

# Modification of Poly(Vinyl Chloride) by IPN Formation with Poly(Ethyl Acrylate)

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Received 9 June 2008; accepted 21 January 2009

DOI 10.1002/app.30095

Published online 8 May 2009 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Semi-1 and semi-2 interpenetrating polymer networks (IPNs) of poly(vinyl chloride) (PVC) and *in situ* formed poly(ethyl acrylate) (PEA) have been synthesized using diallyl phthalate and ethylene glycol dimethacrylate as the crosslinkers of PVC and PEA, respectively. These two types of IPNs have been compared with respect to their physical, mechanical, and thermal properties and an endeavor has been made to find a correlation of these properties with the morphology generated in these systems. The semi-1 IPNs displayed a decrease in their tensile strength and modulus while in contrast; the semi-2 IPNs exhibited a marginal increase with increasing crosslinked PEA incorporation. The semi-1 and semi-2 IPNs containing 10 and 30 wt % of PEA displayed a two-stage degradation typical

of PVC in their thermogravimetric and DSC studies while confirming the increased stability of the samples with higher percentages of PEA. The softening characteristics as detected by the extent of penetration of the thermomechanical probe as has been detected by thermomechanical analysis are in conformity with their mechanicals. The biphasic cocontinuous systems as explicit from the morphological studies reveal fibrillar characteristics in both the systems. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 3450–3459, 2009

**Key words:** Poly(vinyl chloride); poly(ethyl acrylate); interpenetrating networks; mechanical properties; thermal properties

## INTRODUCTION

Crosslinking polymer chains is an important way of diversifying the physical and chemical properties of polymers. Generally, mechanical or thermal properties of the crosslinked polymers are enhanced but the processibility is sacrificed. In the case of poly(vinyl chloride) (PVC) resin, crosslinking technology is investigated as a major tool of enhancing applicability.<sup>1</sup> An IPN is an intimate combination of two polymers both in network form, at least one of which is synthesized or crosslinked in the immediate presence of the other. Characterisation of semi-interpenetrating polymer networks (IPNs) of polyurethane and PVC was carried out by Pielichowski and Janouski.<sup>2</sup> The cure behavior of silicone epoxies and urethane-modified acrylates in IPNs was studied by Price et al. This was done in an attempt to improve the toughness and flexibility of poly(epoxyurethane-acrylic).<sup>3</sup> The ultimate properties of IPNs can be varied to a greater extent by the suitable control of the morphologies of the concerned components. The degree of network interlocking between the components has a measurable effect on the vari-

ous mechanical properties like tensile modulus, hardness, and ultimate tensile strength (UTS) which in turn depends on the type of component crosslinked. Increased network interlocking is expected to improve compatibility.<sup>4</sup> Because of their interlocking configuration, the extent of phase separation is frozen in so the properties are not influenced by subsequent aging. The properties are dependent on the two-phase morphology that develops during IPN formation.<sup>5</sup>

The present study focuses on improving the properties of PVC by incorporating poly(ethyl acrylate) (PEA) as the polymeric modifier in the form of IPN. The inherent problems of poor impact strength and difficult processing of rigid PVC are quite well known and are usually overcome by incorporation of suitable plasticisers and certain rubbery acrylate modifiers.<sup>6</sup> In such cases, there is every possibility of compromising on the mechanical properties of rigid PVC. In this case, we have tried to modify both linear and crosslinked PVC with somewhat rubbery PEA in an attempt to produce tougher IPNs keeping the mechanical parameters at par with original PVC or even better.<sup>7</sup> This can be hinted at from a study by Paul and Barlow<sup>8</sup> in which it was stated that the  $\alpha$  hydrogen of PVC interacts with the ester carboxylate group (H bond acceptor of the acrylic polymer) to form a hydrogen bond and is also the key factor in achieving miscibility.<sup>9</sup> The incorporation of PEA in PVC is

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analogous to the rubber toughening of glassy polymers as the former is well known to be rubbery in character having glass transition of  $-27^{\circ}\text{C}$ .<sup>10,11</sup>

## EXPERIMENTAL

### Materials

PVC (Reon) grade K 67 was procured from M/s Reliance Industries, India and was used as the matrix resin. Dioctyl phthalate (DOP) from M/s Burgoyne (India) and tribasic lead sulfate (TBLS) from M/s Kalpana Industries (Daman, India) were used as suitable plasticisers and stabilizers, respectively. Diallyl phthalate (DAP) from M/s Burgoyne was used as a crosslinker for PVC.

