 10 phr PCNSL (14 J/mol) as compared to that of the unmodified CR (24.3 J/mol) indicate the ease of crosslinking of CR in the presence of PCNSL. This is further substantiated by the higher cure rate ( $dM/dt$ ) and the higher difference in cure modulus ( $M_H - M_L$ ) of CR containing PCNSL at different temperatures. These results clearly indicate that PCNSL promotes the self crosslinking behavior of CR with an increase in temperature.

*Effect of Curatives on Cure Characteristics of CR.* The cure characteristics of a CR mix containing curatives were also determined for comparison with a mix containing no curatives. The rheograph of the mix is given in Figure 3 and the cure characteristics in Table IV. The results show considerable improvement in the cure rate and ultimate state of cure of CR in the presence of the curatives.

#### Chemical crosslink density index

Table V gives the chemical crosslink density index ( $V_r$ ) of unfilled CR containing different dosages of PCNSL. The steady increase in the value of  $V_r$  from 0.096 to 0.1679 with the increase in dosage of PCNSL from 0 to

TABLE VI  
Mechanical Properties of the Unfilled Mixes

Property	Mix Code			
	CRP0	CRP5	CRP10	CRCB0
Hardness (Shore A)	44	36	28	46
Tensile modulus - 300% (MPa)	1.0	0.5	0.4	2.2
Tensile strength (MPa)	4.0	5.0	5.8	7.4
Elongation at break (%)	980	1160	1160	500

10 phr in CR shows the greater extent of crosslinking in CR containing PCNSL.

### IR spectroscopy

In order to understand the nature of the interaction between CR and PCNSL, IR spectra of heat-cured films of CR with and without PCNSL (10 phr) were taken. The FTIR spectra are given in Figure 4. In the spectrum of CR, the absorptions at 609 and 690  $\text{cm}^{-1}$  correspond to the C—Cl group of CR. This is in agreement with the strong absorption at 800–600  $\text{cm}^{-1}$  assigned to C—Cl stretching vibrations of aliphatic compounds.<sup>21</sup> In CR containing PCNSL (10 phr), the intensity of absorption in this range decreases, and only a single absorption is observed at 663  $\text{cm}^{-1}$ . The IR spectrum of CR containing PCNSL (10 phr) shows an absorption at 1007  $\text{cm}^{-1}$ . In phosphorous compounds containing P—O—C (aliphatic) groups, a strong absorption is reported in the 1050–970  $\text{cm}^{-1}$  range.<sup>22</sup> Hence, the absorption at 1007  $\text{cm}^{-1}$  of CR containing PCNSL may be due to the formation of a P—O—C group between the phosphate group of PCNSL and CR. It is reported that in the crosslinking reaction of ZnO in CR, ZnO crosslinks the 1,2 units of CR after an allylic shift of the chlorine atoms.<sup>23</sup> It is probable that a similar reaction may take place between the hydroxyl group in the phosphate group of PCNSL and the allylic chloro group of CR, leading to crosslinking.

### Mechanical properties

The mechanical properties of cured samples of the unfilled mixes of CR with and without PCNSL and curatives are given in Table VI. The steady decrease in hardness from 44 Shore A to 28 Shore A, and tensile modulus from 1.0 MPa to 0.4 MPa, with an increase in dosage of PCNSL from 0 to 10 phr indicates the softening effect of PCNSL on CR. This may be due to the plasticizing effect of the aliphatic  $\text{C}_{15}$  side chain segment of PCNSL in CR, similar to that reported earlier in NR.<sup>12,15</sup> Also, the results show an increase in tensile strength and elongation at break of CR in the presence of PCNSL, possibly due to the higher extent of crosslinking in these systems. The sample containing

curatives shows improvement in hardness, tensile modulus and tensile strength, as expected.

### Filled CR

Since reinforcing fillers are known to improve the mechanical properties of elastomers, the effect of a non black filler (silica) and carbon black in CR containing different dosages of PCNSL was studied. The rheographs at 165°C of CR containing 10 phr each of silica and carbon black and different dosages (0 to 10 phr) of PCNSL are given in Figure 5. The cure parameters of the mixes are given in Table VII.

