

# Evidence of thermally induced chemical reactions in miscible blends of poly(vinyl chloride) and epoxidized natural rubber

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It is evident from Monsanto rheometry, solvent swelling and infra-red spectroscopic studies that miscible blends of poly(vinyl chloride) (PVC) and epoxidized natural rubber (ENR) can be crosslinked during high-temperature moulding for prolonged periods. The crosslinking has no effect on blend miscibility. The physical properties of the blends depend on the blend composition. As the PVC content increases the blend behaviour changes from elastomeric to glassy.

(Keywords: crosslinking; plastic-rubber blend; miscible blend; poly(vinyl chloride); epoxidized natural rubber)

## INTRODUCTION

Poly(vinyl chloride) (PVC) and epoxidized natural rubber (ENR) have recently attracted the attention of many researchers. Margaritis and Kalfoglou<sup>1</sup> reported studies on solution-cast PVC/ENR blends, while Varughese *et al.*<sup>2,3</sup> studied thermoplastic elastomeric blends of PVC and ENR. Earlier workers moulded the samples for short times (about 5 min). It has been subsequently reported that if the moulding is continued for a prolonged time (60 min) at high temperature (180°C) crosslinking between PVC and ENR could occur<sup>4</sup>. Blends which undergo thermally induced crosslinking have been referred to as 'self-crosslinkable plastic-rubber blends'<sup>5-7</sup>. In this paper, we report the results of our studies on stabilized PVC/ENR blends, with special reference to their Brabender Plasticorder processability, physical properties and miscibility. Swelling and infra-red spectroscopic studies were used to confirm the crosslinking reaction in these blends.

## EXPERIMENTAL

Details of the materials used are given in *Table 1*; the formulations of the blends in parts by weight are PVC/ENR: 25/75, 50/50 and 75/25, in each case with a stabilizer concentration of 8 parts per 100 parts PVC.

The mixing was carried out in a Brabender Plasticorder (model PLE-330) using a cam-type mixer at a rotor speed of 60 rev min<sup>-1</sup> and temperature of 180°C. At first, PVC resin along with the stabilizer was allowed to soften for 2 min and ENR was added thereafter and mixed for another 4 min. The total mixing time was thus 6 min in all cases. The hot mix was then quickly removed from the mixing chamber and sheeted on a laboratory two-roll mill.

In order to study the variation in torque and temperature developed during mixing, the mixing was continued for up to 60 min.

Rheographs of the blends prepared in a Brabender Plasticorder (180°C, 60 rev min<sup>-1</sup>, 6 min) were taken at 180°C using a Monsanto rheometer R-100. The processing characteristics were determined using a Mooney shearing disc viscometer, model MK-III (Negretti Automation, UK) according to ASTM D 1646-1963. The blends were moulded for 60 min at 180°C in a Labo press, model 10T, (Toyo Seiki Seisaku-Sho Ltd, Japan) and after moulding the samples, while still under pressure, were immediately cooled down to room temperature by cold water circulation through the platens. In order to study the effect of moulding time on miscibility, the 50/50 PVC/ENR blend was also moulded for 3 min at 180°C.

Infra-red (i.r.) spectra were obtained with a Perkin-Elmer 843 spectrophotometer. Thin film samples of 50/50 PVC/ENR blend were moulded between aluminium foil at 180°C for 3 min, 60 min and 120 min. The difference in spectra due to change in moulding time was recorded using the sample moulded for 3 min as the reference.

Dynamic mechanical analyses were performed in a Rheovibron DDV-III-EP (Orientec Corporation, Japan) at a double strain amplitude of 0.1% and a frequency of 3.5 Hz. The measurements were carried out at a heating rate of 2°C min<sup>-1</sup> over a temperature range of -100° to 150°C.

