

Physicomechanical Properties of Filled Natural Rubber Vulcanizates Modified with Phosphorylated Cashew Nut Shell Liquid

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ABSTRACT: Effect of fillers like carbon black, silica, and china clay on the cure characteristics and physicomechanical properties of natural rubber (NR) modified with phosphorylated cashew nut shell liquid (PCNSL) in various proportions has been studied. Prominent cure retardation has been observed with progressive increase in concentration of PCNSL from 0 to 20 phr. The softening effect of PCNSL on the vulcanizate has been displayed by the linear decrease in hardness and tensile modulus and the increase in elongation at break with the increase in concentration of PCNSL. The results on the tensile and tear strengths of the vulcanizates showed that the reinforcing effect of the fillers were maximized at concentrations of PCNSL ranging from 5 to 10 phr. Also, the PCNSL-modified NR vulcanizates showed improved resistance to thermo-oxidative ageing and decomposition, especially at the higher concentration of 20 phr. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 1303–1311, 1998

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

INTRODUCTION

Natural rubber (NR) has maintained its status since its discovery and subsequent technological revolution, both as a commodity polymer and as an engineering elastomer in a variety of industrial applications. The versatility of its applications is mainly because of its unique combination of physicomechanical properties. Two of its most important properties that need to be considered for any engineering application are its mechanical strength and ageing behavior.¹ The versatility of NR for a wide range of industrial applications and the variety of compounding ingredients available in recent times helps the design of formulations

to meet the severity of service conditions. In this respect, fillers and plasticizers constitute two of the key elements affecting the strength properties of the vulcanizates. A variety of black and non-black fillers of the reinforcing and nonreinforcing types and plasticizers of the reactive and nonreactive types cater to this need.

Cashew nut shell liquid (CNSL) and its derivatives have long been used as rubber compounding additives in various roles as plasticizers, antioxidants, and vulcanizate property modifiers.² Among the many derivatives of CNSL, phosphorylated cashew nut shell liquid (PCNSL) prepolymer³ was found to be suitable as a multifunctional additive for NR vulcanizates. This article reports results of studies on the effect of fillers like carbon black, silica, and clay on the cure characteristics and physicomechanical properties of natural rubber (NR) modified with phosphorylated cashew nut shell liquid (PCNSL) in various proportions.

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Table I Composition of the Mixes

Mix Code ^a	H_0	H_5	H_{10}	H_{20}
HAF black	40	40	40	40
PCNSL	0	5	10	20
Mix Code ^a	S_0	S_5	S_{10}	S_{20}
Silica	40	40	40	40
Ethylene glycol	4	4	4	4
PCNSL	0	5	10	20
Mix Code ^a	C_0	C_5	C_{10}	C_{20}
China clay	40	40	40	40
PCNSL	0	5	10	20

^a Base mix (phr): NR, 100; ZnO, 10; stearic acid, 2; sulphur, 2; MBT, 1.5; TMT, 0.5.

EXPERIMENTAL

Materials

NR (ISNR, 5 grade) was obtained from the Rubber Research Institute of India, Kottayam 9. Technical grade CNSL of Indian Standard specification IS:840 (1964) was obtained from Kerala State Cashew Development Corporation, Quilon. PCNSL was synthesized at the R.R.L. (CSIR), Trivandrum, by the phosphorylation of CNSL with *o*-phosphoric acid at $175 \pm 5^\circ\text{C}$.⁴

Carbon black (HAF N-330), silica (HiSil-233), china clay (soft), zinc oxide, stearic acid, sulfur, mercapto benzothiazole (MBT), tetra methyl thiuram disulfide (TMT), and ethylene glycol were of the commercially available grades.

Methods

The formulations of the mixes are given in Table I. The compounding was carried out on a two-roll open mixing mill (300×150 mm) at room temperature, as per ASTM D-3182-74. Cure characteristics of the compounds were measured at 150°C in an oscillating disk rheometer (Monsanto, R100) as per ASTM D-2084-79. Filler reinforcement index α was calculated from the maximum rheometric torques using the following relation, as reported by Boonstra:⁵

$$\alpha = (\Delta L_{\max(X)} - \Delta L_{\max(\text{gum})}) / \Delta L_{\max(\text{gum})}$$

where $\Delta L_{\max(X)}$ is the maximum change in torque during vulcanization due to the addition of X phr of the filler, and $\Delta L_{\max(\text{gum})}$ is the maximum change in torque during vulcanization of the gum compound.

