

# Studies on Blends of Natural Rubber and Ethylene Propylene Diene Rubber Modified with Phosphorylated Cardanol Prepolymer: Processability, Physico-Mechanical Properties, and Morphology

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**ABSTRACT:** The melt processability and physico-mechanical properties of blends of natural rubber (NR) and ethylene propylene diene rubber (EPDM) containing different dosages (0–10 phr) of phosphorylated cardanol prepolymer (PCP) were studied in unfilled and china-clay-filled mixes. The plasticizing effect of PCP in the blends was evidenced by progressive reduction in power consumption of the mixing and activation energy for melt flow with an increase in the dosage of PCP. The PCP-modified blend vulcanizates showed higher tensile properties and tear strength despite a decrease in the chemical crosslink density (CLD) index. This is presumably due to

the formation of a crosslinked network structure of PCP with the rubbers and improved dispersion of the filler particles in the rubber matrix, as evidenced by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Thermogravimetric analysis showed an increase in thermal stability of the blend vulcanizate in presence of 5 phr of PCP. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 5123–5130, 2006

**Key words:** natural rubber; ethylene propylene diene rubber; phosphorylated cardanol prepolymer; processability; mechanical properties; morphology

## INTRODUCTION

Blends of elastomers are currently being used widely for the manufacture of a variety of rubber products for diverse applications. The major rubber components in an engineered product such as tires are mostly a blend of two or more rubbers.<sup>1</sup> The primary aim in this article is to achieve the best balance of properties required for the part, making use of the desirable attributes of each rubber. Thus, the sidewall compound of a tire must be resistant to flex fatigue, cut growth, weather, and ozone, and be optionally nondiscoloring.<sup>1</sup> Besides, it must have adequate building tack, good processability, and low cost. Ethylene propylene diene rubber (EPDM) is endowed with the former set of attributes but is deficient in the latter. Natural rubber (NR) has excellent tack strength, physical properties, and processability. Extensive studies on blends of NR and EPDM for various applications such as tire side walls, light-colored injection-molded products, extruded profile weatherstrips, and so forth have been reported.<sup>2–9</sup> The incompatibility of EPDM having a lower level of unsaturation with higher unsaturated diene elastomers has been recognized as a major factor limiting the mutual molecular chain interactions and co-crosslinking.<sup>3–5</sup> Baranwal

and Son obtained excellent cure compatibility between EPDM and NR along with improved tensile properties and reduced heat buildup by grafting accelerators on to EPDM.<sup>6</sup> Rubber compounds based on blends of EPDM and NR having good ozone and chemical resistance and reduced compression set have been reported.<sup>7</sup> NR–EPDM blends for high temperature resistance<sup>8</sup> and automotive application<sup>9</sup> have also been reported.

Phosphorylated cashew nut shell liquid (PCNSL)<sup>10</sup> and phosphorylated cardanol prepolymer (PCP)<sup>11</sup> synthesized from cashew nut shell liquid (CNSL) and cardanol, respectively, renewable natural resources obtained from the cashew industry, have been found to be suitable for various applications such as adhesives for bonding plywood, friction modifying additive for automobile brake lining, foundry core oil binder, and flame retardant plasticizer for plastics. Previous studies have shown that PCNSL/PCP<sup>12</sup> could function as a multifunctional additive in NR and synthetic rubbers in various roles as a crosslinkable plasticizer, a softener, a tackifier, an antidegradant, an improver of the thermal stability and mechanical properties of vulcanizates (tensile strength, tear strength, and fatigue resistance), and a coupling agent between silica filler and NR, leading to improvement in resistance to crack propagation.<sup>12–20</sup>

It has been reported previously that carbon-black-filled EPDM vulcanizates containing PCNSL showed improvements in cure rate, tear strength, thermal stability, and resistance to thermo-oxidative decomposi-

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TABLE I  
Composition of Mixes: Blends of NR, EPDM, and PCP

