Interfacial crosslinking in an immiscible plastic/rubber blend based on polyacrylic acid and polychloroprene

P. Ramesh and S. K. De*
Rubber Technology Centre, Indian Institute of Technology, Kharagpur 721302, India
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That the melt-mixed blend of polyacrylic acid and polychloroprene is self-crosslinkable during high temperature moulding is evident from Monsanto rheometric and i.r. spectroscopic studies. Such a system of a self-crosslinkable blend is immiscible at all blend ratios as observed by dynamic mechanical analyses (d.m.a.). Scanning electron microscopic and d.m.a. studies reveal formation of an interfacial layer in the two-phase blend system. The blend possesses high damping characteristics with moderate tensile and tear strength.

(Keywords: polyacrylic acid; polychloroprene; self-crosslinkable blend; interfacial crosslinking; immiscible)

INTRODUCTION

Blending of chemically interactive polymers[1–5] has become an emerging field in polymer research, due to the development of various types of functionally reactive polymers. Crosslinked structure can also be obtained through interchange reactions[6,7]. The interchange reactions in polycarbonate/phenoxy[8] and polyester/phenoxy[9] blends are well established.

Since chemical reaction between the components will change the morphology of the system, efforts have been made to produce compatibilization by interpolymer reactions using functionalized polymers[10–12]. *In situ* reaction polymerization leads to the formation of graft, block or crosslinked polymers as the newly created material primarily at the interface between the two polymers.

The growing interest in multiphase polymer systems is ascribed to the availability of different methods to control the physical and chemical interactions at the interface[13]. A series of chemical and physico-chemical interactions takes place in many polymer blend systems[14,15].

Recently De and co-workers have developed several self-crosslinkable rubber blends wherein the reactive groups of the two rubbers interact chemically to form crosslinks during high temperature moulding for prolonged time in the absence of any crosslinking agent[16–20]. The principle of self-crosslinking was further extended to plastic/rubber blends and we have recently reported the self-crosslinking of plastic/rubber blends based on poly(vinyl chloride)/carboxylated nitrile rubber[21], poly(vinyl chloride)/epoxidized natural rubber[22] and chlorinated natural rubber/carboxylated nitrile rubber[23] systems.

Preliminary studies showed that a melt-mixed blend of polyacrylic acid (PAA) and polychloroprene (CR) can also form such a type of self-crosslinkable plastic/rubber blend, hereinafter referred to as PN. This paper reports the results of our studies on this blend system with respect to the processing characteristics based on Monsanto rheometry, characterization by i.r. spectroscopy, phase morphology by scanning electron microscopy (SEM), component miscibility by dynamic mechanical analyses (d.m.a.) and physical properties, such as stress–strain behaviour, tear strength and hardness.

EXPERIMENTAL

Details of the materials used are given in *Table 1*. *Table 2* gives the blend compositions employed in this study. The blends are designated as PN-1, PN-2 and PN-3 and correspondingly contain PAA and CR in the ratios of 25:75, 50:50 and 75:25 by weight.

The mixing was carried out in a Brabender plasticorder PLE 330, using a cam-type mixer at a rotor speed of 60 rev min^{-1} and temperature of 180°C. Initially PAA was allowed to soften for ~5 min and then CR was added and blended for 6 min. The blended mix was quickly removed from the mixing chamber and sheeted out in the tight nip of a laboratory two-roll mill. The effect of shear history on a 1:1 PAA/CR blend was studied by also mixing the blend at 30 and 90 rev min^{-1} at 180°C.

Rheographs of the blends were taken at 160°C on a Monsanto oscillating disc rheometer R-100 at 3° arc rotation. The rheographs of a 1:1 PPA/CR blend mixed at 30 and 90 rev min^{-1} were also taken at 160°C. Rheographs of a 1:1 blend were also taken at 150 and 170°C in order to study the temperature dependence of the rate of increase in torque. The blends were moulded for 60 min at 160°C, at a pressure of 10 MPa in a Labopress and after moulding the vulcanizates were

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*To whom correspondence should be addressed

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Table 1 Details of the materials used

Materials	Description	Source
CR	Neoprene AC	DuPont Ltd, USA
PAA	Copolymer of methacrylic acid and methyl methacrylate (M_r 500 000–1 000 000)	Fluka, Switzerland

Table 2 Composition of PAA/CR blends (wt%)

	Blend		
	PN-1	PN-2	PN-3
PAA	25	50	75
CR	75	50	25

cooled down to room temperature, under pressure. Tensile stress–strain properties and tear strength were measured at room temperature (25 ± 2°C) using a Zwick universal testing machine (model 1445) according to ASTM D 412-87, method A and ASTM D 624-86, respectively. The rate of separation used was 500 mm min^{-1}. The hardness of the samples was measured according to ASTM D 2240-86 and expressed in shore A or shore D units.

I.r. spectra were obtained with a Perkin Elmer 843 spectrophotometer. Thin films of CR alone and the PN-2 blend were prepared by compression moulding between aluminium foil, in order to obtain the spectra. PAA was mixed with KBr and the mixture was pressed into a pellet to measure the spectra.

D.m.a. were carried out using a Rheovibron (Orientec Corporation, Japan) DDV-III-EP at a strain amplitude of 0.0025 cm and a frequency of 3.5 Hz. For dynamic mechanical studies the samples were moulded for 60 min at 160°C. The 1:1 PAA/CR blend mixed at varying shear rates, i.e. 30 and 90 rev min^{-1}, were also moulded for 60 min at 160°C. The PN-2 blend was also moulded for 3 and 120 min at 160°C in order to study the effect of moulding time on miscibility. The measurements were carried out over a temperature range of −100 to 250°C at a heating rate of 2°C min^{-1}.