Hardness property was measured using an indentation hardness tester (Durometer Shore A) as per ASTM D-2240-75. Tensile properties were measured in a universal testing machine (ZWICK 1435) at a crosshead speed of 500 mm/min, as per ASTM D-412-75 (method A). Tear strength was measured on the Zwick tensile tester with the un-nicked tear test specimens (die C) as per ASTM D-624-73.

Thermogravimetric analysis (TGA) was carried out in a thermogravimetric analyzer (model Du Pont 951) coupled with a data processor (Thermal Analyst 2000) over the temperature range of 25 to 700°C , in air, at a heating rate of $20^\circ\text{C}/\text{min}$. The integral procedural decomposition

Table II Cure Rate at 150°C

Mix Code	H_0	H_5	H_{10}	H_{20}
Scorch time, t_2 (s)	124	120	120	175
Optimum cure time, t_{90} (s)	236	255	285	510
Cure rate (s^{-1})	0.89	0.74	0.61	0.30
Mix Code	S_0	S_5	S_{10}	S_{20}
Scorch time, t_2 (s)	154	98	120	150
Optimum cure time, t_{90} (s)	250	143	195	263
Cure rate (s^{-1})	1.04	2.22	1.33	0.89
Mix Code	C_0	C_5	C_{10}	C_{20}
Scorch time, t_2 (s)	150	210	180	205
Optimum cure time, t_{90} (s)	229	300	285	375
Cure rate (s^{-1})	1.27	1.11	0.95	0.58

Table III Change in Torque During Curing (ΔL_{\max}) and Reinforcement Index (α) at 150°C

Sample PCNSL (phr)	Gum ΔL_{\max} (dNm)	HAF		Silica		China Clay	
		ΔL_{\max} (dNm)	α	ΔL_{\max} (dNm)	α	ΔL_{\max} (dNm)	α
0	54.3	80	0.47	60	0.11	58	0.07
5	43	75	0.74	54	0.26	54	0.26
10	37	62	0.68	48.5	0.31	48	0.30
20	35	42.5	0.21	40.5	0.16	36.5	0.04

temperature (IPDT) of the vulcanizates was calculated from the area under the thermograms as per the method reported by Reich and Levi.⁶ The activation energy for decomposition (E) of the vulcanizates was calculated by the Freeman–Carroll method.⁷

RESULTS AND DISCUSSION

Cure Characteristics

The effect of PCNSL dosage on the cure characteristics of the NR compounds as determined by a Monsanto rheometer (R100) are given in Tables II and III.