Ingredients	Mix code		
	NE	NE-P5	NE-P10
NR	50	50	50
EPDM	50	50	50
PCP	—	5	10

tion as compared to a commercial plasticizer.<sup>18</sup> A recent study on the melt rheology of EPDM modified with 5–10 phr of PCNSL on a capillary rheometer over a wide range of temperatures and shear rates showed the plasticizing effect of the additive on the rubber and the consequent improvement in melt processability.<sup>19</sup> Good compatibility between EPDM and PCNSL was evidenced by lower values of principal normal stress difference versus that of unmodified EPDM.<sup>19</sup> Similar results have been reported for PCNSL-modified NR also, thus establishing the role of PCNSL as a plasticizer.<sup>15</sup> In blends of NR and EPDM the tack strength is known to increase almost linearly as a function of NR content.<sup>21</sup> For applications such as that for passenger tire carcasses, generally 30% to 60% NR is being used.<sup>1</sup> Hence, NR/EPDM blends (50/50) modified with 5–10 phr of PCP are expected to have an ideal combination of desirable properties. The melt processability and physico-mechanical properties of the semi-efficient vulcanization systems of such blends have been studied, the results of which are described in this article.

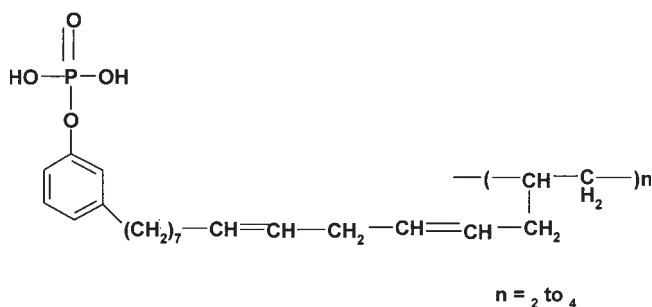
## EXPERIMENTAL

### Materials

PCP (I)—an oligomer of monocardanyl phosphoric acid—was synthesized at Regional Research Laboratory (CSIR), Thiruvananthapuram, India, according to a patented process.<sup>10</sup>

### Prepolymer of PCP

EPDM (grade NORDEL-1046) was obtained from M/s Jal Jyothi International (Mumbai, India). NR (grade, RSS-V) and other rubber chemicals (labora-



Scheme 1 Prepolymer of PCP.

tory reagent grades) were obtained locally. China clay (grade BCK) was obtained from M/s English Indian Clays Ltd. (Thiruvananthapuram, India).

### Methods

Blends of NR, EPDM, and PCP and semi-efficient vulcanization systems of the blends having compositions as given in Tables I and II, respectively, were prepared by mixing in a Brabender Plasticorder (Model PLE 651; Duisberg, Germany) at room temperature and at a rotor speed of 30 rpm for 15 min.

30 g each of the NR/EPDM blends were mixed in the Plasticorder at preset rotor speeds (30 and 60 rpm) and temperatures (60°C, 100°C, and 140°C). The power consumption for mixing ( $P$ ) was obtained from the equilibrium torque at the tenth minute ( $M$ ) in m.kg and the angular velocity of the rotor ( $\omega$ ), using the relation  $P = M\omega$ , where  $\omega = 2\pi S/60$  with  $S$  the rotor speed in rpm. The apparent melt viscosity indexes ( $\eta$ ) of the blends were obtained as,  $\eta = M/S$ . The activation energy for melt flow ( $\Delta E$ ) of the blends at the different rotor speeds was calculated using the Arrhenius relation given as

$$\Delta E = R[d \ln \eta / d(1/T)]$$

where  $R$  is the universal gas constant and  $T$  is the temperature in absolute scale.

The cure time of the mixes was measured using 30 g of the premixes in the Brabender Plasticorder at 150°C and at a rotor speed of 30 rpm. Cure time was taken as the time to reach the maximum value in the torque profile. Test samples were prepared by compression molding the above mixes at 150°C at the respective cure times.

