

Studies on Blends of Polychloroprene and Polybutadiene Rubber Containing Phosphorylated Cardanol Prepolymer: Melt Rheology, Cure Characteristics, and Mechanical Properties

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ABSTRACT: Melt rheology, cure characteristics, and mechanical properties of blends of polychloroprene (CR) and polybutadiene rubber (BR) in the presence and absence of phosphorylated cardanol prepolymer (PCP) were studied. The melt rheology parameters of the blends over a wide range of shear rates and temperatures were studied using a capillary rheometer (Rheoflizer SWO). The plasticizing effect of PCP in the blends was indicated by reduction in apparent melt viscosity and activation energy for melt flow. Good compatibility between the blend components (CR and BR) in the presence of PCP was evidenced by the lower values of principal normal stress difference. The self crosslinking behavior of the blends in the presence and absence of PCP was studied at different temperatures, using a Brabender Plasticorder and the kinetic parameters of

crosslinking were evaluated. The cure characteristics of blends of CR and BR containing different dosages of PCP (0–10 phr) in a semi efficient vulcanization system were also studied at temperatures ranging from 150°C to 180°C, using an oscillating disk rheometer. The increase in tensile modulus, tensile strength, and tear strength of the vulcanizates in the presence of 5 phr of PCP is presumed to be an indication of reinforcement resulting from accelerated crosslinking reaction as evidenced by higher chemical crosslink density index. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 3195–3200, 2006

Key words: melt rheology; cure characteristics; mechanical properties; blends; polychloroprene; polybutadiene; phosphorylated cardanol prepolymer

INTRODUCTION

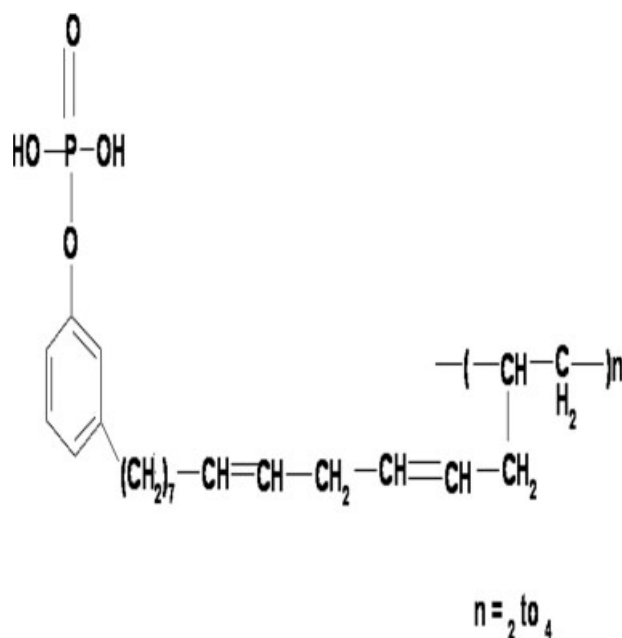
Blends of elastomers are widely used for industrial applications because of the desirable unique combination of superior performance properties, improved processability, and cost advantage imparted by them.¹ It is reported that the incorporation of polybutadiene rubber (BR) in polychloroprene rubber (CR) will result in improved low temperature properties, abrasion resistance, and heat ageing characteristics.² Thus, addition of 10–20 parts of emulsion BR to a neoprene compound was found to give better processing compounds having an improved overall balance of physical properties. CR is endowed with a combination of desirable properties such as resistance to oils and chemicals, flame resistance, etc. Hence blends of BR and CR can be expected to possess the desirable qualities of each of them enabling the design of rubber com-

pounds for various applications such as cover compounds of coal mine conveyor belts, railway brake hoses, etc.

It has recently been found that phosphorylated cardanol prepolymer (PCP) can serve as an excellent 'multifunctional additive' in natural rubber in various roles such as a crosslinkable plasticizer, a tackifier, a coagent for vulcanization, and an improver of filler dispersion and physicomechanical properties of vulcanizates such as tensile and tear strengths, elongation at break, thermal stability, and resistance to fatigue failure and thermo-oxidative decomposition at dosages ranging from 5–20 phr.^{3–6} However, it seems that the properties inherent in the peculiar structural features of PCP have not been fully exploited. PCP is amphiphilic in nature. It has a polar phosphate group and a nonpolar C₁₅ 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 a polar elastomer such as CR and a nonpolar rubber such as BR. The authors have reported recently that PCP could accelerate the heat

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Scheme 1 Prepolymer of PCP.

induced self crosslinking reaction of CR along with an improvement in tensile properties.⁷ Hence, it was anticipated that these improvements could be obtained in a blend of CR and BR upon suitable modification with PCP, thereby leading to cost effective, easily processable, high performance compositions for potential industrial applications. So, the melt rheology, cure characteristics, and mechanical properties of blends of CR and BR modified with different dosages of PCP was studied and the results of which are reported in this article.

