

Chemical Crosslink Density and Network Structure of Natural Rubber Vulcanizates Modified with Phosphorylated Cardanol Prepolymer

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SYNOPSIS

The chemical crosslink density (CLD) and network structure of natural rubber (NR) vulcanizates, modified with phosphorylated cardanol prepolymer (PCP), have been studied by equilibrium swelling and other chemical methods. The PCP-modified NR vulcanizates showed lower CLD, as compared to the unmodified NR samples, the decrease being lesser for the semiefficient vulcanization (SEV) system, as compared to the conventional (CV) and efficient (EV) vulcanization systems. The superior tensile characteristics of the PCP-modified vulcanizates of the SEV system is presumed to be partly due to the presence of an entangled network structure between the aliphatic segment of PCP and the isoprene chains, as evident from X-ray diffraction studies. The critical role of Zn⁺⁺ ions in the crosslinking reactions, especially at higher concentrations of PCP, was evident from the increase in CLD at higher concentrations of ZnO. The reduction in the IR absorption intensity, in the presence of ZnO, indicated the probable complex formation of Zn⁺⁺ ions with the phosphate groups of PCP. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The excellent combination of physicomechanical properties of natural rubber (NR) has made it a versatile material that is capable of meeting the challenging demands of the present times. Its range of utility is being extended still further by the judicious selection of additives for crosslinking and other modifications. The properties of a vulcanizate are dependent on the nature or type of crosslinks and the crosslink density.¹⁻³ In addition, it is possible that modification of an elastomer, with additives such as process-aids or flame-retardants, may alter the crosslink density and, hence, the network structure of the vulcanizates. Therefore, a knowledge of the nature and degree of crosslink formation in an elastomer, modified with such additives, would reasonably correlate the observed properties with its structural characteristics.

There are a number of reports on the use of additives prepared from cashew nut shell liquid (CNSL, 8007-24-7) and its distillation product, cardanol (37330-39-5), in modifying the properties of elastomers.⁴ It has been shown that the addition of a phosphorylated prepolymer of CNSL (PCNSL) and Cardanol (PCP)⁵ affect the processability, curing, and vulcanizate properties of NR. Significant improvements have been observed in tensile and tear strength, elongation at break, resistance to heat aging, fatigue failure,⁶ and ozone resistance.⁷ Further studies on the effect of variations in the concentration of curatives, in the presence of PCP, have strengthened the belief that PCP affects the crosslink density and hence the network structure of NR. The aim of the present study is, therefore, to achieve insight into the detailed network structure of NR vulcanizates, modified with PCP, through the determination of chemical crosslink density. This is expected to lead to a better understanding of the role of additives in the vulcanizate structure and properties, which may be useful in the design of multifunctional single additives for NR. This article,

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in particular, discusses: (a) the effect of PCP content and the curing system on the total chemical crosslink density of NR vulcanizates, (b) the effect of variations in the dosage of the cure activator (ZnO) on the crosslink density, and (c) the elucidation of the network structure of the vulcanizates through the determination of proportions of mono, di, and poly sulfidic crosslinks, network combined sulfur, and sulfur-inefficiency parameter.

MATERIALS AND METHODS

Materials

Natural rubber, of grade ISNR-5, obtained from the Rubber Research Institute of India, Kottayam, was used in this study. PCP was synthesized as reported earlier.⁵ The chemicals for vulcanization, such as zinc oxide, stearic acid, sulfur, mercaptobenzothiazole (MBT), tetra methyl thiuramdisulfide (TMTD), and the solvents, such as benzene, *n*-heptane, piperidine, propane-2-thiol, and 1-hexanethiol, were products of E. Merck and were used without further purification.