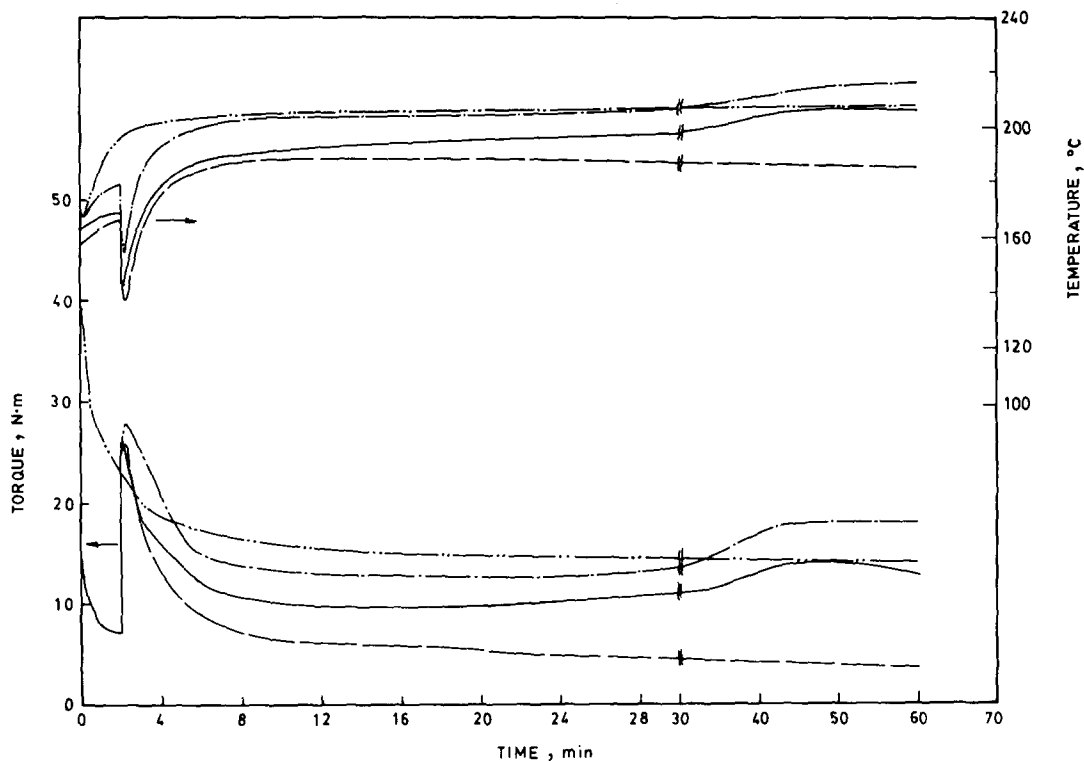
The tensile stress-strain properties were measured at room temperature (27 ± 2°C) according to ASTM D 412-87 in an Instron Universal Testing Machine, model 1195, at 500 mm min<sup>-1</sup> rate of grip separation. Tear strength was also measured under the same conditions according to ASTM D 624-86. The hardness was determined according to ASTM D 2240-86 and expressed in Shore D units.

The volume fraction of rubber ( $V_r$ ) in the swollen vulcanizate was determined by equilibrium swelling<sup>8</sup> in tetrahydrofuran at room temperature (27 ± 2°C). The blends were solvent extracted using a Soxhlet extraction apparatus using both chloroform (solvent for ENR alone) and tetrahydrofuran (common solvent) for 12 h each and

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**Table 1** Details of the materials used

Materials	Abbreviation	Description	Source
Poly(vinyl chloride)	PVC	Suspension-polymerized PVC (NOCIL PVC Polymer S 67-311); $K = 66-69$ , $\bar{M}_w = 3.5 \times 10^5$	National Organic Chemical Industries Ltd, Bombay, India
Epoxidized natural rubber	ENR	ENR-50, 50 mol% epoxidized natural rubber, specific gravity 1.03, $\bar{M}_w = 4.7 \times 10^5$	The Malaysian Rubber Producers' Research Association, Herts, UK
Naperak-2201	PVC stabilizer	Solid meta complex PVC stabilizer, barium-cadmium type	National Peroxide Ltd, Bombay, India


**Figure 1** Torque and temperature dependence on time of mixing. Neat PVC with stabilizer (— · — ·), PVC/ENR blend: 25/75 (— — —), 50/50 (— — —) and 75/25 (— · — ·)

the extracted samples were dried and weighed until consistent weight was obtained.

## RESULTS AND DISCUSSION

Figure 1 shows the variation of mixing torque and temperature with mixing time in the Brabender Plasticorder at 180°C. The results are summarized in Table 2. The minimum torque increases with increase in PVC content. The Plasticorder scorch time, defined as the time (after the addition of the rubber) for a torque rise of two units above the minimum, is quite long, showing the processing safety of the blends. In the case of 25/75 PVC/ENR after the initial reduction, there is little rise in torque, showing the low level of reactivity in this blend. This is further confirmed by Monsanto rheometric studies, as discussed later. The difference between maximum and minimum torque (Table 2) shows that the extent of interaction follows the order 75/25 > 50/50 > 25/75 PVC/ENR. It was also noted that stabilized PVC alone (containing 8 parts by weight of stabilizer per 100 parts PVC) does not show

**Table 2** Processing characteristics using a Plasticorder

	PVC/ENR blend			
	25/75	50/50	75/25	100/0
Minimum torque (N m)	3.5	9.5	12.5	14.0
Plasticorder scorch time (min)	> 60	31	32	> 60
$\Delta$ Torque <sup>a</sup> (N m)	0.75	4.5	5.5	0
Temperature rise (°C)	10	26	37	26

<sup>a</sup> Difference between maximum and minimum torque values

any rise in torque. This indicates that the torque rise in the case of these blends is due to the chemical crosslinking between the two polymers (PVC and ENR). The temperature *versus* time plots show that the 25/75 blend shows the smallest rise in temperature, while the greatest rise is seen in the case of 75/25 PVC/ENR.