EXPERIMENTAL

Materials

CR (Neoprene W) supplied by Du Pont, Dow Elastomers, LLC. was used for the study. BR (Grade BR Nd 40) was obtained from Petroflex[®] Industria e Comercio S.A, Brazil.

PCP (I), an oligomer of monocardanyl phosphoric acid⁸ was synthesized at Regional Research Laboratory (CSIR), Thiruvananthapuram, according to a patented process⁹ (Scheme 1).

Chemicals such as zinc oxide, magnesium oxide, stearic acid, sulfur, tetramethyl thiuram disulfide, and

diorthotolyl guanidine and solvent benzene were of the laboratory reagent grade.

Methods

Blends of BR and CR as given in Table I were prepared by mixing on a Brabender Plasticorder fitted with a mixer measuring head (cam type rotor) at room temperature at a rotor speed of 30 rpm, and their cure characteristics were measured at 150°C and 180°C on the same instrument.

The melt rheology of the blends was studied on a capillary rheometer (Rheoflizer SWO), using a circular die (dia 1 mm, L/D 20) over the temperature range from 60–100°C and shear rate range from 50 to 1000 s⁻¹. The activation energy for melt flow at constant shear rate (E_a) of the mixes over the temperature range 60–100°C was determined using the Arrhenius relationship given as $\eta_a = K e^{E_a/RT}$, where η_a is apparent viscosity. The principal normal stress difference ($\tau_{11} - \tau_{22}$) was determined from the die swell ratio (D_e/D_0) and apparent shear stress (τ_a) using the Tanners equation^{4,10} given as

$$\tau_{11} - \tau_{22} = 2 \tau_a [2(D_e/D_0)^6 - 2]^{1/2}.$$

The activation energy for crosslinking (E_a) of the blends over the temperature range 150–180°C was determined using the Arrhenius relationship given as $t_{\max} = K e^{E_a/RT}$, where t_{\max} is the peak cure time, R is the universal gas constant, and T is the temperature in absolute scale.

The CR/BR mixes containing curatives (compositions of which are given in Table II) were prepared on an open two roll mixing mill (300 mm × 150 mm) at preset roll temperature of 60°C for 10 min as per ASTM D-3182-74. Test specimens were made by compression molding the mixes at preset temperatures for the respective optimum cure time (t_{90}) as determined using the oscillating disk rheometer. 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.

The cure rate was calculated as, cure rate = $(M_h - M_l) / (t_{Mh} - t_{Ml})$ where M_h is the maximum torque, M_l is the minimum torque, and t_{Mh} and t_{Ml} are the time for maximum and minimum torques, respectively.

TABLE I
Composition of CR/BR Blends

Composition	Mix code									
	C ₄ B ₀	C ₃ B ₁	C ₂ B ₂	C ₁ B ₃	C ₀ B ₄	C ₄ B ₀ P	C ₃ B ₁ P	C ₂ B ₂ P	C ₁ B ₃ P	C ₀ B ₄ P
CR	100	75	50	25	–	100	75	50	25	–
BR	–	25	50	75	100	–	25	50	75	100
PCP	–	–	–	–	–	10	10	10	10	10

TABLE II
Composition of CR/BR Mixes Containing Curatives^a

Composition	Mix code								
	(100/0) P0	(90/10) P0	(80/20) P0	(100/0) P5	(90/10) P5	(80/20) P5	(100/0) P10	(90/10) P10	(80/20) P10
CR	100	90	80	100	90	80	100	90	80
BR	0	10	20	0	10	20	0	10	20
PCP	0	0	0	5	5	5	10	10	10

^a Base mix: ZnO, 5; MgO, 4; stearic acid, 0.5; sulphur, 1; TMTD, 0.5; DOTG, 0.5.