Sample Preparation

The formulations of the mixes, based on NR, are presented in Table I. Compounds were prepared on a two-roll mixing mill with a size of 150 mm × 300 mm, at a friction ratio of 1 : 1.12, as per ASTM-D 3182. Tensile sheets with a size of 140 mm × 130 mm × 2.5 mm were molded in a compression molding press at 150°C, under 65 kg/cm pressure, for the respective optimum cure times, as obtained from a Monsanto Oscillating Disk Rheometer, R-100.

Test specimens in duplicate (10 mm dia) were punched out from the center portion of the vulcanized sheets for the determination of the crosslink density.

Thermal Aging

Thermal aging of the vulcanizates was carried out in an air oven, at 70°C for 48 h, as per the standard ASTM-D-573-78, and the crosslink density was measured after aging.

Determination of Chemical Crosslink Density

The chemical crosslink density (CLD) of the vulcanizates (before and after aging and after thiol-amine treatments) was determined by following the procedure of equilibrium swelling in benzene.⁸⁻¹⁰ The volume fraction of the rubber, V_r , was calculated from the swollen and deswollen weights.⁸ The chemical crosslink density, expressed as $(2 M_c \text{ chem})^{-1}$ was calculated using the Flory-Rehner equation.¹¹ The number-average molecular weight of NR was determined from the intrinsic viscosity data, with the relation reported by Mullins and Watson,¹² as

$$[\eta] = 2.29 \times 10^{-7} M_n^{1.33}$$

Propane-Thiol Treatment

For the selective cleavage of the polysulfidic linkage of the vulcanizates, the specimens were treated with a mixture of propane-2-thiol and piperidine, under nitrogen atmosphere, for a period of 2 h, as per the method reported by Campbell and Saville.^{13,14}

Table I Composition of the Mixes

Vulcanization System ^a	CV		SEV						EV	
	1	2	3	4	5	6	7	8	9	10
Mix Code										
Composition (phr)										
NR	100	100	100	100	100	100	100	100	100	100
ZnO	10	10	10	10	10	15	20	25	10	10
Stearic acid	2	2	2	2	2	2	2	2	2	2
S	2.5	2.5	2	2	2	2	2	2	0.5	0.5
MBT	0.6	0.6	1.5	1.5	1.5	1.5	1.5	1.5	2.5	2.5
TMTD	0.2	0.2	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
PCP	0	10	0	10	20	20	20	20	0	10

^a (CV) Conventional, (SEV) semiefficient, and (EV) efficient.

Hexane-Thiol Treatment

To cleave both di- and polysulfidic crosslinks, leaving mono sulfidic crosslinks intact, the vulcanizates were treated with a solution of 1-hexane thiol in piperidine, under nitrogen atmosphere for 48 h, according to the method of Campbell and Saville.^{13,14}

The amount of sulfur, combined within the polymer network (Sc), was determined by estimating the zinc-sulfide sulfur and free-sulfur of the vulcanizates,¹⁵ as follows. The free-sulfur of the vulcanizate was determined by following the procedure as per ASTM-D-297-72 A. The sulfur, present as ZnS, was estimated iodimetrically after converting it to CdS by reaction with HCl and absorption of the liberated H₂S in CdCl₂. The sulfur inefficiency parameter E was defined as

$$E = \frac{(Sc)}{(2 M_c \text{ chem})^{-1}}$$

where $(2 M_c \text{ chem})^{-1}$ is the chemical crosslink density of the vulcanizate.¹⁶

The IR spectra of PCP, NR/ZnO, NR/PCP, and NR/PCP/ZnO blends were taken by casting thin films of the samples (from a solution in chloroform) on KBr plates, by an IR spectrophotometer (Model, Perkin-Elmer 843).

The X-ray diffraction characteristics of the specimens were measured by an XRD spectrometer (Model, Philips-A 1710) with a Cu-K_α source 35 KV, 15 mA.