The Monsanto rheographs of the PVC/ENR blends, prepared in Brabender Plasticorder (180°C, 60 rev min<sup>-1</sup>, total 6 min mixing) are shown in Figure 2. The blends register a composition-dependent rise in torque at 180°C,

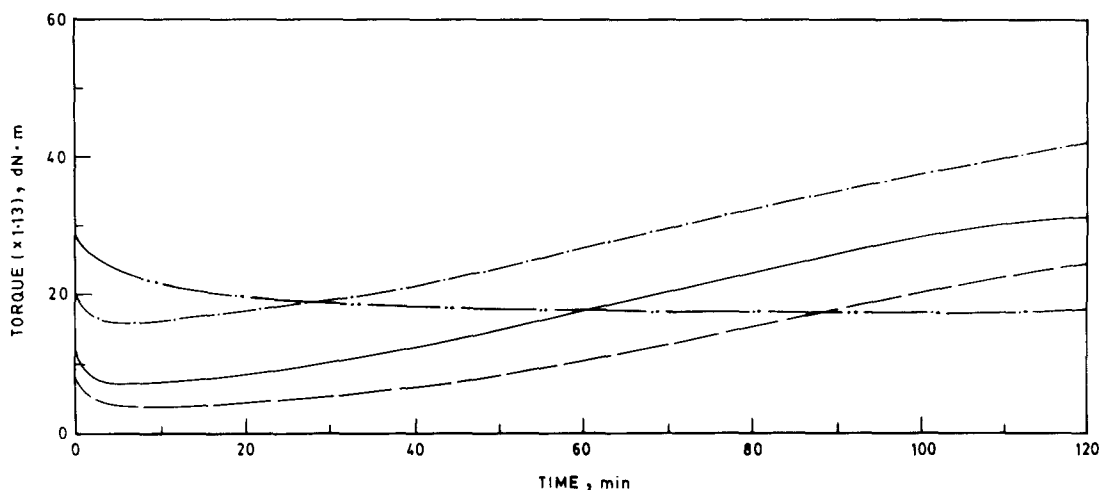


Figure 2 Monsanto rheographs of PVC/ENR blends at 180°C; curves as in Figure 1

Table 3 Processing characteristics of PVC/ENR blends

	PVC/ENR blend			
	25/75	50/50	75/25	100/0
Mooney viscometer data				
ML(1+4), 120°C	41	104	166	277
Scorch time, at 120°C (min)	>60	>60	>60	>60
Monsanto rheometer data				
Minimum torque, ( $\times 1.13$ ) at 180°C (dN m)	4.0	7.0	16.0	18.0
Scorch time at 180°C (min)	33	22	20	>120

showing the chemical interaction between the two polymers. The pure polymers do not show such an increase in torque, thus eliminating the possibility of thermovolcanization of the pure polymers in the blend. The processing characteristics studied from the Monsanto rheometer are summarized in Table 3. The minimum torque increases with increase in PVC content in the blend (approximately a linear function of the PVC weight fraction). This trend is the same as that observed in the Brabender Plasticorder studies. This indicates that the chemical interaction increases with increasing PVC concentration which ensures availability of more allylic chlorine sites. The difference between the Plasticorder and rheometric scorch times may be attributed to the difference in the shear fields of the two machines.

Results of the Mooney shearing disc viscometer studies are given in Table 3. Mooney viscosity increases with increase in PVC content. The blends possess very long scorch times, indicating extraordinarily good processing safety.