Chemical crosslink density (CLD) indexes of the vulcanizates ( $V_r$ ) were determined by the equilibrium swelling method using benzene as solvent.<sup>13,22</sup> The volume fraction of rubber ( $V_r$ ) in the swollen sample of the vulcanizate is given as,

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

TABLE II  
Composition of Mixes: SEV Systems

Ingredients	Composition (phr)					
	U	U-P5	U-P10	F	F-P5	F-P10
NR	50	50	50	50	50	50
EPDM	50	50	50	50	50	50
ZnO	5	5	5	5	5	5
St. acid	2	2	2	2	2	2
Sulphur	2	2	2	2	2	2
MBT	1.5	1.5	1.5	1.5	1.5	1.5
TMT	0.5	0.5	0.5	0.5	0.5	0.5
PCP	—	5	10	—	5	10
China clay	—	—	—	20	20	20

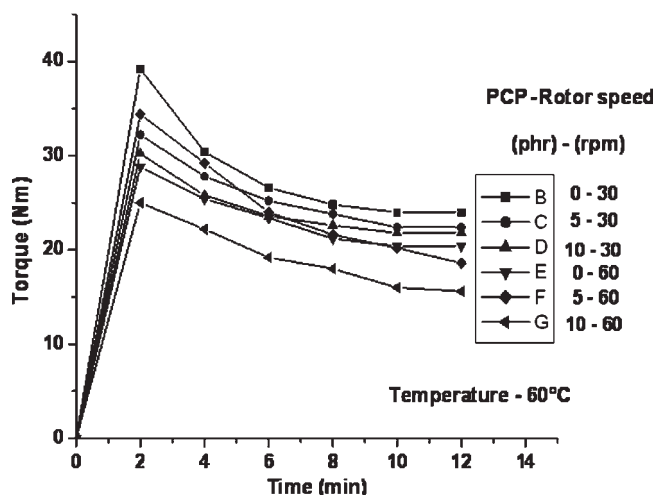


Figure 1 Brabender torque profiles at 60°C of NR/EPDM blends containing different dosages of PCP.

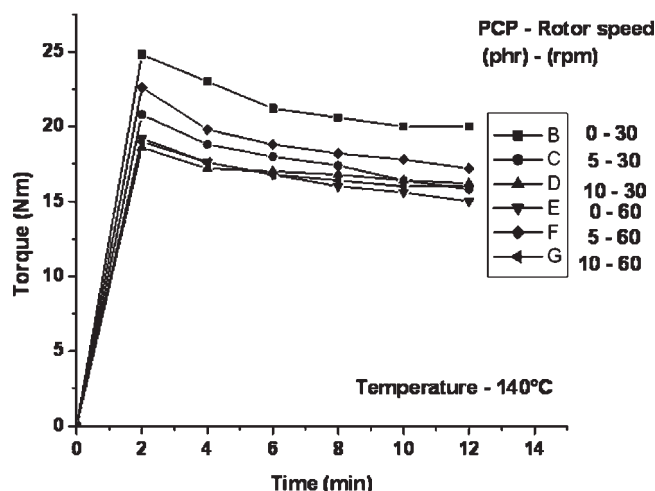


Figure 3 Brabender torque profiles at 140°C of NR/EPDM blends containing different dosages of PCP.

where  $D$  is the deswollen weight of the vulcanizate,  $F$  is weight fraction of insoluble components of the vulcanizate,  $T$  is the initial weight of the test specimen,  $\rho_r$  is the density of the rubber vulcanizate,  $A_o$  is the weight of the solvent absorbed under equilibrium condition, and  $\rho_s$  is the density of the solvent ( $0.941 \text{ g ml}^{-1}$ ).

The tensile properties of the vulcanizates were measured using a Universal Testing Machine (Hounsfield Model H5 KT; Surrey, UK) at a crosshead speed of 500 mm/min as per ASTM D-412-1978. Tear strengths of the samples were also measured on the same equipment as per ASTM D-624-86.

The morphology of the cut surfaces of the specimens was studied using a scanning electron microscope (Model JEOL-JSM 5600LV SEM, Tokyo, Japan) after sputter coating the surfaces with a fine coater (Model JEOL-JFC 1200). Also, the cut surfaces of the vulcani-

zate specimens were observed using an atomic force microscope (AFM, Nanoscope IV, Digital Instruments, VEECO Instruments, Santa Barbara, CA) under tapping mode.

Thermogravimetric analysis (TGA) of the vulcanizates was carried out in nitrogen atmosphere at a heating rate of 20°C/min on a thermogravimetric analyzer (Model Shimadzu DTG 60).