RESULTS AND DISCUSSION

Effect of PCP on the Chemical Crosslink Density of NR Vulcanizates

The CLD and the related mechanical properties of NR vulcanizates are dependent on the nature of the

vulcanization system employed.¹⁶⁻¹⁸ The relatively higher tensile properties, observed for the PCP-modified NR vulcanizate in the semiefficient vulcanization system (SEV), as compared to that of the Conventional (CV) and Efficient (EV) systems,⁶ made it imperative to determine the effect of variation of PCP content in these systems on the chemical crosslink density and network structure of these vulcanizates.

The results of the CLD and the distribution of different types of crosslinks are presented in Table II. In all the vulcanization systems, there was a reduction in the CLD in the presence of PCP; this reduction was comparatively lower for the SEV system. Table II shows that, in the presence of PCP (10 phr), the original CLD decreased by 41.45% for CV, 27.56% for EV, and 12.30% for SEV systems. The decrease in CLD is analogous to that of similar NR systems containing lignin^{16,18} (10 phr). It has been suggested that lignin increases the structural complexity of the vulcanizate by masking portions of the vulcanization sites of the polymer chains and causing higher modification of the main chain, which inhibits strain-induced crystallization.¹⁸

PCP is a prepolymer that contains a mixture of oligomers.⁵ The structure of the triene component of the monomer and oligomer of PCP is shown in Figure 1. Possible interactions between PCP and NR can thus be envisaged as follows:

1. the interactions between the aliphatic segment of PCP and NR,
2. hydrogen bonding between the phosphate group of PCP, and
3. the phosphate-metal (e.g., Zn⁺⁺) interaction.

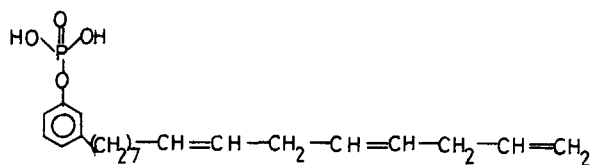
Thus, it is probable that many of the interactions listed above may be operating simultaneously, as shown schematically in Figure 2. The involvement

Table II CLD and Distribution of Different Types of Crosslinks

Vulcanization System Mix Code	CV		SEV						EV	
	1	2	3	4	5	6	7	8	9	10
1. Total Crosslink Density ^a										
a. Original	6.78	3.97	7.48	6.56	2.97	6.02	6.81	5.12	4.50	3.26
i. Polysulfidic Crosslinks	2.48	1.22	1.78	2.00	0.46	1.71	2.67	1.46	0.77	0.66
ii. Disulfidic Crosslinks	0.72	2.75	2.06	1.74	2.51	1.36	1.73	0.89	0.97	0.58
iii. Monosulfidic Crosslinks	3.58	—	3.64	2.82	—	2.95	2.41	2.77	2.76	2.02
b. Total CLD After Aging	6.45	4.68	7.10	7.00	3.64	6.07	6.65	5.98	4.67	3.09

^a CLD × 10⁵ mol/g RH.

Monomer of phosphorylated cardanol (triene component)



Phosphorylated Cardanol Prepolymer (PCP)

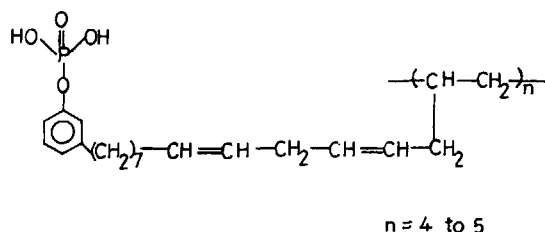


Figure 1 Monomer and prepolymer of phosphorylated cardanol.