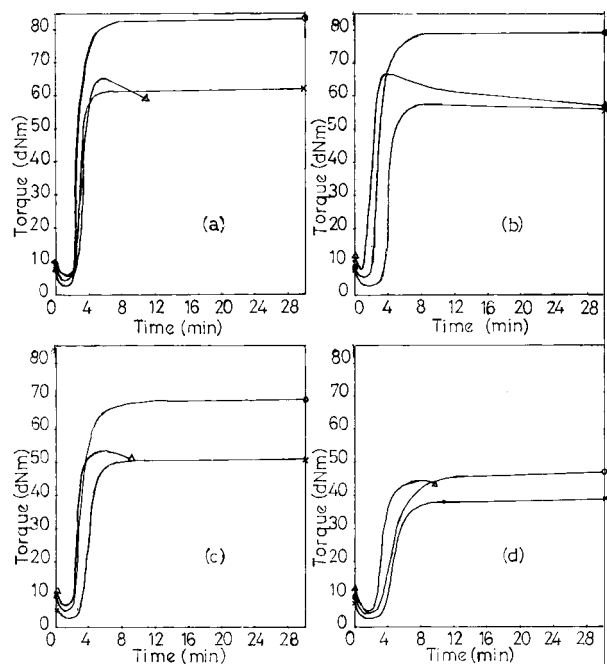


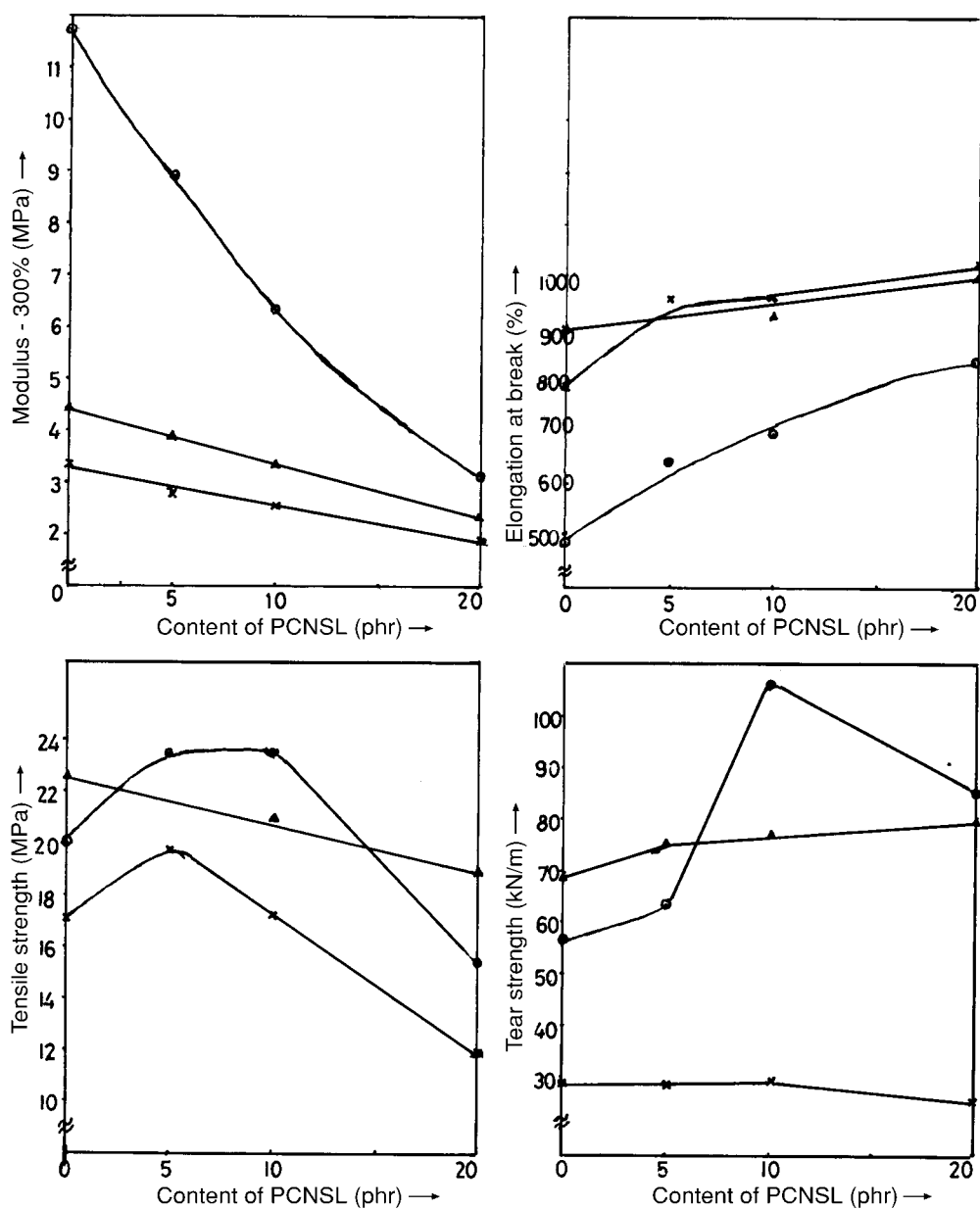
Figure 1 Rheographs of the NR formulations. PCNSL (phr): (a) 0, (b) 5, (c) 10, and (d) 20. ○, HAF; △, silica; ×, china clay.