The morphology of cryogenically fractured samples was examined using a Philips scanning electron microscope.

RESULTS AND DISCUSSION

The Monsanto rheographs of the blends at 160°C are shown in *Figure 1*. The rheographs show a gradual increase in torque with time. The single components did not show such an increase in torque with time which eliminates the possibility of thermovulcanization of the individual components in the blend. The 1:1 blend registers a maximum rise in torque compared with other blend ratios. The rise in rheometric torque indicates possible crosslinking between PAA and CR in the melt mixed blend and the reaction rate depends on the blend ratio. *Figure 1* also shows the Monsanto rheographs of the PN blend at different temperatures, namely, 150, 160 and 170°C. The rheometer curves show a temperature dependence of the increase in torque which indicates an increased rate of chemical reaction with an increase in temperature. At 160°C, the rheometric torque attains a constant value at 112 min, while at 170°C a plateau was reached at 54 min.

The rheographs of a 1:1 PAA/CR blend mixed at 30 and 90 rev min^{-1} at 180°C is also given in *Figure 1*. The minimum rheometric torque and rate of increase in torque increases with increase in shear rate. It has been earlier reported that in the blends of carboxylated nitrile rubber and oxazoline functionalized polystyrene the speed of the chemical reaction is a function of temperature and the intensity of mixing[11,24]. It is well known that with increase in shear history the rise in temperature will be higher. Therefore, it is clear that the increase in minimum rheometric torque with increase in shear history was due to increased chemical interaction during blending. The increase of the reaction rate with increase in shear rate of mixing is attributed to the increased level of molecular mixing which will enhance the possibility of chemical crosslinking between the components.

The processing characteristics of the blend, as studied from Monsanto rheometer curves, are summarized in *Table 3*. The minimum rheometric torque is highest for the 1:1 blend which shows that the interaction is a maximum at this blend ratio. As expected, for the 1:1 blend scorch time and minimum rheometric torque decreases with increase in temperature. Again, the 1:1 blend possesses shorter rheometric scorch time indicating a higher level of interaction between the components even during the mixing stage.

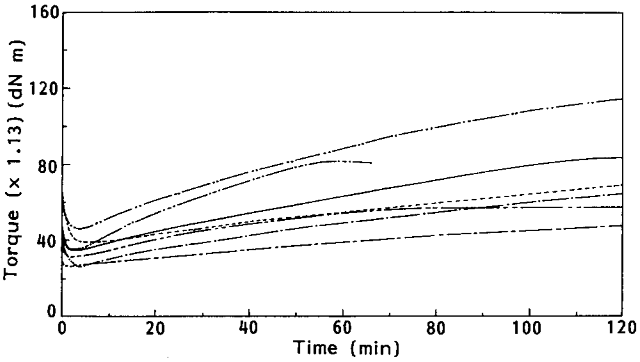

Figure 1 Monsanto rheographs of PAA/CR blends PN-1 (— — —), PN-2 (——) and PN-3 (— — — —) at 160°C; the 1:1 PAA/CR blend at 150°C (- - -) and 170°C (—·—·—); and the 1:1 PAA/CR blend mixed at 30 rev min^{-1} (—·—) and 90 rev min^{-1} (—··—)

Table 3 Processing characteristics of PAA/CR blends

	Blend		
	PN-1	PN-2	PN-3
Minimum rheometric torque (× 1.13) (dN m) at			
150°C	–^{b}	39.0	–^{b}
160°C	26	35.0	32
170°C	–^{b}	34.5	–^{b}
Rheometer scorch time^{a} (min) at			
150°C	–^{b}	15	–^{b}
160°C	11	8	9
170°C	–^{b}	6	–^{b}

[a] Time to increase the rheometer torque by two units from the minimum value

[b] Rheograph not taken at this temperature

The i.r. spectra of PAA, CR and a 1:1 blend of PAA/CR are given in *Figure 2*. PAA shows carbonyl stretching of carboxylic acid at 1720 cm^{-1}. The PN-2 blend shows the presence of carbonyl stretching of the ester group at 1740 cm^{-1} arising from crosslinks formed in the blend. The proposed crosslinking mechanism between PAA and CR is shown in *Figure 3*.

The miscibility of the components in the PN blends which are moulded for 60 min at 160°C is analysed using d.m.a. (*Figures 4–6*). At all blend ratios, two transitions were observed in the damping *versus* temperature plot; one in the low temperature rubbery region and a broad transition in the higher temperature region. The temperatures corresponding to the maximum damping or loss modulus are taken as the glass transition temperature (T_g) of the blend and the values are summarized in *Table 4*. The dynamic storage modulus for the blend decreases sharply in two stages confirming the presence of immiscible phases in the blend. The dynamic loss modulus for the blend also shows the presence of two transitions in the blend. Thus it is evident that the blend shows characteristics of the individual components. The 1:1 blend is unique in that it exhibits maximum damping efficiency for a broad temperature range of 59–241°C.