of hydrogen bonding in the interaction between phosphate groups of the oligomer of PCP has been revealed by John et al.¹⁹ They observed that a broadening of the IR spectra of neat film, in the region 1250 cm^{-1} , and a shifting by 10 cm^{-1} of the peak, occurs as compared to that of a dilute solution in CCl_4 . This is an indication of the presence of hydrogen bonding between phosphate groups of the adjacent oligomers of PCP. It is likely true that the

physical interactions between the aliphatic side chain of PCP and the main chains of NR are formed in the PCP-modified NR vulcanizates. This may be facilitated by an increase in the effective length of the PCP oligomer unit through intermolecular hydrogen bonding, as explained earlier. The presence of the oligomeric moieties of PCP, between the unsaturation sites of NR, is thought to be responsible for the reduced CLD of the vulcanizates containing PCP. The high tensile strength and elongation at break of these vulcanizates is thus expected to be partly due to (a) the formation of virtual crosslinks between NR and PCP, similar to that reported for polyurethanes,²⁰ and possibly (b) the contribution of the chelation effects of Zn^{2+} ions as described elsewhere. Kramer has observed that chain-entanglement contributes significantly to the equilibrium modulus of the rubber networks made by crosslinking linear polymeric chains, e.g., polybutadiene.²¹

X-ray study shows a reduction in the intensity of peaks for the PCP-modified NR sample, as compared to that of the unmodified sample. This is evident from Figures 3(a) and (b). The absence of any strain-induced crystallization in the NR that was modified with PCP is clear from the reduced intensity of the peaks for the PCP-modified NR sample (ii), compared to that of unmodified NR (i), as shown in Figure 3(b). This, along with the increase in the proportion of the amorphous region for the PCP-modified sample, is supposed to be due to the presence of a higher proportion of the entangled network structure, hindering the formation of crystallites.

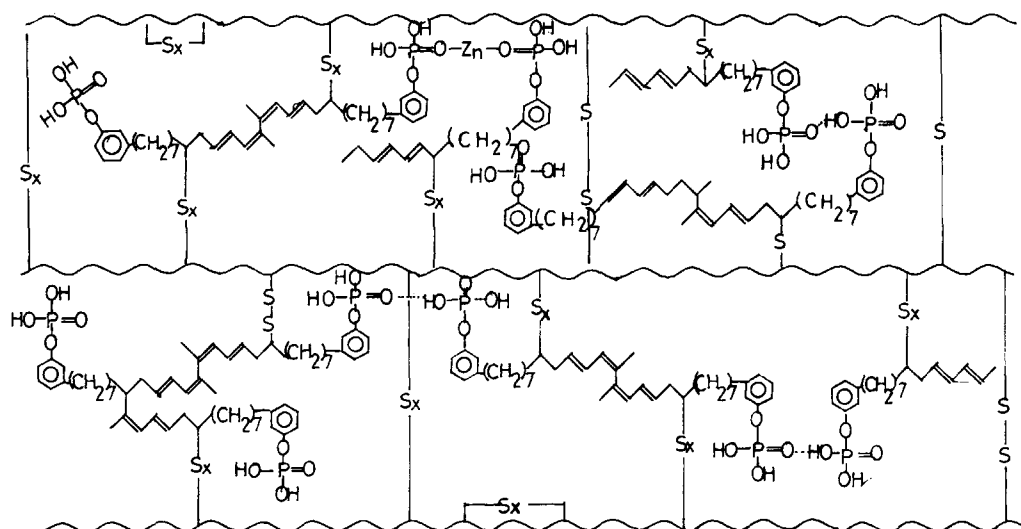


Figure 2 A schematic representation of the possible chemical linkages in the network structure of PCP-modified NR vulcanizates.