Table II shows, in general, a decrease in the cure rate with an increase in concentration of PCNSL. This is very much pronounced at the higher concentration of PCNSL (20 phr). This is analogous to the results reported earlier⁸ for unfilled NR vulcanizates modified with PCNSL wherein considerable cure retardation has been observed at concentrations of PCNSL above 10 phr. This has been ascribed to the residual acidity of PCNSL and the probable complex formation of Zn^{2+} ions of the cure activator (ZnO) with the phosphate groups of PCNSL.⁹

The rheographs of the mixes are given in Figure 1. It shows a progressive decrease in the cure plateau with an increase in concentration of PCNSL from 0 to 20 phr for the compounds containing different types of fillers. The reinforcement index⁵ α of various fillers at different concentrations of PCNSL, calculated from the change in torque values of the gum and filled compounds, are given in Table III. The results show that the reinforcement index α reaches a maximum in all the compounds at concentrations of PCNSL ranging from 5 to 10 phr. This may be due to better dispersion of the filler in the NR matrix in presence of 5 to 10 phr of PCNSL, which helps in wetting the filler and lowering the interfacial energy. It is also presumed that there is interaction between active functional groups such as carboxyl groups on the surface of carbon black particles with phenolic hydroxyl groups of PCNSL. Therefore, α is the highest in carbon black filled stocks. The lower α value at higher dosage of PCNSL (20 phr) may be due to the dilution effect and plasticization effect. The higher degree of softening action of PCNSL on NR at the concentration of 20 phr may lead to a reduction in shear-induced dispersion of the filler, leading subsequently to a lower state of cure. The probability for poor dispersion of fillers in low-viscosity rubbers has been proposed by Boonstra.⁵

Table IV Hardness of the Vulcanizates

Mix Code	Hardness (Shore A)	Mix Code	Hardness (Shore A)	Mix Code	Hardness (Shore A)
H_0	65	S_5	58	C_0	47
H_5	63	S_{10}	57	C_5	43
H_{10}	59	S_{20}	55	C_{10}	37
H_{20}	52		43	C_{20}	35