The d.m.a. of the PAA/CR blend moulded for 3 and 120 min at 160°C are shown in *Figures 7–9*. The mechanical damping plots show an intermediate relaxation due to the interfacial layer formed at the interface through the chemical reaction between the two components. This intermediate peak is merged with the

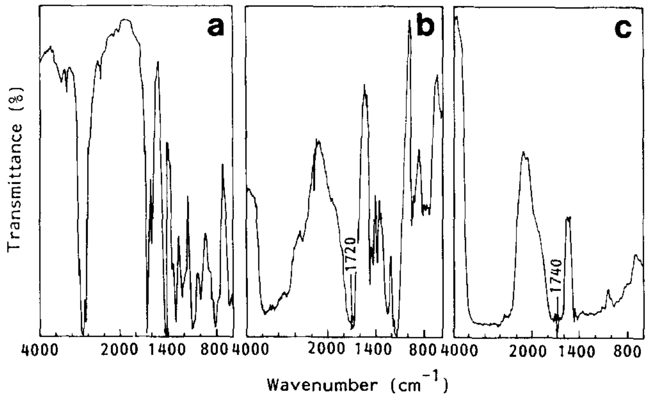

Figure 2 I.r. spectra of (a) CR, (b) PAA and (c) 1:1 PAA/CR blend

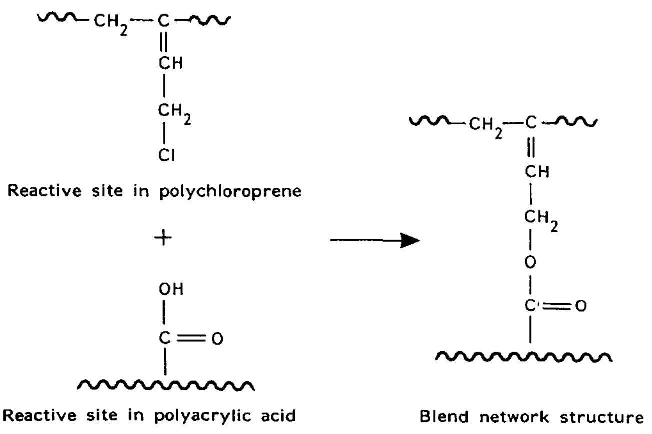

Figure 3 Possible crosslinking mechanism between PAA and CR

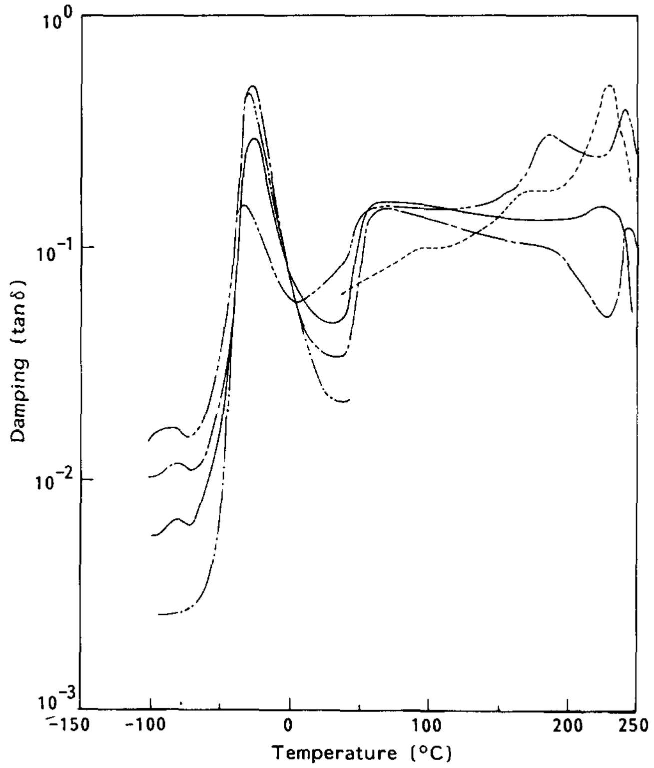

Figure 4 Effect of temperature on mechanical damping of CR (—·—·—), PAA (– – –), PN-1 (— — —), PN-2 (——) and PN-3 (– – – –)

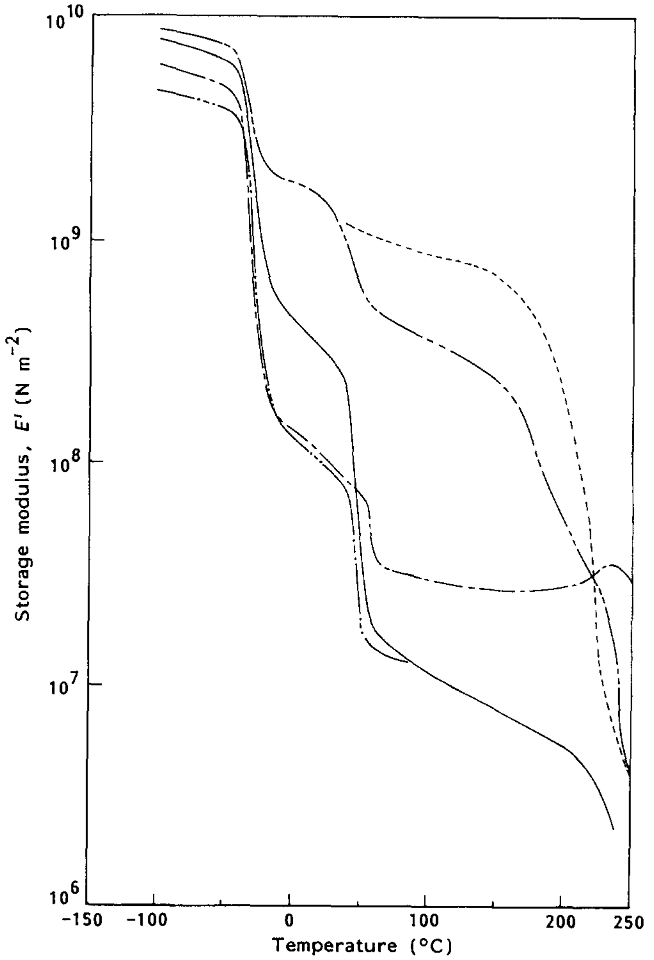

Figure 5 Effect of temperature on storage modulus of CR (—·—·—), PAA (– – –), PN-1 (— — —), PN-2 (——) and PN-3 (– – – –)