Ethyl acrylate (EA) from M/s Burgoyne was purified by washing first with 2% aqueous sodium hydroxide (NaOH) solution and then by thorough and repeated washing with distilled water (to make alkali free as tested by litmus paper) and dried over fused calcium chloride ( $\text{CaCl}_2$ ). It was finally vacuum distilled. Benzoyl peroxide from Loba Chemie (India) was purified by repeated crystallization from chloroform and was used as an initiator for acrylate polymerization. Ethylene glycol dimethacrylate (EGDM) from Aldrich Chemical Company, USA, was used as the crosslinker for PEA.

### Synthesis of semi-1 and semi-2 IPNs

A weighed amount of purified EA was charged and thoroughly mixed with 2% by weight (based on EA) of recrystallised  $\text{Bz}_2\text{O}_2$ . PVC resin was weighed such that the ratio with respect to the monomer as weighed was maintained. The PVC resin was taken in an airtight warm dry blender and mixed with 30 parts of DOP and two parts of TBLS with respect to PVC resin taken. Five parts by weight of crosslinker DAP with respect to PVC was then added. The monomer PEA containing initiator  $\text{Bz}_2\text{O}_2$  was then added to the pre-mix of PVC in case of semi-1 IPN (Table 1).

Crosslinker of the monomer EGDM in the ratio of 2% by weight of EA taken was initially added to the

monomer mix in case of semi-2 IPN. Dry mixing with PVC resin in proportionate quantity of the monomer with TBLS (2 parts), DOP (30 parts), and EGDM-mixed monomer was continued until a thoroughly mixed powder was obtained. The mix in each case was then compression molded into sheet by subjecting a three-piece mold under pressure and two stages heating.

### Conditions of molding

Initially, the mold was compressed under a pressure of  $15 \text{ tons/cm}^2$  at a temperature of  $80^{\circ}\text{C}$  to initiate and propagate acrylate polymerization. This was allowed to continue for 30 min. Subsequently, the temperature was raised to  $160^{\circ}\text{C}$  while the pressure was maintained at the same level. This condition was maintained for 5 min to ensure complete sintering of PVC and acrylic polymerization. The whole combination was kept in an oven at  $100^{\circ}\text{C}$  for further 20 min to ensure complete polymerization and crosslinking of residual EA or PVC or both as the cases may be. The mold was then allowed to cool down at room temperature and the molded sheet ejected.

## MEASUREMENTS

### Physicomechanical properties

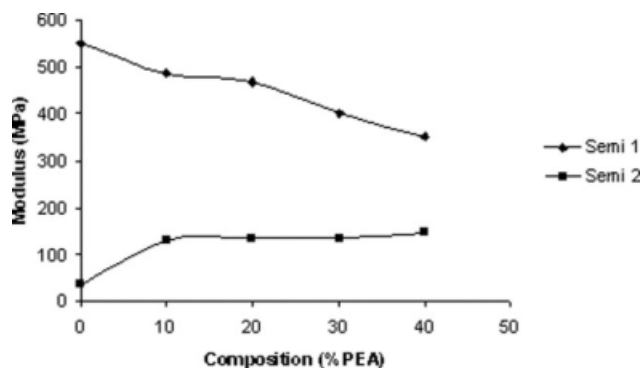
An Instron Universal Testing Machine (Model 4204) was used for measuring the tensile properties like UTS, percent elongation at break (%EB), modulus, and toughness. ASTM D 638 method was followed. A crosshead speed of 3 mm/min was maintained. All testings were carried out at room temperature ( $27^{\circ}\text{C}$ ). Toughness of the samples was determined from the area under the load *vs.* elongation plot. The samples were visually inspected before measurements and were found to be free from pores or nicks. The data reported were averages of at least six measurements and typical scattering range of the results was  $\pm 5\%$ . Hardness of different samples was measured by means of Durometer in Shore D scale following ASTM D-2240-64T. Specific gravity values of the different samples were measured at room temperature using hydrostatic technique following ASTM D-792.