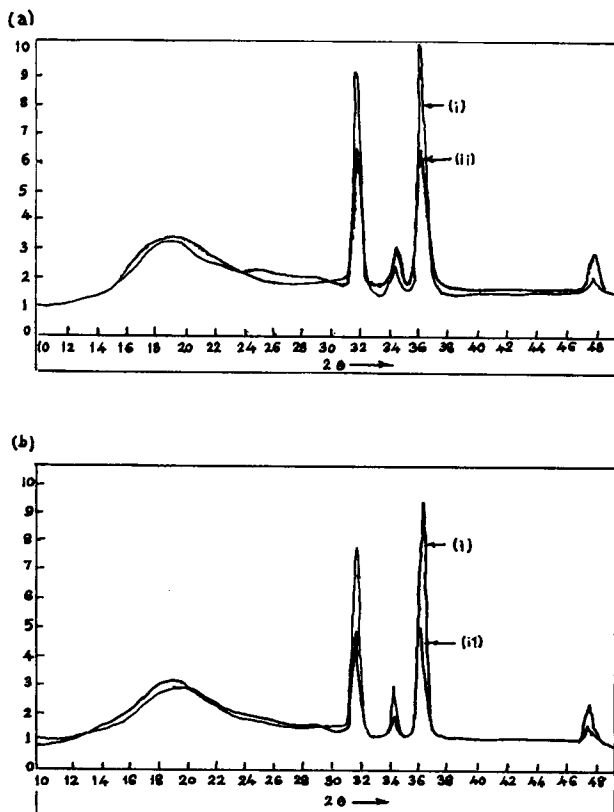


Figure 3 X-Ray diffraction patterns of PCP-modified NR vulcanizates. (a) unstretched, (b) after stretching 300%, 30 min, (i) PCP, 0 phr, (ii) PCP, 10 phr.

Effect of Aging

After aging at 70°C for 48 h, it was found that there was an increase in the CLD of the samples containing 10 phr of PCP for the CV (17.88%) and SEV (6.71%) systems. However, the CLD of the unmodified NR samples decreased by 4.87% for the CV and 5.08% for the SEV system. These results support the observed increase in tensile strength of the PCP-modified samples and the decrease in tensile strength of the unmodified samples, after aging.⁶ The increase in CLD of the PCP-modified samples, after aging, may be attributed to the formation of additional crosslinks during postcuring in both the CV and SEV systems.

Effect of ZnO on the Crosslink Density

The authors have reported a significant retardation in the cure of unfilled NR compounds, taking place at higher concentrations of PCP (20 phr and above) and at the normal ZnO concentration of 5 phr.⁶

However, a restoration in cure was achieved by an increase in the dosage of ZnO, which is the primary cure activator. The CLD of similar formulations, containing 20 phr of PCP, were measured for the range of ZnO content varying from 10 to 25 phr. The results for the original samples, and the samples after thermal aging, are shown in Table II. On increasing the concentration of ZnO, a characteristic increase in the CLD was observed in all cases, up to the 1 : 1 ratio of ZnO/PCP.

The above results show that ZnO plays a vital role, in the thiazole-accelerated NR vulcanization, especially in the presence of higher concentrations of PCP. This may be explained on the basis of the mechanism proposed by Coran²² for the thiazole-accelerated vulcanization of NR. It has been proposed that, in a thiazole-accelerated sulfur vulcanization system of NR, an increase in the concentration of soluble Zn^{++} causes an increase in the overall rate of formation of rubber- S_x -Ac. This increase, on the other hand, increases the extent of crosslink formation due to Zn^{++} -forming complexes with accelerator and accelerator-polysulfides. The chelated form of the accelerator terminated polysulfidic chain-modified rubber was postulated to be more reactive than the free accelerator-derived polysulfidic moiety, resulting in the formation of a higher extent of crosslinks. Because of the zinc chelation, the S—S bond is most likely to break in the rubber- S_x -Ac complex, resulting in monomeric rubber radical that is highly sulfurated² and that can recombine to form again crosslinks.