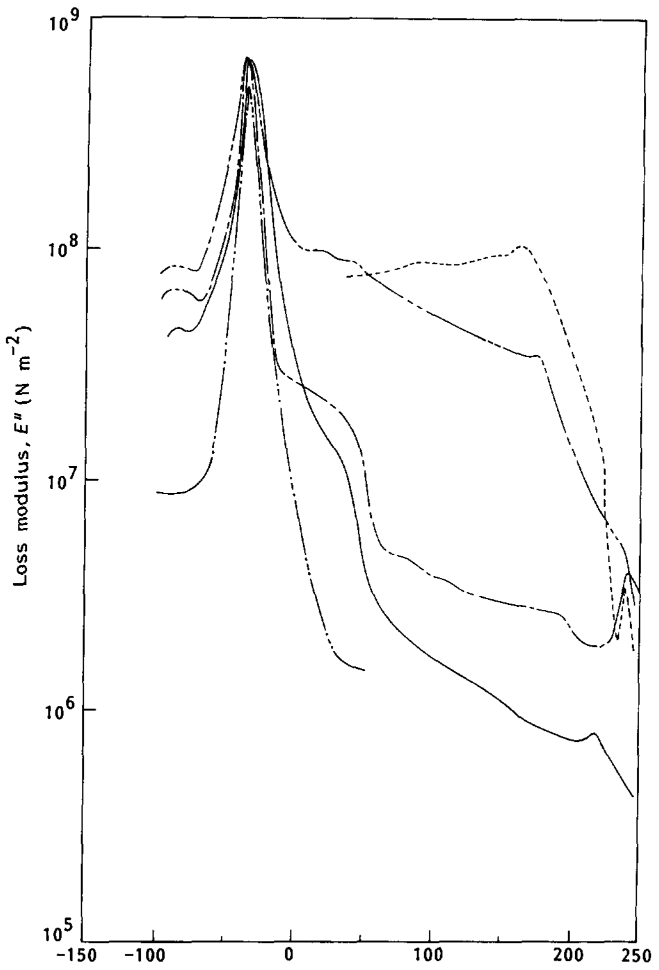

Figure 6 Effect of temperature on loss modulus of CR (—·—·—), PAA (- - -), PN-1 (— — —), PN-2 (——) and PN-3 (– – – – –)

Table 4 Glass transition temperature as obtained from d.m.a.

Sample	T_g (°C) Loss modulus (N m^{-2})	Damping (tan δ)
PAA	164	173, 231
PN-1	−35, broad and 243	−27, broad and 243
PN-2	−33.5, 42	−25, 59 to 241 (broad transition)
PN-2 (3 min moulded)	−33 and broad	−25 and broad
PN-2 (120 min moulded)	−33 and broad	−25 and 51 to 241 (broad transition)
PN-3	−35 and broad	−32 and broad
CR	−34	−28

higher temperature transition to give a broad transition in the 60 min moulded sample. Thus in this PAA/CR blend, the crosslinked structure occupies the interface between PAA and CR. Hence this system will be conceptually similar to the *in situ* emulsifying systems reported by Saleem and Baker[12].

By varying the shear history we studied the miscibility of the PAA/CR blend system. Morphological differences in compression and injection moulded samples of an immiscible blend of bisphenol-A polycarbonate and styrene acrylonitrile copolymer have been reported recently[25]. *Figures 10–12* show the dynamic mechanical

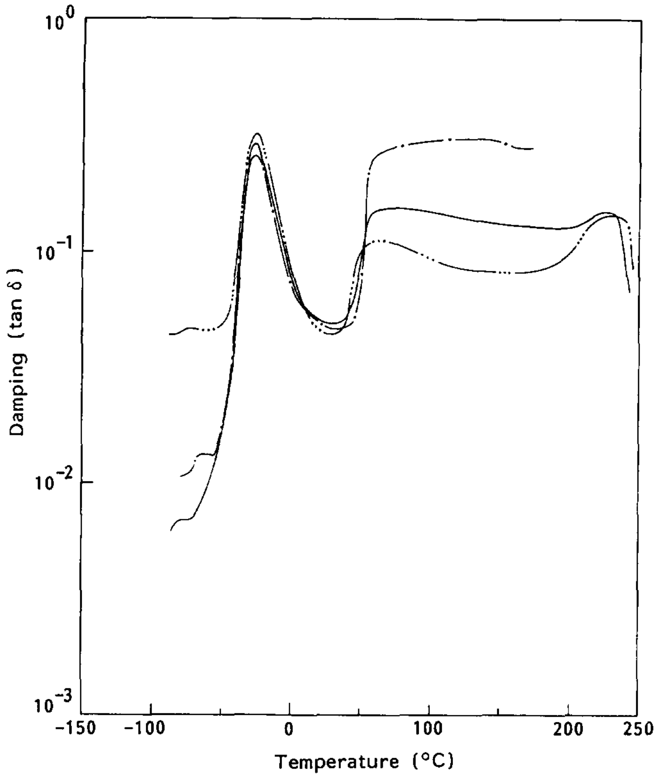

Figure 7 Temperature dependence of mechanical damping of a 1:1 PAA/CR blend moulded for different moulding times at 160°C: PN-2 blend moulded for 3 (—·—), 60 (——) and 120 min (—···—)