### Determination of crosslink density in PVC-PEA semi-IPNs

When a crosslinked polymer is placed in a suitable solvent, the polymer imbibes the solvent and undergoes swelling to an extent determined by the crosslink density of the polymer, nature of the polymer, and the nature of the solvent used. The following Flory-Rehner equation [eq. (1)] may be applicable at

TABLE I  
Table of Materials

Material type	Ingredients by parts
Major matrix	PVC (polyvinyl chloride) 100–60 parts
Heat stabilizer	TBLS (tribasic lead sulfate) 2 parts
Plasticiser	DOP (dioctyl phthalate) 30 parts
Crosslinker of PVC	DAP (diallyl phthalate) 5 parts
Minor dispersing phase	PEA (polyethyl acrylate) 0–40 parts in proportion to PVC
Initiator	$\text{Bz}_2\text{O}_2$ (benzoyl peroxide) 2 parts
Crosslinker of acrylate	EGDM (ethylene glycol dimethacrylate) 2 parts



**Figure 1** Variation of Young's modulus of PVC-PEA semi-IPNs with variation of PVC-PEA blend ratio (w/w).

equilibrium swelling of such polymer system by a good solvent.<sup>12</sup>

$$\frac{1}{\bar{M}_C} = \frac{V_P + \chi V_P^2 + \ln(1 - V_P)}{V_S dr (V_P^{1/3} - V_P/2)} \quad (1)$$

where,  $\bar{M}_C$  = molecular weight between crosslinks;  $V_P$  = volume fraction of polymer in the swollen mass;  $V_S$  = molar volume of the solvent;  $dr$  = density of the polymer;  $\chi$  = polymer-solvent interaction parameter.

The polymer-solvent interaction parameter ( $\chi$ ) was calculated as follows. Equilibrium swelling was performed at 27°C using seven different liquids ranging in their solubility parameter ( $\delta$ ) from 14.9 to 29.7.

The swelling coefficient  $Q$  was calculated using the following equation [eq. (2)]

$$Q = \left( \frac{m - m_0}{m_0} \right) \times \frac{dr}{ds} \quad (2)$$

where,  $m$  = weight of the swollen samples;  $m_0$  = original weight of the sample;  $ds$  = density of the solvent.

In the subsequent plots of  $Q$  vs.  $\delta$  values for different solvents, the solubility parameter corresponding to the maximum value of  $Q$  was noted and this value was taken as the solubility parameter of the concerned blend system. The polymer-solvent interaction parameter was then calculated from the Bristow and Watson equation as follows<sup>13</sup>:

$$\chi = \beta + (V_S/RT) \times (\delta_S - \delta_P)^2 \quad (3)$$

where,  $\beta$  = lattice constant = 0;  $R$  = Universal gas constant;  $T$  = absolute temperature;  $\delta_S$  and  $\delta_P$  = solubility parameters of the solvent and the prepared samples, respectively.

### Thermal properties

The thermomechanical analysis of the various samples were carried out in a TMA apparatus from Shi-

madzu (model TMA 50) in the presence of oxygen. The thermo-oxidative characteristics were studied under a constant load of 8 g throughout the experiment using a compressive mode of probe upto a temperature limit of 180°C following a temperature program in which a heating rate of 10°C/min was maintained right from the ambient temperature.

The differential scanning calorimetry (Mettler 822e) of the samples were carried out upto a limit of 350°C at a heating rate of 10°C/min right from the ambient temperature. The transition behavior above ambient temperature and the temperature ranges of degradation were only studied. The weights of the samples were maintained between 0.005 and 0.008 g.

Thermogravimetric analyses (TGA) of the various samples were obtained using a Perkin-Elmer Delta Series TGA-7 thermogravimetric analyser under nitrogen atmosphere at a heating rate of 20°C/min. The samples ranging between 6 and 10 mg in weight were used for the TGA analysis.

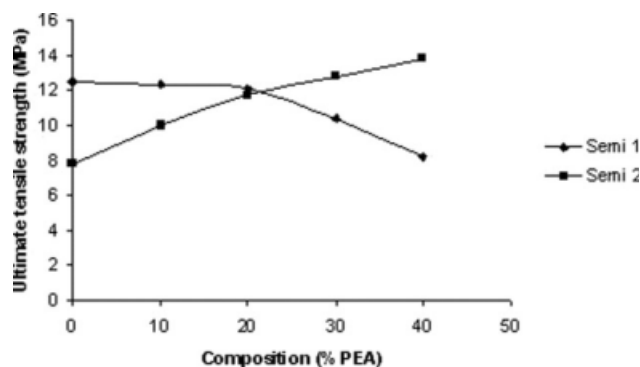
### Morphology

Scanning electron micrographs of the semi-1 and semi-2 IPNs were obtained after gold coating the samples using scanning electron microscope (Hitachi model S415A). Completely dried samples were coated with a thin layer of gold using a high-vacuum gold sputterer. The fractured surface of a tensile fracture specimen was inspected for morphology. The scale of magnification was 500×.