## RESULTS AND DISCUSSION

### Melt processability

#### Mixing

The variations in mean value of the torque with time obtained during mixing of the NR/EPDM (50/50) blends containing different dosages of PCP in the

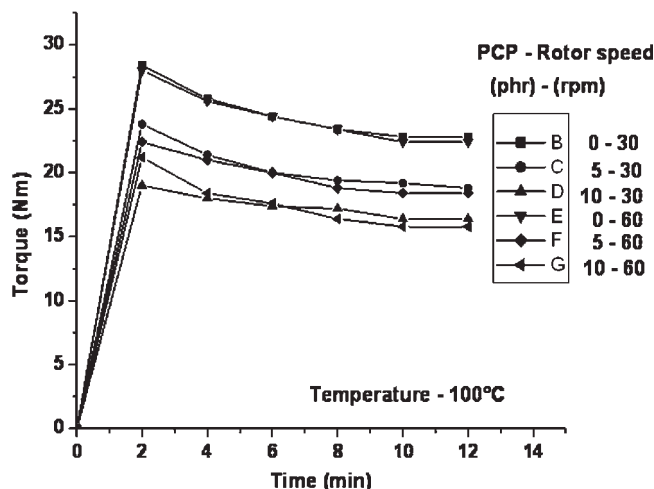


Figure 2 Brabender torque profiles at 100°C of NR/EPDM blends containing different dosages of PCP.

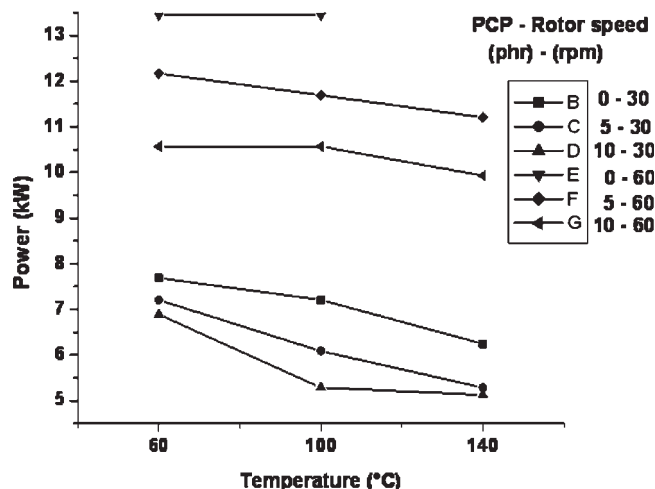


Figure 4 Power consumption for mixing NR/EPDM mixes containing different dosages of PCP.

**TABLE III**  
Activation Energy For Melt Flow at Constant Shear Rate ( $E_a$ ) of PCP-Modified NR/EPDM Blends<sup>a</sup>

Mix code	Rotor speed $S$ (rpm)	Activation energy $E_a$ (kJ)
NE	30	11.101
	60	10.284
NE-P5	30	10.284
	60	2.986
NE-P10	30	9.621
	60	1.991

<sup>a</sup>  $T = 333\text{--}413^\circ\text{K}$ .

Brabender Plasticorder at  $60^\circ\text{C}$  are shown in Figure 1. The corresponding torque profiles obtained at  $100^\circ\text{C}$  and  $140^\circ\text{C}$  are given in Figures 2 and 3, respectively. Figure 4 shows the variations in power consumption for mixing of the blends with respect to temperature at different rotor speeds. The values of activation energy for melt flow at constant shear rate of the blends over the temperature range from  $60^\circ\text{C}$  to  $140^\circ\text{C}$  are given in Table III.

Figures 1–3 show progressive decreases in the equilibrium value of the Brabender torque with the increase in dosage of PCP from 0 to 10 phr at the different preset rotor speeds and temperatures. However, this decrease is more prominent at the lower rotor speed (30 rpm) and at the lower temperatures ( $60^\circ\text{C}$  and  $100^\circ\text{C}$ ). Figure 4 also shows a similar decrease in power consumption for mixing with the increase in dosage of PCP and increase in temperature. The lower values of activation energy for melt flow ( $E_a$ ) of the PCP-modified blends and its steady decrease with increase in rotor speed, as given in Table III, indicate the softening effect and the consequent improvement in melt processability in the presence of PCP. This is presumably due to the plasticizing effect of PCP on the rubber phase similar to that observed earlier for NR<sup>15</sup> and EPDM<sup>19</sup> separately. It is believed that the unsaturated hydrocarbon side-chain fraction of PCP facilitates the segmental motion of elastomers in the blends, leading to the observed improvement in melt processability.