The chemical crosslink density (CLD) index, V_r of the CR/BR vulcanizates was determined by equilibrium swelling measurement using benzene, where V_r is given as $V_r = [(D - FT) \rho_r^{-1}] / [(D - FT) \rho_r^{-1} + A_0 \rho_s^{-1}]$, where T is the initial weight of the sample, D is the deswollen weight of the sample, F is the fraction of the insoluble components in the vulcanizate, A_0 is the molar volume of the solvent and ρ_r^{-1} and ρ_s^{-1} are the densities of the vulcanizate and solvent, respectively.^{5,7}

The tensile properties of the cured samples (as per ASTM D-416) and tear strength (as per ASTM D-624-86) were measured on a Universal Tensile testing Machine (model INSTRON - 1145).

RESULTS AND DISCUSSION

CR/BR blends

Melt rheology

The variations in apparent viscosity of the CR/BR blends at 60, 80, and 100°C with apparent shear rates are shown in Figures 1-3, respectively. These show

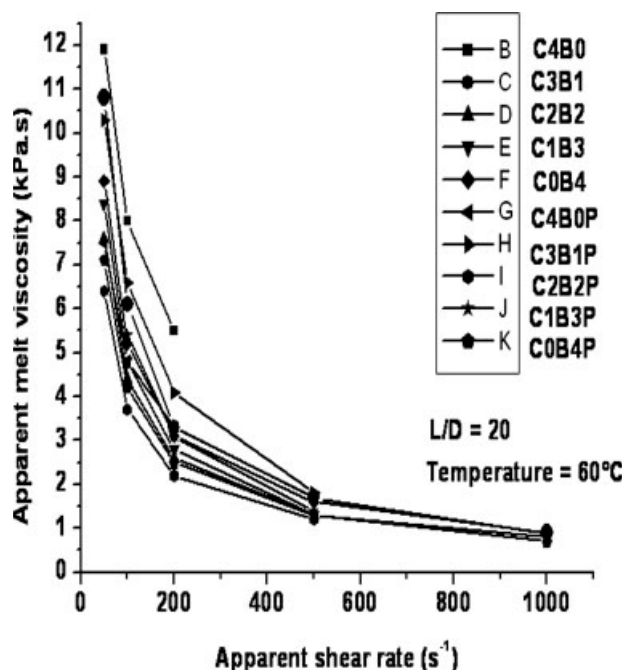


Figure 1 Variation in apparent melt viscosity (η_a) with apparent shear rate (γ_a) of CR/BR mixes at 60°C.

that there is a distinct exponential reduction in viscosity with increases in dosage of BR, temperature, shear rate, and dosage of PCP. Figure 4 shows the variations in activation energy for melt flow of the mixes at constant shear rate (E_a) with dosage of BR in the blends. It can be noted that at the different shear rates and dosages of BR, the PCP modified mixes show lower activation energy for melt flow when compared with the unmodified mixes. Thus, the reduction in apparent melt viscosity and activation energy for melt flow in presence of PCP in the blends is a clear indication of the plasticizing effect of PCP in the blends. It is expected that the C₁₅ aliphatic side chain fraction of PCP enhances the segmental mobility of the base polymers in the blends resulting in the plasticization effect.

Principal normal stress difference

Principal normal stress difference is a good indicator of the compatibility of different components in a

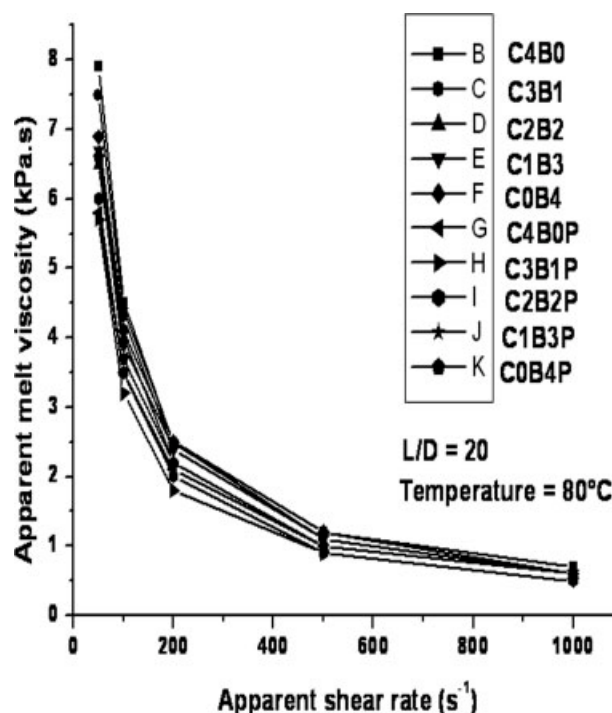


Figure 2 Variation in apparent melt viscosity (η_a) with apparent shear rate (γ_a) of CR/BR mixes at 80°C.