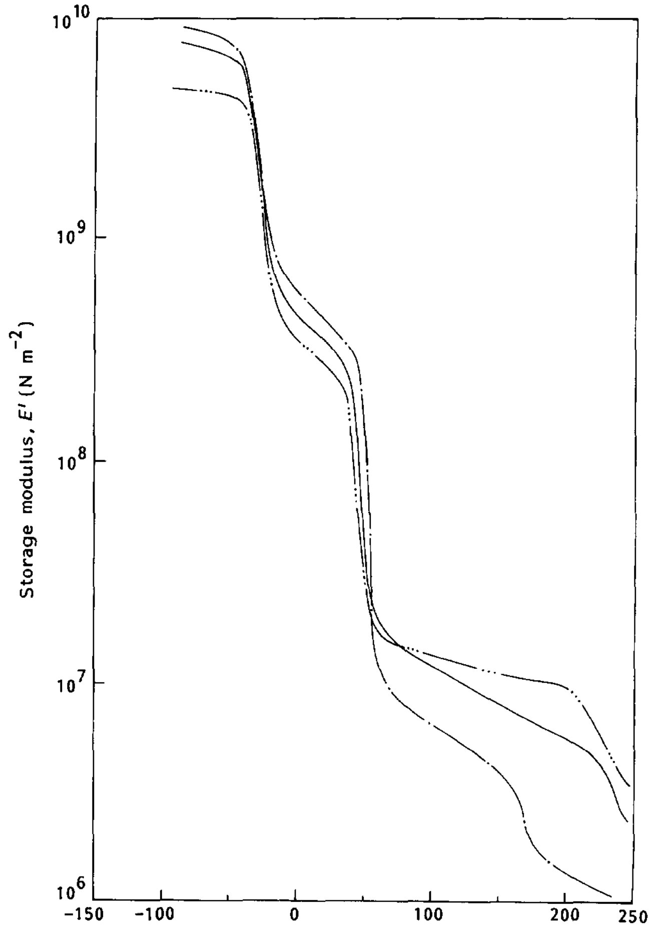

Figure 8 Temperature dependence of storage modulus of a 1:1 PAA/CR blend moulded for different moulding times at 160°C: PN-2 blend moulded for 3 (—·—), 60 (——) and 120 min (—···—)

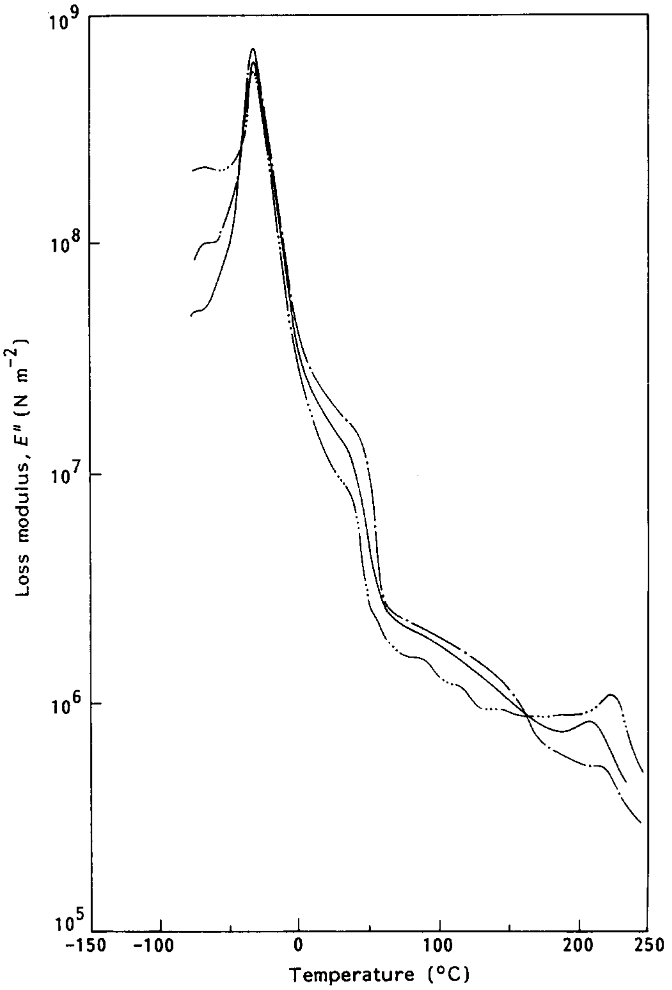

Figure 9 Temperature dependence of loss modulus of a 1:1 PAA/CR blend moulded for different moulding times at 160°C: PN-2 blend moulded for 3 (— · —), 60 (——) and 120 min (— · · · —)