**TABLE IV**  
Cure Time of the Mixes at  $150^\circ\text{C}$

Mix code	U	U-P5	U-P10	F	F-P5	F-P10
Cure time (min)	5'30"	5'	5'30"	8'30"	5'	5'

#### Cure characteristics

The results given in Table IV show a decrease in cure time with the increase in dosage of PCP in the unfilled and filled mixes. However, this is particularly prominent in the filled mixes. Also, the CLD index of the unfilled vulcanizates decrease with increase in dosage of PCP, as shown in Table V. The higher cure rate of the mixes containing PCP (dosage up to 10 phr) is analogous to that reported earlier for an unfilled NR system.<sup>14</sup> This could be due to the enhanced mobility of the rubber chains in the presence of PCP along with immediate access to sufficient unsaturation sites of the side chains of PCP, for crosslink formation with the main chains of NR/EPDM. The lower CLD index of the vulcanizates in the presence of PCP may be due to their participation in the crosslinking reaction, probably leading to the formation of a crosslinked network structure similar to the one reported earlier for PCP-modified NR.<sup>13</sup>

It is possible that the phosphate group of PCP can have interaction with the polar groups on the surface of china clay and the unsaturated side-chain fraction of PCP may become co-crosslinked with the unsaturation of NR/EPDM via formation of sulphidic linkages. A similar crosslinking reaction leading to an entangled structure was suggested earlier for PCP-modified NR vulcanizates.<sup>13</sup> Such a reaction could probably enhance the cure rate of the PCP-modified system, thus leading to a reduction in cure time as shown in Table IV.

#### Physico-mechanical properties

##### Mechanical properties

Table V shows the results on the CLD index ( $V_r$ ), tensile properties and tear strength of the blend vulcanizates. It can be seen that the tensile strength and elongation at break of the unfilled and filled blend vulcanizates

**TABLE V**  
Physico-Mechanical Properties of the Vulcanizates

Mix code	U	U-P5	U-P10	F	F-P5	F-P10
Cure time (min)	5'30"	5'	5'30"	8'30"	5'	5'
Property	Mix code					
	U	U-P5	U-P10	F	F-P5	F-P10
CLD index $V_r$	0.540	0.537	0.485	—	—	—
Tensile strength (MPa)	19.4	—	22.4	20.9	21.4	25.1
Elongation at break (%)	330	—	430	240	310	270
Tear strength (kN/m)	83.6	86.5	106.7	88.8	130.5	94.3

increase simultaneously with the increase in dosage of PCP from 0 to 10 phr. Also, the vulcanizates containing PCP show a similar steady increase in tear strength.