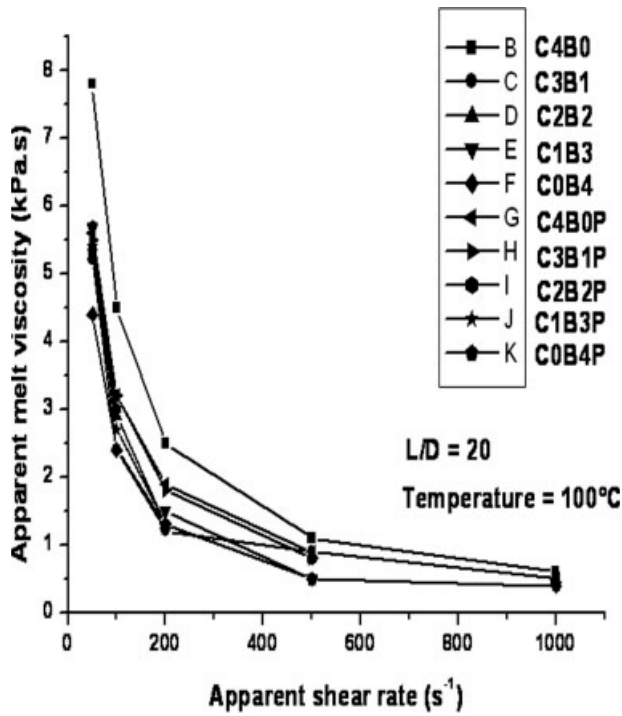


Figure 3 Variation in apparent melt viscosity (η_a) with apparent shear rate (γ_a) of CR/BR mixes at 100°C.

polymer blend; a lower value indicating a high degree of compatibility.^{11,12} Figures 5 and 6 show the variations in principal normal stress difference with dosage of BR in unmodified and PCP modified CR/BR blends. These results show a significant lowering in the principal normal stress difference of the

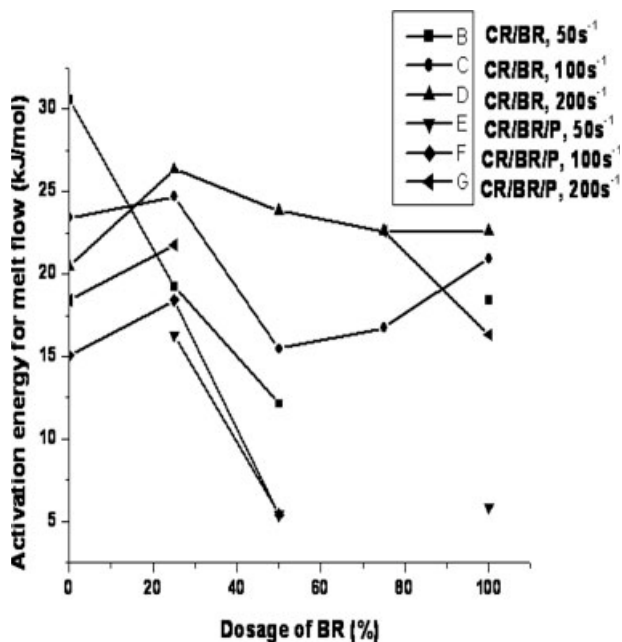


Figure 4 Variation in activation energy for melt flow at constant shear rate (E_a) of CR/BR mixes with dosage of BR.