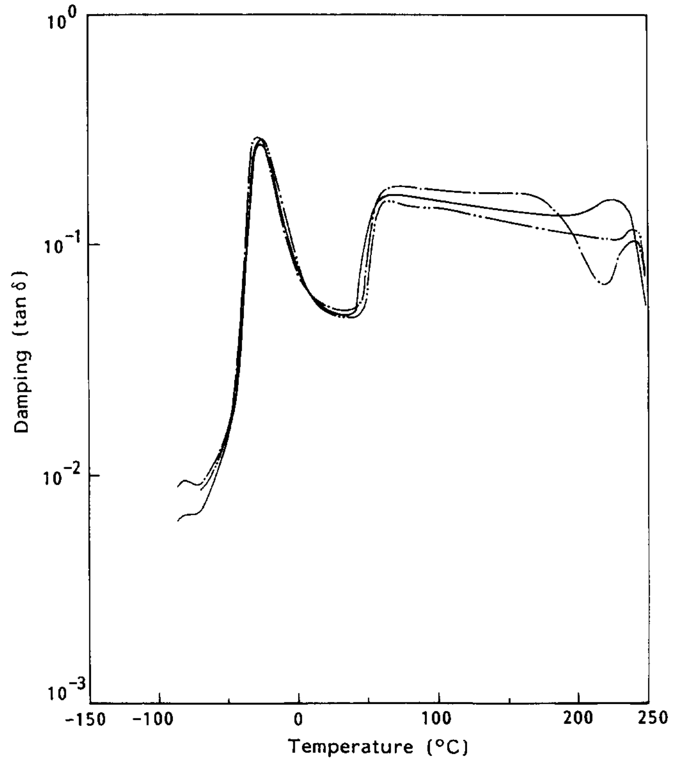

Figure 10 Temperature dependence of mechanical damping of a 1:1 PAA/CR blend mixed at different shear rates and moulded for 60 min at 160°C: PN-2 blend mixed at 30 (— · —), 60 (——) and 90 rev min^{-1} (— · · —)

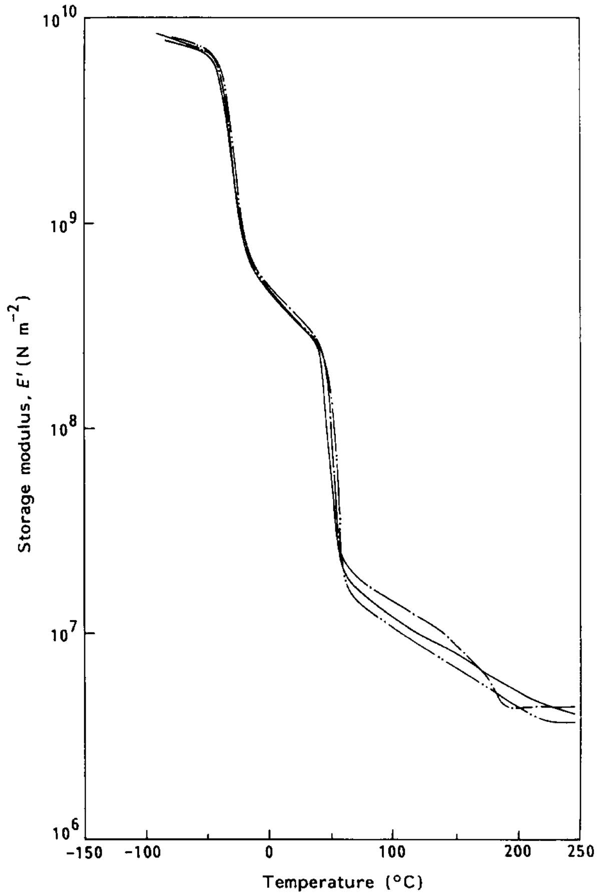

Figure 11 Temperature dependence of storage modulus of a 1:1 PAA/CR blend mixed at different shear rates and moulded for 60 min at 160°C: PN-2 blend mixed at 30 (— · —), 60 (——) and 90 rev min^{-1} (— · · —)

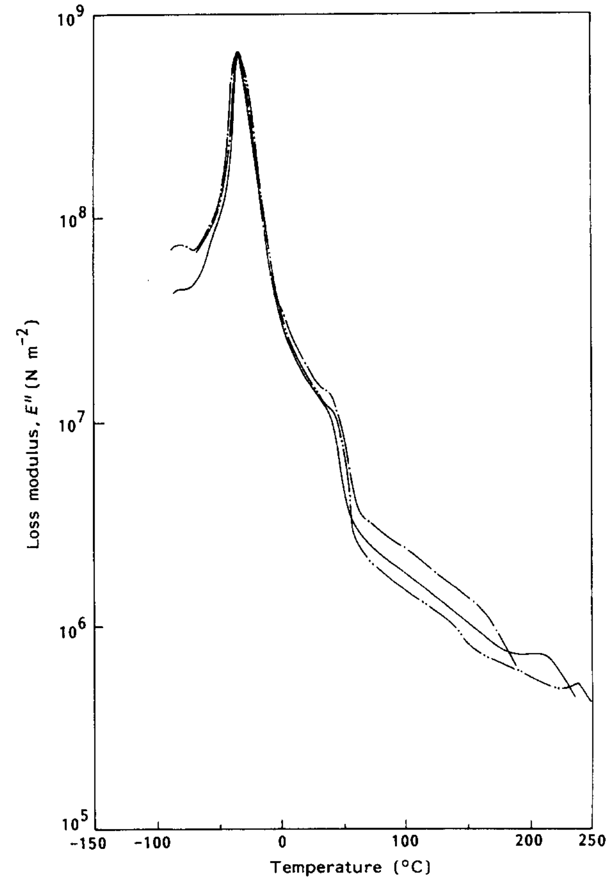

Figure 12 Temperature dependence of loss modulus of a 1:1 PAA/CR blend mixed at different shear rates and moulded for 60 min at 160°C: PN-2 blend mixed at 30 (— · —), 60 (——) and 90 rev min^{-1} (— · · —)