**Figure 2** Mechanical properties of the vulcanizates. O, HAF; Δ, silica; ×, clay.

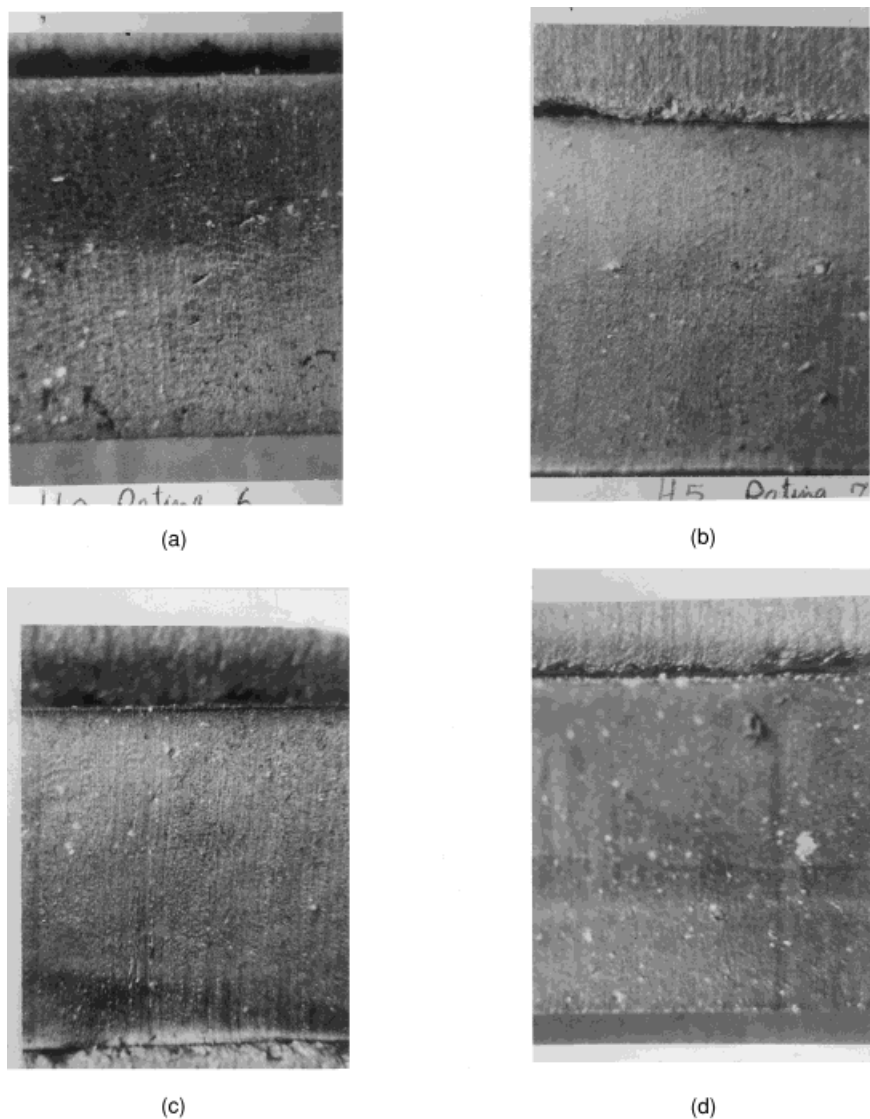
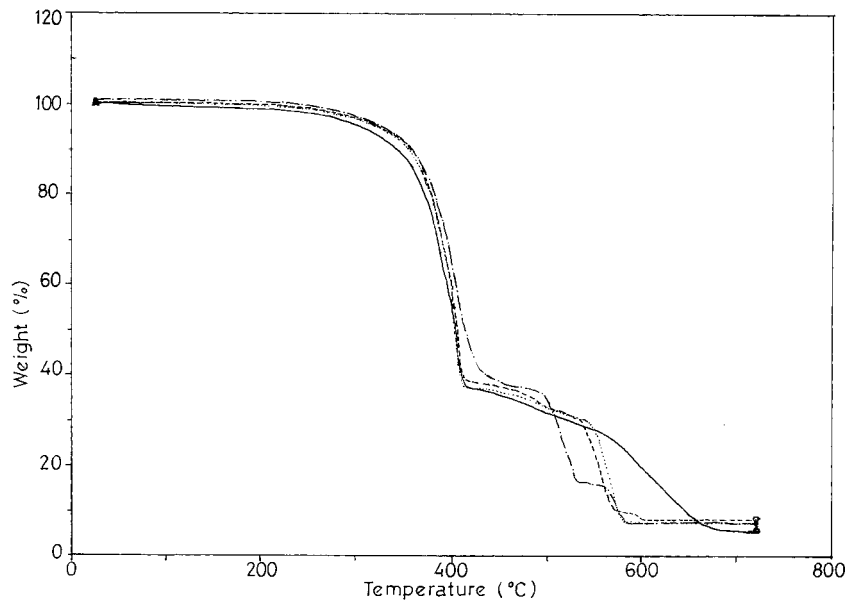


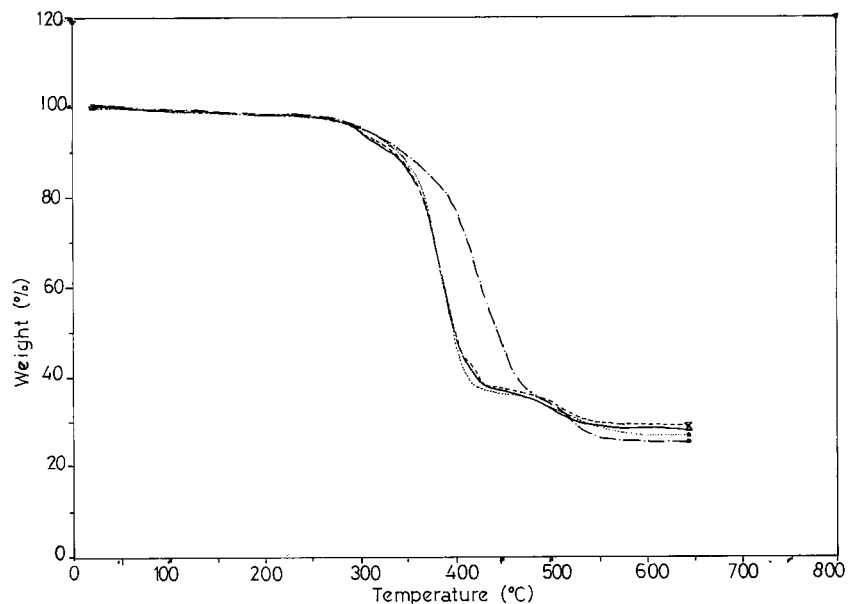
Figure 3 Polaroid dispersion photographs of black-filled NR vulcanizates. PCNSL (phr): (a) 0, (b) 5, (c) 10, and (d) 20.