At a ZnO/PCP ratio of less than 1 : 1 (especially at the higher PCP concentration), it is most likely that sufficient soluble Zn^{++} ions are not available for the chelate formation, due to the interaction of Zn^{++} ions with the phosphate groups of PCP, as shown in Figure 2. This is evident from the reduction in the intensity of IR absorption at 1250 cm^{-1} , for the NR sample containing 10 phr each of ZnO and PCP [Fig. 4(a)], compared to the one having only 10 phr of PCP [Fig. 4(b)]. The IR spectrum of the neat film of PCP from $CHCl_3$ [Fig. 4(c)] showed higher absorption intensity at 1250 cm^{-1} , due to the higher extent of hydrogen bonding, as explained earlier.¹⁹ The reduced availability of Zn^{++} ions, in turn, leads to a reduction in the extent of crosslink formation, as per the mechanism of Coran, discussed earlier.²² However, at higher concentrations of ZnO (ZnO/PCP ratio 1 : 1 and above) it is expected that sufficient free Zn^{++} ions are available to influence the vulcanization reactions, even if a part of the ions are not available because of the complex formation with PCP.

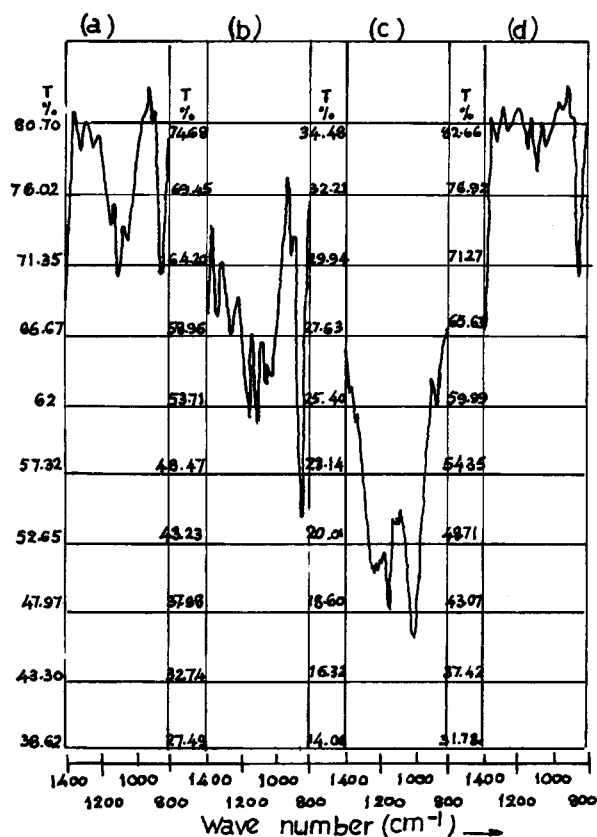


Figure 4 IR spectra of blends of NR, PCP, and ZnO (NR/PCP/ZnO), (a) 100/10/10, (b) 100/10/0, (c) 0/100/0, and (d) 100/0/10.

Effect of PCP on the Network Structure

The distribution of different types of crosslinks (mono-, di-, and polysulfidic), as compared to the original CLD of the vulcanizates, is presented in

Table II. The estimated values of the network combined sulfur and sulfur inefficiency parameter of the different vulcanizates are presented in Table III.

The CV and SEV systems, containing PCP, showed a relatively higher proportion of poly sulfide crosslinks (30%) and network combined sulfur (6 to 7×10^{-4} mol S/g RH), as compared to that of the EV system (20% and 1.2×10^{-4} mol S/g RH, respectively). The higher values of sulfur-inefficiency parameter for the CV and SEV systems (18.3 and 9.3, respectively) are indicative of the lesser amount of chemically effective combined sulfur. This is in conformity with the fact that higher concentrations of sulfur yield both more polysulfidic crosslinks and more sulfur, combined with the rubber chains in cyclic modifications.² However, upon changing from the conventional to the semiefficient vulcanization system in the presence of PCP, the proportion of polysulfidic and monosulfidic crosslinks increases, at the expense of disulfidic linkages, leading to an overall increase in CLD from 3.97×10^{-5} mol/g RH to 6.56×10^{-5} mol/g RH. This is expected, due to the improved efficiency of the SEV system.