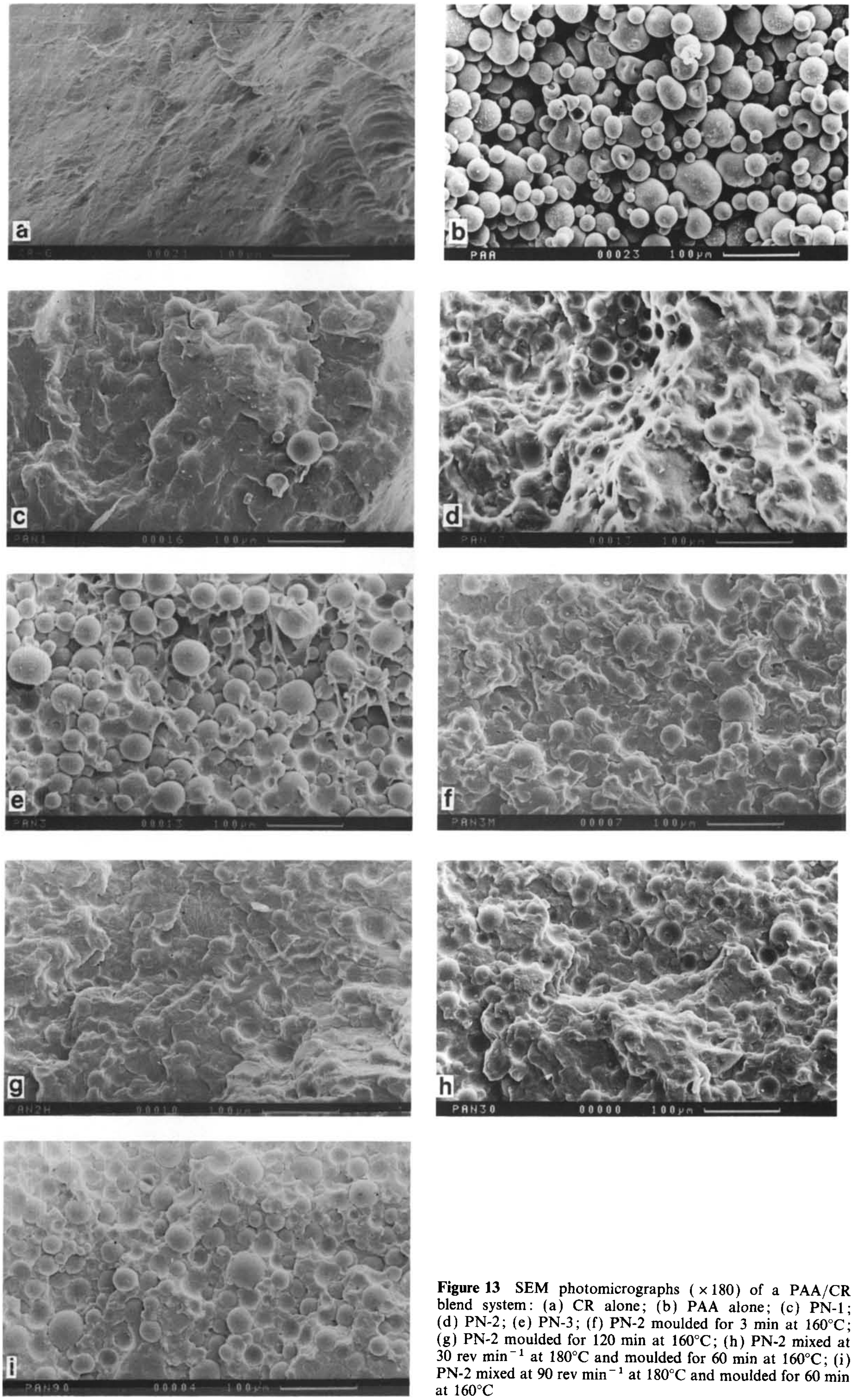

Figure 13 SEM photomicrographs (×180) of a PAA/CR blend system: (a) CR alone; (b) PAA alone; (c) PN-1; (d) PN-2; (e) PN-3; (f) PN-2 moulded for 3 min at 160°C; (g) PN-2 moulded for 120 min at 160°C; (h) PN-2 mixed at 30 rev min^{-1} at 180°C and moulded for 60 min at 160°C; (i) PN-2 mixed at 90 rev min^{-1} at 180°C and moulded for 60 min at 160°C

plots for the 1:1 PAA/CR blend mixed at different shear rates, namely, 30, 60 and 90 rev min^{-1} at 180°C and moulded for 60 min at 160°C. All these blends are immiscible and show one low temperature transition corresponding to CR segmental motion and a broad high temperature transition which consists of both the interfacial layer transition and the PAA transition. At 30 rev min^{-1} there is separate transition for the boundary layer and PAA, but at 60 and 90 rev min^{-1} these two transitions have merged together to give a broad high temperature transition.