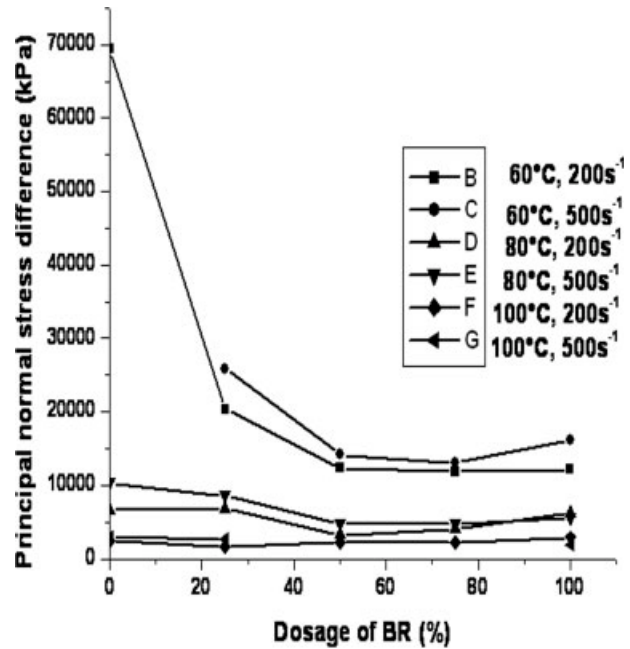


Figure 5 Variation of principal normal stress difference of CR/BR mixes with dosage of BR in CR/BR blends.

blends in presence of PCP at the different shear rates and temperatures. This shows a good level of compatibility between the CR and BR phases in presence of a small amount of PCP. This could probably be the result of PCP acting as a compatibiliser between the polar and nonpolar rubbers essentially due to its amphiphillic nature.

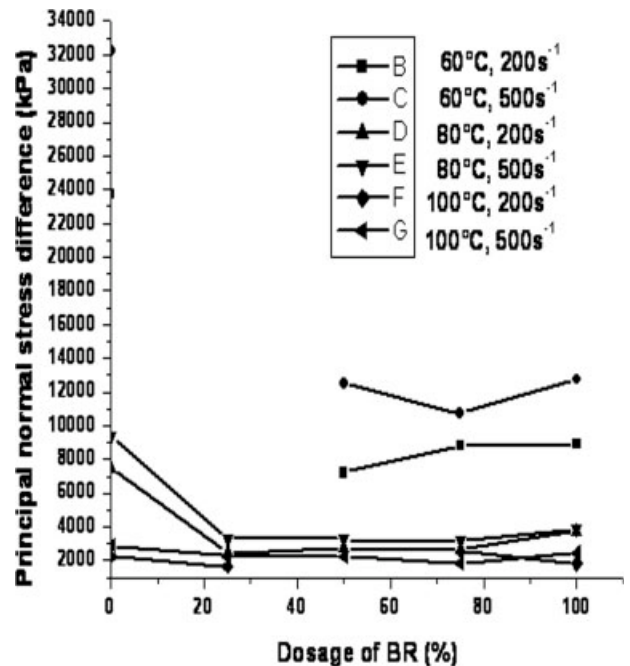


Figure 6 Variation of principal normal stress difference of CR/BR mixes with dosage of BR in CR/BR blends containing PCP.

TABLE III
Cure Characteristics of CR/BR Blends on Brabender Plasticorder

Temperature (°C)	Parameter	Mix code							
		C ₄ B ₀	C ₃ B ₁	C ₂ B ₂	C ₁ B ₃	C ₄ B ₀ P	C ₃ B ₁ P	C ₂ B ₂ P	C ₁ B ₃ P
150	Cure time, t_{100} (min)	22	24.5	27	27	9	9	8.5	8
	Max. torque, M_H (Nm)	16	13	12	11	18	15	16	17
	Cure rate, (M_H /min)	0.7	0.6	0.5	0.4	2.0	1.7	1.9	2.1
180	Cure time, t_{100} (min)	5.5	8	7	5	3	3	3	4
	Max. torque, M_H (Nm)	20	20	23	23	21	19	21	22
	Cure rate, (M_H /min)	3.6	2.6	3.3	4.6	7.1	6.4	7.0	5.4
150–180	Activation energy for crosslinking, E_a (kJ/mol)	–	62.8	75.3	93.3	59.8	59.8	57.3	38.5

Cure characteristics

The results on the cure characteristics of the CR/BR blends as obtained from Brabender Plasticorder at different temperatures are given in Table III. These results show that upon modification of the blends with PCP, there is considerable decrease in cure time and increases in cure rate and maximum torque due to cure. Also, the values for activation energy for crosslinking of PCP modified blends are lower than that of the unmodified blends. This shows the accelerating effect of PCP on thermally induced self crosslinking reaction of CR in the CR/BR blends. Previously, similar results have been observed by the authors in phosphorylated cashew nut shell liquid prepolymer (PCNSL) modified CR.⁷ A probable crosslinking reaction between the hydroxyl group in the phosphate group of PCNSL and the allylic chloro group of CR has been suggested, based on IR spectroscopy data.