The infra-red spectra of the 50/50 PVC/ENR blend moulded for 3 min were deducted from those of blends moulded for 60 and 120 min (at 180°C) and are shown in Figure 3. The blend shows C–O stretching vibration of ethers at 1072  $\text{cm}^{-1}$  and reduction in epoxy ring vibration at 875  $\text{cm}^{-1}$ . The ether peak intensity increases when moulded for 120 min and there is reduction in epoxy ring peak. It has been reported earlier that epoxy resin can crosslink PVC<sup>9</sup>. Also, it has been shown that the allylic moieties of 4-chloro-2-hexene and 2-chloro-3-hexene (as the prototype for the reactive segments of the PVC chains) can react with cyclohexene oxide (as the

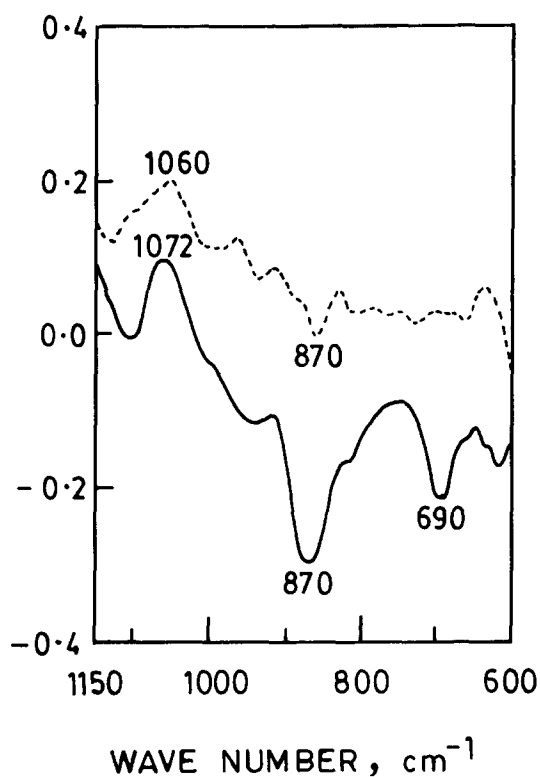
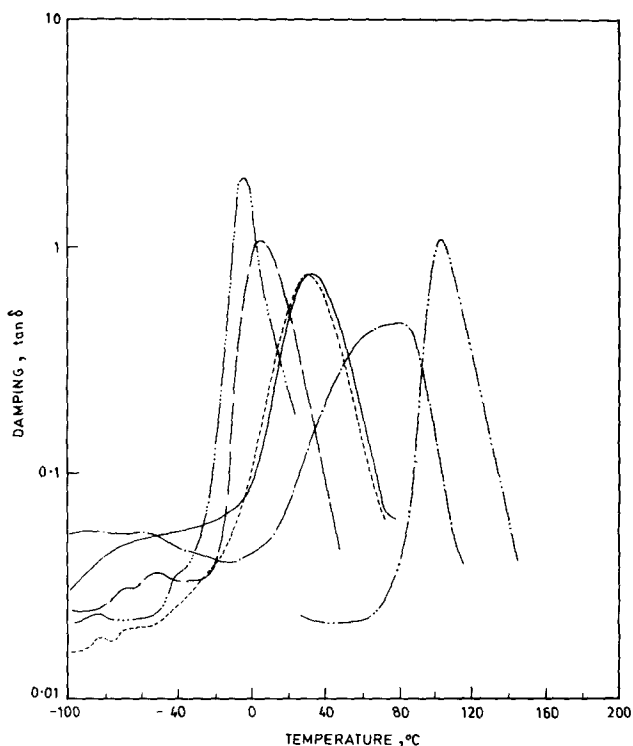


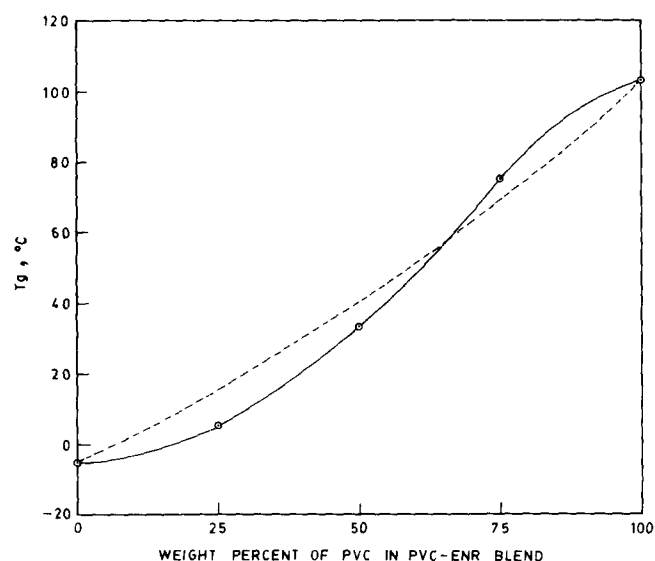
Figure 3 Infra-red spectra of 3 min moulded 50/50 PVC/ENR blend subtracted from 60 min moulded 50/50 PVC/ENR blend (---) and 120 min moulded 50/50 PVC/ENR blend (—)

prototype for the epoxy resin) to form an ether<sup>10</sup>, thereby confirming that epoxy resin and PVC can react together to form ether crosslinks. Thus it is clear that PVC and ENR can also react together through the allylic chlorine sites in PVC and the epoxy moieties in ENR. The blend network structure, however, consists of furanized ENR and crosslinked ENR along with the crosslinked PVC/ENR.