Table V Retention in Mechanical Properties of the PCNSL-Modified NR Vulcanizates after Ageing at 70°C for 48 h (%)

Mix Code	Hardness	Mix Code	300% Modulus	Mix Code	Tensile Strength	Mix Code	Tear Strength
H_5	97	H_5	127	H_5	82	H_5	71
H_{10}	94	H_{10}	134	H_{10}	90	H_{10}	87
H_{20}	79	H_{20}	98	H_{20}	93	H_{20}	106
S_5	84	S_5	145	S_5	104	S_5	95
S_{10}	80	S_{10}	138	S_{10}	109	S_{10}	96
S_{20}	94	S_{20}	159	S_{20}	105	S_{20}	87
C_5	104	C_5	129	C_5	45	C_5	55
C_{10}	115	C_{10}	131	C_{10}	93	C_{10}	83
C_{20}	103	C_{20}	142	C_{20}	136	C_{20}	93



(a)



(b)

Figure 4(a) TGA curves of the black-filled NR vulcanizates. PCNSL (phr): (a) 0, (b) 5, (c) 10, and (d) 20. (b) TGA curves of the silica-filled NR vulcanizates. PCNSL (phr): (a) 0, (b) 5, (c) 10, and (d) 20. (c) TGA curves of the china-clay-filled NR vulcanizates. PCNSL (phr): (a) 0, (b) 5, (c) 10, and (d) 20: (···) 0; (---) 5; (—) 10; (-·-·) 20.

Mechanical Properties of the Vulcanizates

Hardness

Hardness of the vulcanizates decreased steadily with an increase in concentration of PCNSL, as shown in Table IV. Similar softening effect be-

cause of plasticization has also been reported in gum NR compounds.⁸

Tensile Properties

Variations in the tensile properties of the vulcanizates, such as modulus at 300% elongation, elon-

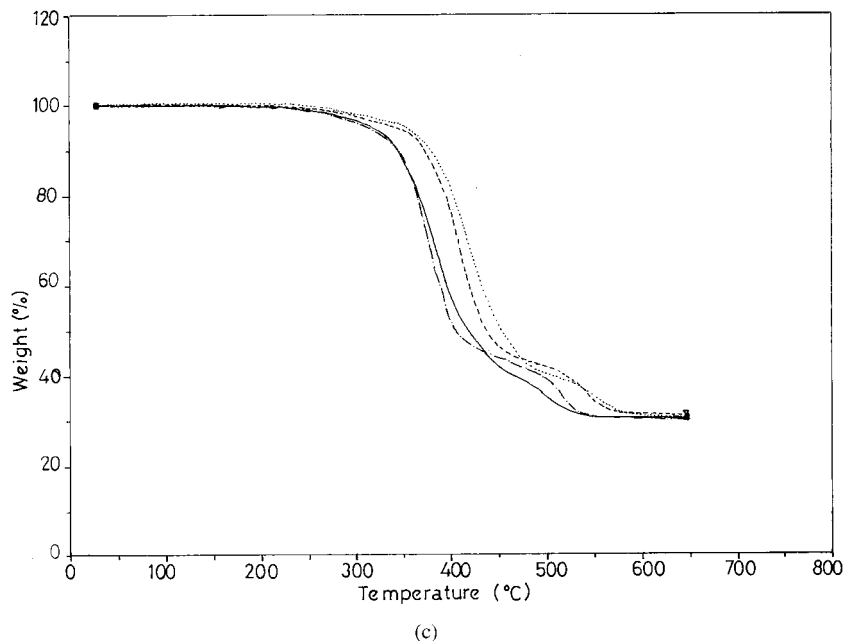


Figure 4 (Continued from the previous page)

gation at break, and tensile strength with concentration of PCNSL are given in Figure 2.