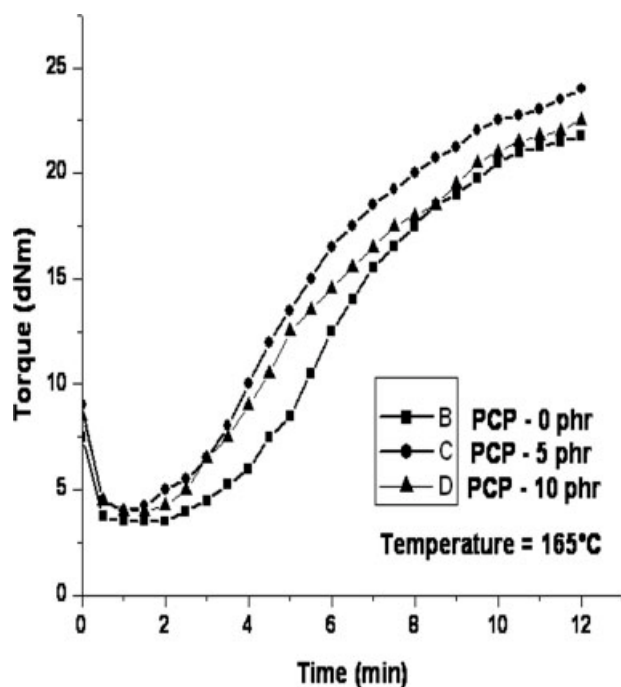


Figure 7 Rheographs at 165°C of CR/BR (90/10) mixes modified with different dosages of PCP.

CR/BR mixes containing curatives

Cure characteristics

The rheographs of CR/BR (90/10) mixes modified with 0–10 phr of PCP at 165°C are shown in Figure 7. The PCP modified mixes show higher cure rate and higher state of cure when compared with the unmodified mix. The results on chemical crosslink density index (V_r) of the CR/BR vulcanizates are given in Table IV. The higher values of V_r for the PCP modified CR/BR vulcanizates further substantiates the higher extent of crosslinking in these systems. The above results show the accelerating effect of PCP in the crosslinking reaction of CR/BR mixes containing curatives.

Mechanical properties

The results on the tensile properties and tear strength of the CR/BR vulcanizates are shown in Table V. With the increase in dosage of BR from 0–20 phr, a decrease in tensile modulus and tensile strength is observed in the unmodified blend vulcanizates, which is a reflection of the reduction in CLD. However, it could be noted that the vulcanizates containing up to 10 phr of BR and 5 phr of PCP show an improvement in the tensile properties and tear strength, when compared with the unmodified CR/BR vulcanizates, which is an indi-

TABLE IV
Chemical Crosslink Density Index (V_r) of CR/BR Vulcanizates^a

Mix code	V_r
100/0 P0	0.181
90/10 P0	–
80/20 P0	0.169
100/0 P5	0.195
90/10 P5	0.176
80/20 P5	–
100/0 P10	0.224
90/10 P10	0.19
80/20 P10	0.171

^a Cure: 10 min at 180°C.

TABLE V
Mechanical Properties of CR/BR Vulcanizates^a

Property	Mix code								
	(100/0) P0	(90/10) P0	(80/20) P0	(100/0) P5	(90/10) P5	(80/20) P5	(100/0) P10	(90/10) P10	(80/20) P10
Modulus-100% (MPa)	0.581	0.449	0.419	0.541	0.520	0.318	0.742	0.457	0.352
Modulus-300% (MPa)	1.871	1.476	1.426	2.255	1.822	1.537	2.461	2.113	1.711
Tensile strength (MPa)	4.938	4.528	4.017	6.946	9.354	3.395	4.540	3.629	1.969
Elongation at break (%)	550	580	580	540	680	510	440	430	320
Tear strength (N/mm)	20.3	15.6	22.1	25.1	27.2	25.9	20.7	23.3	19.0

^a Cure: 10 min at 180°C.

cation of the reinforcing effect of PCP in these systems. Suitability of such systems for industrial applications could be explored.

CONCLUSIONS

The results on the melt rheology of CR/BR blends modified with PCP indicate that PCP acts as a plasticizing additive and compatibilizer in the blends. PCP was also found to accelerate the heat induced self crosslinking reaction of CR in the blends. Besides, the reinforcing effect of PCP in the blends was evident from the increase in mechanical properties at an optimal dosage of 5 phr of PCP.

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