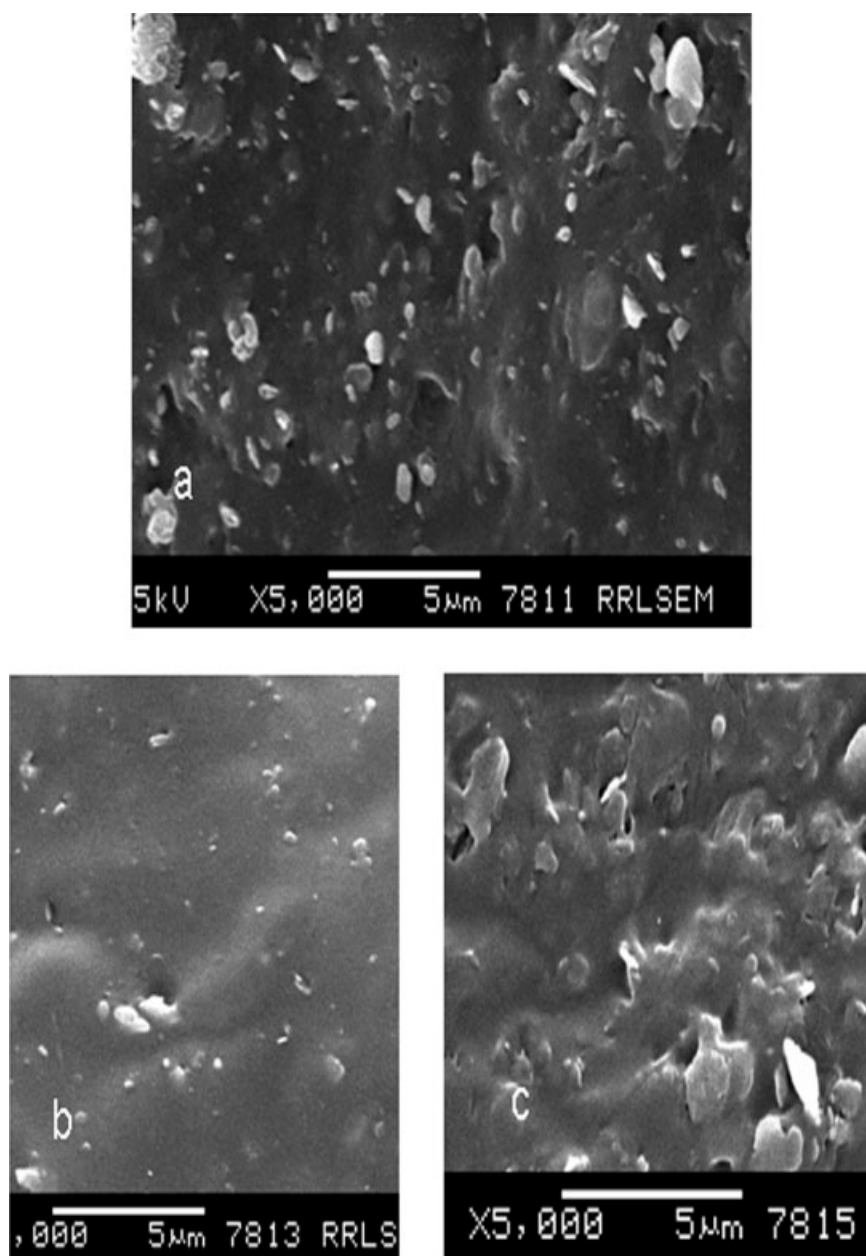
The increase in the mechanical properties of the PCP-modified vulcanizates (despite the reduction in CLD index) is presumably due to the possible formation of a network structure between PCP and NR/EPDM, similar to the one reported earlier<sup>13</sup> for PCP-modified unfilled NR. Such a structure could allow higher elongations to be reached before failure in tensile or tear modes.<sup>12</sup>

In the china-clay-filled mixes of the blend vulcanizates a maximum elongation of the break and tear

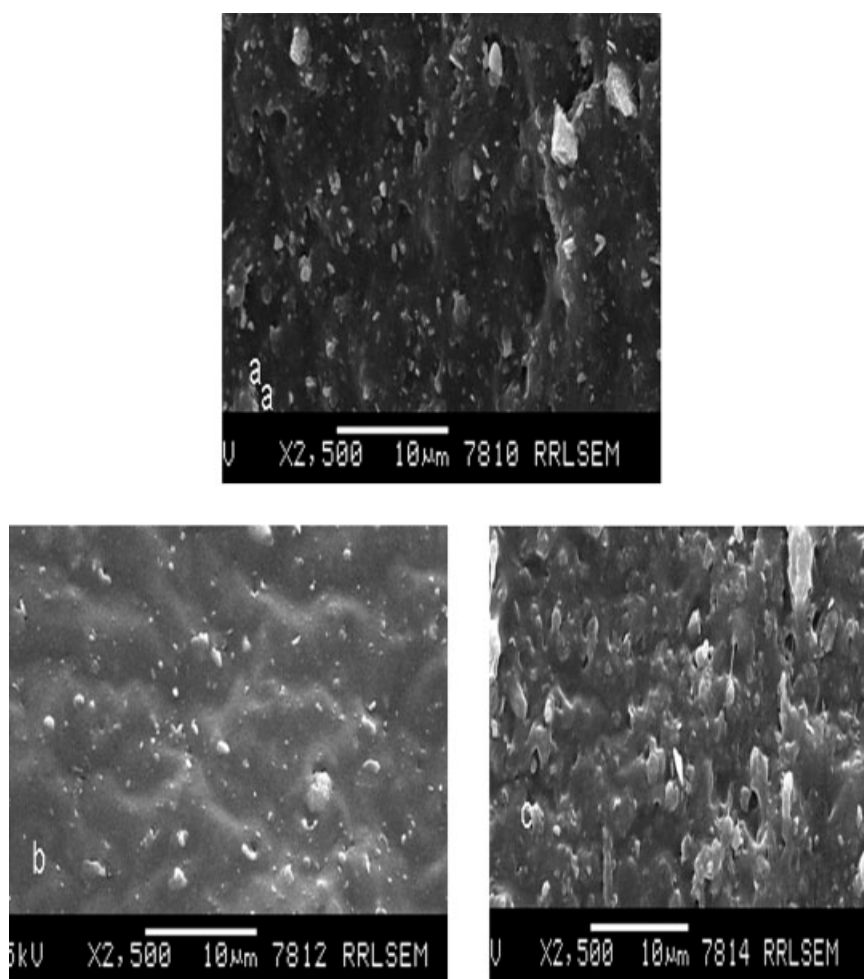
strengths is observed in the presence of 5 phr of PCP. This could probably be due to the better dispersion of the filler particles in the rubber matrix, assisted by higher shear forces during mixing. A similar behavior was reported earlier in carbon-black-filled NR vulcanizates containing PCP.<sup>20</sup>