Table IV shows some of the mechanical properties of PCP-modified NR vulcanizates of the SEV system. The superior tensile characteristics of the PCP-modified NR vulcanizates in the SEV system, as compared to that of the CV and EV systems,⁶ can thus be understood on the basis of the comparatively higher proportion of polysulfidic linkages present in it. This is in agreement with the findings of Nasir and Teh,²³ in that the tensile strength, modulus, and elongation at break of vulcanizates, with predominantly polysulfidic crosslinks, were superior to those of the corresponding vulcanizates with mono-

Table III Combined Sulfur and Sulfur-Inefficiency Parameter

Vulcanization System	Mix Code	Network Combined Sulfur (S_c) $\times 10^4$ mol S/g RH	Sulfur Inefficiency Parameter (E) Atoms/Chem Crosslink
CV	1	7.37	10.9
	2	7.27	18.3
	3	5.90	7.9
	4	6.09	9.3
	5	5.90	19.9
SEV	6	5.85	9.7
	7	5.88	8.6
	8	5.75	11.2
EV	9	1.30	2.9
	10	1.24	3.8

Table IV Mechanical Properties of PCP-Modified NR Vulcanizates⁶

No.	Property	Mix Code		
		3	4	7
1	Modulus-200% (MPa)	1.5	1.4	1.4
2	Tensile Strength (MPa)	2.35	25.28	21.90
3	Elongation at Break (%)	290	1090	1030
4	Hardness (Shore A)	41	38	38.5
5	Tear Strength (KN/m)	32.4	35.8	32.1
6	Monsanto Fatigue-to-Failure (KC)	74	125	147

sulfidic crosslinks. The higher effectiveness of polysulfidic crosslinks (as compared to other types) in producing high strength networks has also been shown in vulcanized polyisoprenes.¹⁷

The improved fatigue life of the SEV system, containing 10 phr of PCP,⁶ may be attributed to its higher content of polysulfidic crosslinks, which are capable of relieving rapidly the localized stresses associated with the growth of a flaw.²

The better retention of tensile properties, after aging of the PCP-modified NR vulcanizates of the SEV system,⁶ may be explained, considering the relatively high proportion of polysulfidic linkages, which, upon thermal decomposition, can reform into crosslinks having lower sulfidity (mono- or disulfides), thereby increasing the CLD.

At the high concentration of PCP (20 phr), the increase in the ZnO/PCP ratio of up to 1 : 1 resulted in an increase in the proportion of polysulfidic linkages from 15.50 to 39.23% and the total CLD from 2.97×10^{-5} mol/g RH to 6.81×10^{-5} mol/g RH, along with a reduction in the sulfur inefficiency parameter from 19.9 to 8.6. It is expected that the higher proportion of polysulfidic crosslinks and the higher CLD, at the ZnO/PCP ratio of 1 : 1 are responsible for the observed improvement in the mechanical properties of these vulcanizates.⁶

CONCLUSIONS

1. PCP decreases the crosslink density of NR vulcanizates in all the vulcanization systems studied; the decrease is marginal in the case of SEV system.

2. Thermal aging of the NR vulcanizates, containing PCP, increases the CLD in CV and SEV systems, only because of the formation of additional crosslinks during aging.
3. The higher tensile strength and elongation at break of the PCP-modified NR vulcanizates is attributed to the enhanced physical interactions between the side chain of PCP and the isoprene main chain, along with hydrogen bonding between the phosphate groups in adjacent PCP molecules, as well as in the phosphate-Zn⁺⁺ ion interaction. This also substantiates the reduced crystallinity of the PCP-modified NR vulcanizates, as observed from X-ray studies.
4. An increase in the concentration of ZnO in PCP (20 phr)-modified NR mixes increases the CLD and an optimum CLD was observed at the ZnO/PCP ratio of 1 : 1. The non-availability of ZnO for cure reactions at lower concentrations is attributed to the PCP-Zn⁺⁺ ion complex formation.
5. Modification of NR with PCP results in an increase in the relative proportion of polysulfidic crosslinks, over mono- and disulfidic linkages in the SEV system.

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