### Cure characteristics

*Silica as Filler.* In the compositions containing silica as filler, an increase in dosage of PCNSL leads to a decrease in the maximum torque value and a slight increase in the optimum cure time. This cure retardation in silica-filled compositions in the presence of PCNSL is analogous to the one observed earlier in PCNSL modified NR containing silica as a filler.<sup>15</sup> In the silica filled compositions, it is possible that ionic interactions between the polar groups of PCNSL and silica filler may prevent the effective utilization of PCNSL in cure reaction with CR.

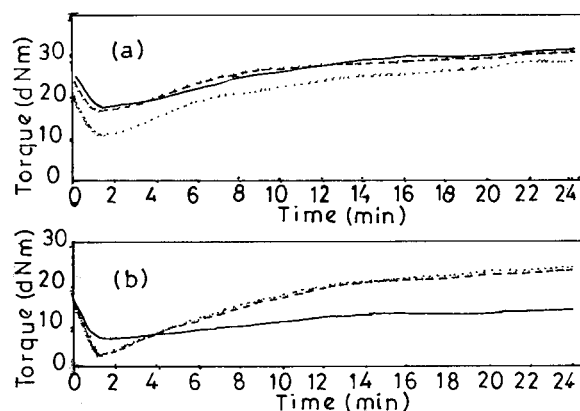


Figure 5 Rheographs at 165°C CR containing different dosages of PCNSL and filled with: (a) silica and (b) carbon black.

**TABLE VII**  
Cure Parameters of CR Containing PCNSL and Different Fillers

Parameter	Mix Code					
	S10P0	S10P5	S10P10	B10P0	B10P5	B10P10
Min. torque, $M_1$ (dNm)	18.8	18.3	12.8	9.7	8.5	8.1
Max. torque, $M_h$ (dNm)	33.0	31.8	29.0	15.7	23.7	25.8
Scorch time, $t_{s2}$ (min)	4.0	2.9	3.4	10.9	3.5	2.9
OCT <sup>a</sup> , $t_{90}$ (min)	19.4	20.1	19.5	21.8	19.7	19.8
Cure rate, (dNm/min)	0.654	0.606	0.732	0.270	0.672	0.774

<sup>a</sup> OCT = Optimum cure time

**TABLE VIII**  
Mechanical Properties of the Filled Mixes

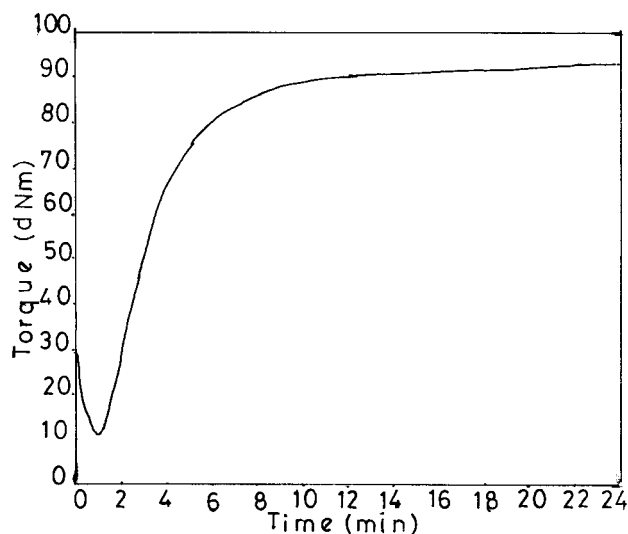
Property	Mix Code						
	S10P0	S10P5	S10P10	B10P0	B10P5	B10P10	CRCB10
Hardness (Shore A)	66	62	58	50	46	42	50
Tensile modulus - 300% (MPa)	0.7	0.7	0.6	0.6	0.4	0.2	5.4
Tensile strength (MPa)	6.8	8.6	8.6	4.6	9.6	11.4	14
Elongation at break (%)	1120	1080	1160	900	1140	1320	460