The tensile modulus at 300% elongation of the HAF-black-filled vulcanizate decreased at a higher rate compared to that containing silica and china clay with the increase in concentration of PCNSL. This shows the higher degree of efficiency of PCNSL in reducing the stiffness of the vulcanizate when HAF black is used as the reinforcing filler.

The elongation at break of the vulcanizates increased steadily with the increase in the content of PCNSL, with the rate of increase being higher for the black filled vulcanizates compared to that of the others.

The tensile strength of the black-filled vulcanizate reached a maximum (23.5 MPa) in the presence of 5 to 10 phr of PCNSL. The maximum tensile strength for the china-clay-filled vulcanizate (19.8 MPa) was obtained with 5 phr of PCNSL in the vulcanizate. The silica-filled vulcanizates did not show any improvement in tensile strength on modification with PCNSL.

The simultaneous increase in tensile strength and elongation at break of gum NR vulcanizates modified with 5 to 20 phr of PCNSL has been reported earlier.⁸ The tensile strength of these vulcanizates increased from 13 to 21 MPa and elongation at break from 920 to 1250% with the increase in concentration of PCNSL from 0 to 20 phr. This was attributed to the presence of higher

proportions of polysulfidic linkages in the PCNSL-modified vulcanizates and the probable formation of an entangled network structure between PCNSL and the isoprene chains of NR.⁹ It is possible that these mechanisms may also operate in the filled samples. Besides, the plasticizing effect of PCNSL on NR, as reported earlier,¹⁰ may facilitate the proper dispersion of the filler in NR with accompanying improvements in tensile characteristics. Thus, the improved dispersion of HAF black in the NR matrix in presence of PCNSL is evident from the polaroid dispersion photographs of the vulcanizates containing 0 to 20 phr of PCNSL [Fig. 3(a)–(d)]. As the figures show, the vulcanizates containing 5 and 10 phr of PCNSL show a numerical dispersion rating of 7, compared to the rating of 6 for the unmodified NR vulcanizate and that containing 20 phr of PCNSL. The numerical rating of 7 shows the good dispersion of black in the former, as against the fair dispersion in the latter, according to the grading of Stumpe and Railsback.¹¹

Tear Strength

The variations in the tear strength of the vulcanizates with the concentration of PCNSL are given in Figure 2. The increase in tear strength of the vulcanizates with the increase in concentration of PCNSL is much more prominent for the black-filled vulcanizate with a higher value (106 kN/m)

Table VI Thermal Stability and Activation Energy for Decomposition (TGA)

Mix Code	T_{50} (°C)	IPDT (°C)	Activation Energy (kCal/mol)
H_0	404	420	2.0
H_5	405	404	1.8
H_{10}	402	401	0.6
H_{20}	445	426	12.9
S_0	399	384	2.1
S_5	399	383	3.7
S_{10}	401	382	14.3
S_{20}	444	413	13.4
C_0	451	429	3.9
C_5	424	400	7.3
C_{10}	418	393	4.3
C_{20}	405	392	1.9

in presence of 10 phr of PCNSL, as against 57 kN/m for the control. The higher tear strength for the PCNSL modified vulcanizates may be due to the lateral deviations in the major tear path of these vulcanizates as a result of enhanced flexibility of NR matrix in the presence of PCNSL. These observations are analogous to the pattern of results reported elsewhere for unfilled NR vulcanizates modified with 10 to 20 phr of PCNSL.⁸

Resistance to Ageing

The retention in mechanical properties of the vulcanizates after ageing in a hot air oven at 70°C for 48 h are given in Table V.

The vulcanizates containing PCNSL showed good retention in hardness and tensile modulus after ageing. The retention in tensile strength and elongation at break of the vulcanizates containing HAF and china clay increased with the increase in content of PCNSL from 5 to 20 phr. The significantly high retention, especially with 20 phr of PCNSL, may be due to the post-curing reactions during the ageing period. Unfilled NR vulcanizates modified with PCNSL also showed similar high retention in tensile properties after ageing,⁸ along with an increase in crosslink density.⁹

Thermal Stability and Thermo-Oxidative Decomposition Characteristics

The decomposition characteristics of the vulcanizates in air were determined by TGA over the tem-

perature range from 25 to 700°C, the results of which are given in Table VI and Figure 4(a)–(d).