#### Morphology of filled vulcanizates

The SEM micrographs of the china-clay-filled vulcanizates containing different dosages of PCP are given in Figures 5 and 6. The micrographs of the vulcanizate not containing PCP show filler particles of nonuniform size



**Figure 5** Scanning electron micrograph of the cut surface of NR/EPDM (50/50) blend vulcanizate ( $\times 5000$ ) containing (a) china clay (20 phr), (b) china clay (20 phr) and PCP (5 phr), and (c) china clay (20 phr) and PCP (10 phr).



**Figure 6** Scanning electron micrograph of the cut surface of NR/EPDM (50/50) blend vulcanizate ( $\times 2500$ ) containing (a) china clay (20 phr), (b) china clay (20 phr) and PCP (5 phr), and (c) china clay (20 phr) and PCP (10 phr).

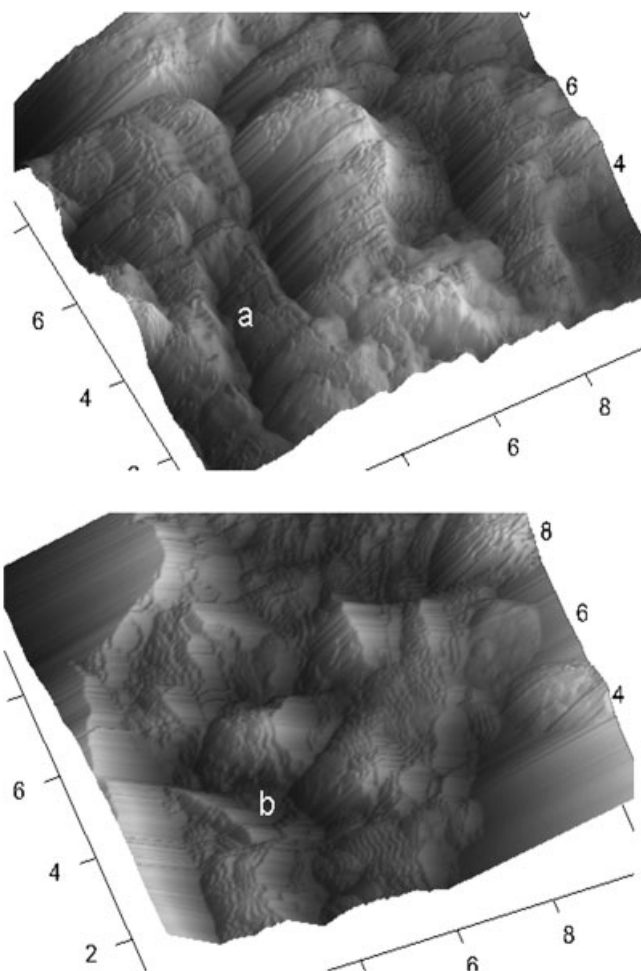
dispersed unevenly in the matrix along with improper wetting of the filler by rubber. In sharp contrast to this, the micrographs of the vulcanizates containing 5 and 10 phr of PCP show a larger number of smaller filler particles dispersed more uniformly in the matrix along with better 'wetting' by the rubber matrix. This could also be another reason for the higher mechanical properties of the PCP-modified vulcanizates. Figure 7(a,b) shows the AFM of the china-clay-filled blend vulcanizates not containing PCP and with 10 phr of PCP, respectively. The vulcanizate not containing PCP shows particles of nonuniform size (around 430 nm) as compared to the uniform particles around 400 nm in size for the PCP-modified vulcanizate.