*Carbon Black as Filler.* Figure 3 and the results in Table IV show that, unlike the nonblack fillers, the black-filled CR mixes containing different dosages of PCNSL show progressive cure acceleration with increasing dosage of PCNSL. Thus, the addition of 5 phr of PCNSL in carbon black filled CR resulted in an increase in its maximum torque by 8 dNm. Also, an increase in maximum torque by 10.1 dNm was obtained in the presence of 10 phr of PCNSL in the same base compound. Also, the cure rate increased steadily, from 0.270 dNm/min to 0.774 dNm/min with an increase in dosage of PCNSL from 0 to 10 phr. The higher rate of curing of black filled CR containing

PCNSL indicates the active role of PCNSL in cure reactions with CR.

#### Mechanical properties

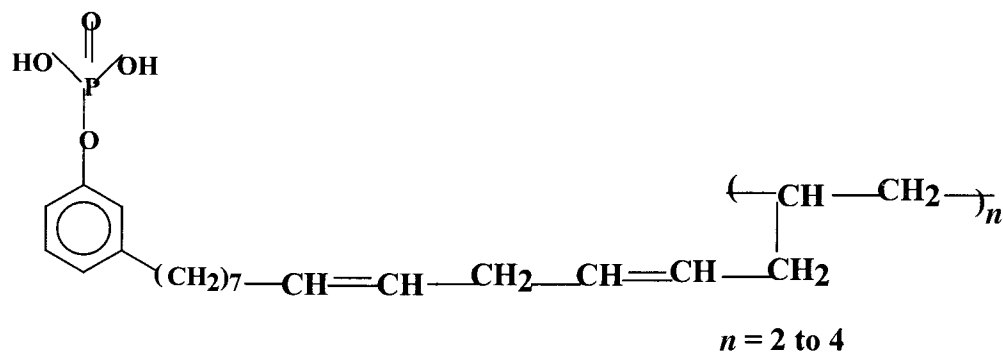
The results on the mechanical properties of the filled mixes are given in Table VIII. The progressive decreases in hardness and tensile modulus of the mixes show the softening effect of PCNSL, similar to that in the unfilled systems. It is interesting to note that the increases in tensile strength and elongation at break of the carbon black filled mixes are considerably higher than those of the silica filled mixes. This is probably due to the better dispersion of carbon black in the polymer matrix in the presence of PCNSL. Similar results have been obtained earlier in carbon black filled NR systems containing PCNSL.<sup>15</sup> Also, the results in Table VIII show that, in the presence of 10 phr each of carbon black and PCNSL in CR, a high value of tensile strength (11.4 MPa) can be obtained, which is approximately 81.43% of the value for mixes containing curatives in addition.



**Figure 6** Rheograph at 165°C of carbon black filled CR containing curatives.

**TABLE IX**  
Cure Parameters of Carbon Black Filled CR Containing Curatives

Parameter	Mix Code CRCB10
Min. Torque, $M_1$ (dNm)	13.2
Max. torque, $M_h$ (dNm)	95
Scorch time, $t_{s2}$ (min)	1.3
OCT*, $t_{90}$ (min)	7.8
Cure rate, (dNm/min)	3.540



(I) Prepolymer of PCNSL

Scheme 1

### Carbon Black Filled CR Containing Curatives

#### Cure characteristics

Figure 6 shows the rheograph at 165°C of carbon black filled CR containing curatives. The cure parameters of the mix at 165°C, as obtained from ODR, are given in Table IX. The considerably high values of maximum torque and cure rate of this system indicate a higher extent of crosslinking, leading to higher tensile modulus and tensile strength.

### CONCLUSIONS

The cure characteristics and mechanical properties of CR containing different dosages of PCNSL (0 to 10 phr) have been studied in unfilled and filled mixes. The results of the present work lead to the conclusion that, at concentrations up to 10 phr, PCNSL accelerates the self-crosslinking behavior of unfilled and carbon black filled CR at high temperatures, leading to cured samples with a high degree of crosslink density and tensile strength.

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