In the case of the black- and silica-filled samples, an initial decrease in the thermal stability indices, namely, T_{50} and IPDT were observed followed by an increase at 20 phr of PCNSL. However, the thermal stability indices of the china-clay-filled samples decreased with the increase in concentration of PCNSL. Previous thermogravimetric studies on unfilled NR vulcanizates modified with 10 phr of PCNSL in air and nitrogen showed a marginal improvement in thermal stability in air for the PCNSL-modified vulcanizate and the probable formation of thermally stable structures subsequently decomposing at higher temperatures.¹² Also, further improvement in thermal stability was observed with 20 phr of PCNSL in the vulcanizate.

The activation energy for thermal decomposition of the black-filled vulcanizate reached a maximum (12.9 kcal/mol) in presence of 20 phr of PCNSL (Table VI). The maximum value (14.3 kcal/mol) was obtained for the silica-filled sample with 10 phr of PCNSL. The china-clay-filled NR vulcanizate containing 5 phr of PCNSL decomposed with a maximum activation energy of 7.3 kcal/mol. The higher values of T_{50} , IPDT, and activation energy for decomposition of the black- and silica-filled vulcanizates modified with 20 phr of PCNSL indicate their improved resistance to thermo-oxidative decomposition over that of the samples not modified with PCNSL.

CONCLUSIONS

1. An increase in the concentration of PCNSL in the black-, silica-, and china-clay-filled NR formulations leads to a progressive cure retardation, as shown by the decrease in rates and states of cure.
2. The softening effect of PCNSL in the filled vulcanizates is shown by a steady decrease in hardness and tensile modulus and an increase in elongation at break of the vulcanizates with the increase in concentration of the resin.
3. The reinforcing effect of HAF black and china clay on NR maximizes in presence of 5 to 10 phr of PCNSL, as shown by the higher values of reinforcement factor, tensile, and tear strengths.
4. Resistance to thermo-oxidative ageing and decomposition of the vulcanizates, in general,

improves in presence of PCNSL, particularly at the higher concentration of 20 phr.

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REFERENCES

1. E. Southern, in *Elastomers: Criteria for Engineering Design*, C. Hepburn and R. J. W. Reynolds, Eds., Applied Science, London, 1979, p. 273.
2. A. R. R. Menon, C. K. S. Pillai, J. D. Sudha, and A. G. Mathew, *J. Sci. Ind. Res.*, **44**, 324 (1985).
3. C. K. S. Pillai, V. S. Prasad, J. D. Sudha, S. C. Bera, and A. R. R. Menon, *J. Appl. Polym. Sci.*, **41**, 2487 (1990).
4. C. K. S. Pillai, J. D. Sudha, V. S. Prasad, S. C. Bera, A. R. R. Menon, A. D. Damodaran, S. Alwan, S. K. Lakshmidasan, and K. N. Govinda Raman, Ind. Pat. 176,069.
5. B. B. Boonstra, in *Rubber Technology and Manufacture*, C. M. Blow and C. Hepburn, Eds., Butterworth, London, 1982, p. 269.
6. L. Reich and D. W. Levi, in *Characterization of Polymers*, N. M. Bikales, Ed., John Wiley and Sons, New York, 1971, p. 221.
7. E. S. Freeman and B. Carroll, *J. Phys. Chem.*, **62**, 394 (1958).
8. A. R. R. Menon, C. K. S. Pillai, and G. B. Nando, *Kauts. Gummi Kunst.*, **45**, 708 (1992).
9. A. R. R. Menon, C. K. S. Pillai, and G. B. Nando, *J. Appl. Polym. Sci.*, **51**, 2157 (1994).
10. A. R. R. Menon, C. K. S. Pillai, A. K. Bhattacharya, and G. B. Nando, in *Polymer Science—Recent Advances*, Vol. 2, I. S. Bharadwaj, Ed., Allied Publ., New Delhi, 1994, p. 657.
11. N. A. Stumpe Jr. and H. E. Railsback, *Rubber World*, **151**, 41 (1964).
12. A. R. R. Menon, C. K. S. Pillai, and G. B. Nando, *Polym. Degrad. Stab.*, **52**, 265 (1996).