The SEM photomicrographs of the cryogenically fractured samples are shown in *Figure 13*. *Figures 13a* and *b* are the SEM photomicrographs of CR conventionally vulcanized with zinc oxide and magnesium oxide and PAA moulded for 5 min at 180°C. The CR gives the typical appearance of a homogeneous single-phase system and the PAA shows the presence of spherical domains. The PAA has no melting point and will degrade without melting at high temperatures[26]. *Figures 13c*, *d* and *e* are photomicrographs of 25/75, 50/50 and 75/25 PAA/CR blends moulded for 60 min at 160°C. The existence of two phases can be clearly seen from the photomicrographs. In the 50/50 PAA/CR blend, the PAA domains are found to be uniformly dispersed in the rubber matrix. The concentration of the PAA dispersed phase in the rubber matrix depends on the blend ratio and it is evident from *Figures 13c* and *e* that the concentration of the PAA dispersed phase is more in PN-3 than in PN-1. Furthermore, in PN-1 the PAA domains are embedded in the rubber matrix.

It is well documented that the phase morphology of incompatible blends varies significantly with the processing history of the blends[27–31]. In this work the dependence of blend morphology on moulding time and shear history has been studied using SEM. For a thorough understanding of the morphological features, SEM photomicrographs of a 1:1 PAA/CR blend, moulded for 3 and 120 min are given in *Figures 13f* and *g*. The 3 min moulded specimen shows a very low level of adhesion between the two phases but at 120 min, even though the system is heterogeneous, there is an increased adhesion between the phases. Thus with increased moulding time the thickness of the interface is increased. This is due to the increased chemical reaction taking place between the components at the interface. This statement can be supported by the fact that the Monsanto rheometric torque increases with increase in time.

The change in shear history will also affect the morphology of the blend. *Figures 13h* and *i* are SEM photomicrographs of a 1:1 PAA/CR blend mixed at 30 and 90 rev min^{-1} at 180°C. The Monsanto rheographs show increased chemical reaction with increased shear rate. It can be seen from the photomicrographs of the moulded samples (160°C, 60 min) that the system remains heterogeneous even with high shear history (i.e. at 90 rev min^{-1}).

The stress–strain plots of the blends are shown in *Figure 14*. The stress–strain behaviour changes from rubbery to glassy as the weight percentage of PAA in the blend is increased. The 1:1 PAA/CR blend registers a leather-type behaviour[32]. The modulus increases with increase in PAA content. PN-1 possesses maximum tensile strength due to the strain crystallization behaviour of CR rubber. The elongation at break decreases dramatically with increase in PAA content. The physical properties of the vulcanizates are summarized in *Table 5*. The tear strength is a maximum for PN-1 compared to PN-2 and PN-3. The hardness values increase as the percentage of PAA in the blend is increased.

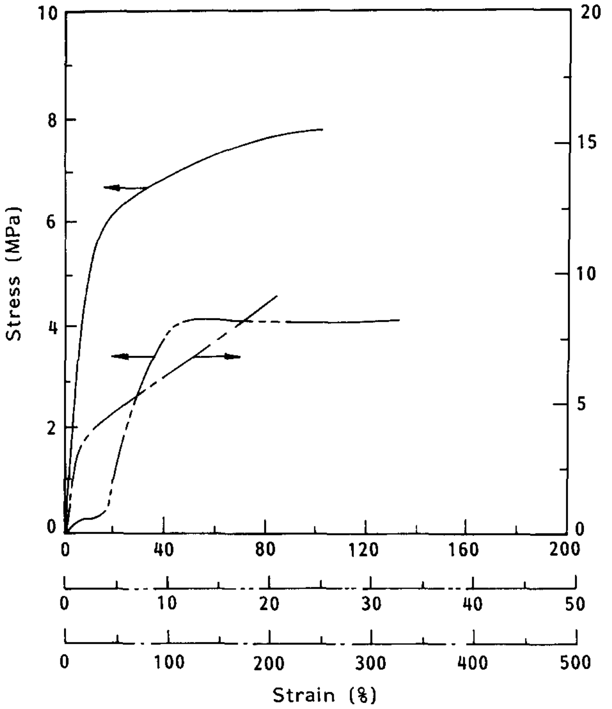

Figure 14 Stress–strain plots of PAA/CR blends PN-1 (— — —), PN-2 (——) and PN-3 (- - - -)

Table 5 Physical properties of PAA/CR blends moulded at 160°C for 60 min

Properties	Blend PN-1	 PN-2	 PN-3
50% modulus (MPa)	4.6	7.0	–
100% modulus (MPa)	6.0	7.7	–
Tensile strength (MPa)	8.9	7.8	4.2
Elongation at break (%)	216	109	36
Tear strength (N mm^{-1})	69	42	23
Hardness (shore A or shore D)	60 A	44 D	61 D

CONCLUSIONS

The PAA/CR blend is self-crosslinkable. This is evident from Monsanto rheometric and i.r. spectroscopic studies. The blend possesses good processing safety. The blend is not miscible at the molecular level as evident from d.m.a. The increase in moulding time increases the interfacial crosslinked layer thickness as observed by SEM. The system is found to be immiscible at all the processing conditions employed in this study. The blends exhibit high damping characteristics. The vulcanizate properties depend on the blend ratio. The 25/75 PAA/CR blend possesses maximum tensile strength and tear strength among the blend ratios studied. The 75/25 PAA/CR blend shows characteristics of a brittle polymer with low strength. The 50/50 PAA/CR blend behaves like a leathery material.

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