It is well known that filler dispersion to an adequate level is needed for the development of optimum properties.<sup>23</sup> In an earlier work on silica-filled NR vulcanizates containing PCP, the improved mechanical properties was ascribed partly to the better dispersion of the filler particles in the presence of PCP and to the role of PCP as a coupling agent between the filler and the elastomer matrix.<sup>16</sup> Probably, a similar interaction in the

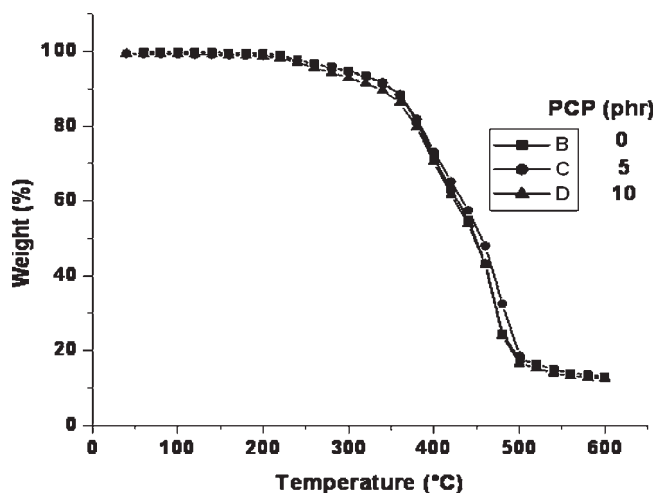
china-clay-filled mixes containing PCP may contribute to the observed improvements in morphology and mechanical properties of the NR/EPDM blends.

#### Thermal stability

Thermograms of unfilled NR/EPDM blend vulcanizates containing different dosages of PCP as obtained from TGA are shown in Figure 8. Table VI shows the calculated values of thermal stability index ( $T_{50}$ ) of the vulcanizates. The shifting of the TGA profile of the vulcanizate containing 5 phr of PCP towards higher temperature and the corresponding higher value of  $T_{50}$  indicate an increase in thermal stability. This may possibly be due to the formation of some thermally stable structure in this vulcanizate decomposing subsequently at a later stage. A similar behavior has been observed in an earlier work in unfilled NR vulcanizates containing different dosages of PCP.<sup>24</sup> The slight reduction in thermal stability at the higher dosage of PCP (10 phr) could be due to the decomposition of the aliphatic segment of PCP.



**Figure 7** AFM of the cut surfaces of NR/EPDM (50/50) blend vulcanizate containing (a) china clay (20 phr) and (b) china clay (20 phr) and PCP (10 phr).



**Figure 8** Thermograms of unfilled NR/EPDM blend vulcanizates containing different dosages of PCP.

**TABLE VI**  
Thermal Stability Index  $T_{50}$  of the Unfilled Vulcanizates

Mix code	U	U-P5	U-P10
Thermal stability index $T_{50}$ (°C)	450.1	456.6	448.4

## CONCLUSION

The effect of variations in the dosage of PCP on melt processability and physico-mechanical properties of unfilled and china-clay-filled NR/EPDM blends has been studied. The decreases in power consumption of the mixing and activation energy for melt flow indicate an improvement in the processability of the blends in the presence of PCP, which is presumed to be due to the plasticization effect of the additive on the rubbers. The increase in tensile properties and tear strength of the blend vulcanizates in the presence of PCP, despite a reduction in the CLD index, is presumably due to the participation of PCP in the crosslinking reaction with the rubbers and better dispersion of the filler particles in the rubber matrix in the presence of PCP. Also, at a dosage of 5 phr PCP is found to improve the thermal stability of the blend vulcanizate.

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