The damping (loss tangent) versus temperature plots of the blends are shown in Figure 4. The temperature corresponding to the loss tangent maxima is taken as the glass transition temperature ( $T_g$ ) of the blends. The  $T_g$  for ENR is  $-5^\circ\text{C}$  and that of stabilized PVC is  $103^\circ\text{C}$ . The  $T_g$ s of the 25/75, 50/50 and 75/25 PVC/ENR blends moulded for 60 min at 180°C, are 5, 33 and  $75^\circ\text{C}$



**Figure 4** Temperature dependence of damping for ENR (— · — · —); PVC (— · — · —); PVC/ENR blends: 25/75 (— · — · —); 50/50 (— · — · —) and 75/25 (— · — · —). (— · — · —) 50/50 PVC/ENR blend moulded for 3 min



**Figure 5** Composition dependence of  $T_g$  for PVC-ENR system by Fox relation (---) and experimental value from  $\tan \delta$  maxima (—)

respectively. The composition-dependent single glass transitions of the moulded blends clearly indicate that the system is miscible at all blend ratios in the crosslinked stage. The 3 min moulded blend of 50/50 PVC/ENR also gives a single transition and the  $T_g$  of this blend is 31°C. Thus it can be concluded that the system is miscible in the uncured state and the miscibility does not change with crosslinking.

The compositional dependence of the  $T_g$  of the blend can be given by the Fox relation<sup>11</sup>:

$$1/T_{gb} = W_1/T_{g1} + W_2/T_{g2} \quad (1)$$

where  $W$  is the weight fraction of the component and  $T_{gb}$

**Table 4** Physical properties of PVC/ENR blends<sup>a</sup>

	PVC/ENR blends	
	50/50	75/25
50% modulus (MPa)	9.4	—
100% modulus (MPa)	12.4	—
200% modulus (MPa)	14.3	—
300% modulus (MPa)	15.6	—
Tensile strength (MPa)	17.4	36.4
Elongation at break (%)	375	12
Tear strength (kN m <sup>-1</sup> )	106	189
Hardness (Shore D units)	30	70
$V_r$ , in tetrahydrofuran <sup>b</sup>	0.02	0.01
Percentage weight loss in:		
Chloroform	21	15
Tetrahydrofuran	38	68

<sup>a</sup> For the 25/75 PVC/ENR blend, the experiment was not conducted because of bubble formation in the moulded sheet

<sup>b</sup>  $V_r$ , volume fraction of rubber

is the glass transition temperature of the blend.  $T_{g1}$  and  $T_{g2}$  are the glass transition temperatures for the components. Figure 5 shows the experimental compositional dependence of  $T_g$  and also the prediction on the basis of the Fox equation. Slight deviations from the Fox relationship were observed. It has been reported that such deviations can be attributed to the chemical interaction between the components<sup>12-14</sup>.

Table 4 summarizes the physical properties of the blends. The tensile strength, tear strength and hardness increase and the elongation at break decreases with increase in the PVC content. In general, the blend behaviour changes from the elastomeric to the glassy type as the PVC content is increased.

The 25/75 blend is soluble in tetrahydrofuran and chloroform, indicating that the crosslinking in this blend is negligible. This observation supports the results of rheometric studies. However, the  $V_r$  values for the 50/50 and 75/25 PVC/ENR blends show a moderate extent of crosslinking in these blends. The percentage weight loss in chloroform is proportional to the weight of unreacted ENR in the blend and that in tetrahydrofuran to that of unreacted PVC and ENR together. The percentage weight loss values (Table 4) in chloroform and tetrahydrofuran show that PVC/ENR mostly exists in a crosslinked form. The  $V_r$  values together with the percentage weight loss results after extraction indicate that the crosslink density is greater in the 50/50 blend than in the 75/25 PVC/ENR blend.

## CONCLUSIONS

It was observed that chemical reactions occur in miscible blends of PVC and ENR on high-temperature moulding for prolonged times. This was confirmed from the results of processability studies using a Brabender Plasticorder and Monsanto rheometer, and by infra-red spectroscopic and swelling studies. The blends were still found to be miscible in the crosslinked condition. The blend behaviour changes from elastomeric to glassy with increasing PVC content.

## ACKNOWLEDGEMENT

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