## RESULTS AND DISCUSSION

### Physicomechanical properties

The modulus and UTS of semi-1 IPN (PVC cross-linked) as depicted in Figures 1 and 2 show a decreasing trend with increasing proportion of PEA, although there is an initial sharp reduction in modulus in going from pure crosslinked PVC to PVC-PEA (10%). The semi-2 IPNs, however, show steady



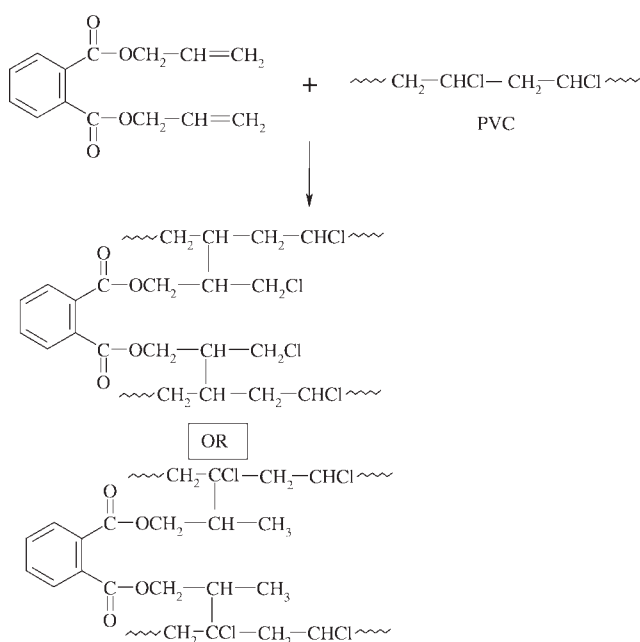
**Figure 2** Variation of UTS of PVC-PEA semi-IPNs with variation of PVC-PEA blend ratio (w/w).

increasing tendency in UTS values with increasing proportion of PEA incorporation.

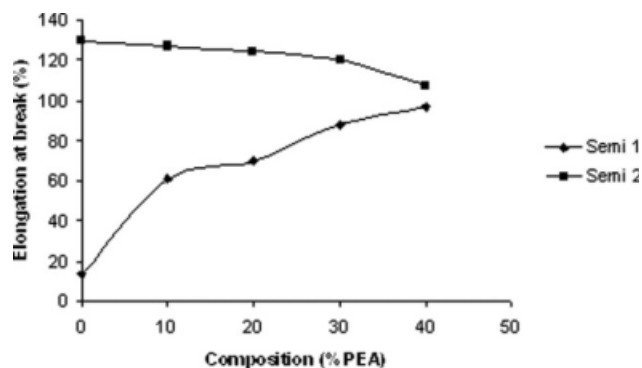
The reduction in tensile characteristics can possibly be explained by the presence of linear PEA chains that not only disrupts the regular chain structure of PVC in attaining its characteristic chain stiffness and rigidity but also does not allow the complete crosslinking of the matrix as they occupy the interstitial spaces of the PVC chains as the conditions of synthesis demand and increases the intermolecular distances. The somewhat plasticisation of PVC by the already incorporated DOP in the base formula is found to be augmented steadily with the *in situ* formation of PEA which occupies the interstices of the PVC chains, thus nullifying any antiplasticisation effect of DOP due to its presence.<sup>14</sup> Thus, the overall plasticisation effect due to the presence of the conventional plasticiser DOP and relatively elastomeric PEA gets a boost. The flexibility imparted by the long-chain crosslinks is predicted from the following postulated structure.

The crosslinking of PVC taking place by a thermally initiated free-radical process, which is assumed to take place after *in situ* formation of PEA, might occupy the interchain spaces and inhibit the complete crosslinking process of PVC (Scheme 1). The gradual steady decrease in modulus and UTS may thus be attributed to the decreasing proportion of homogeneous crosslinked PVC in various semi-IPN samples under study.

In contrast to the observation of semi-1 IPN systems, the semi-2 IPNs of PVC-PEA of different composition display an increasing behavior of modulus and UTS with increasing proportions of crosslinked in a linear matrix of PVC. The influence of crosslink-



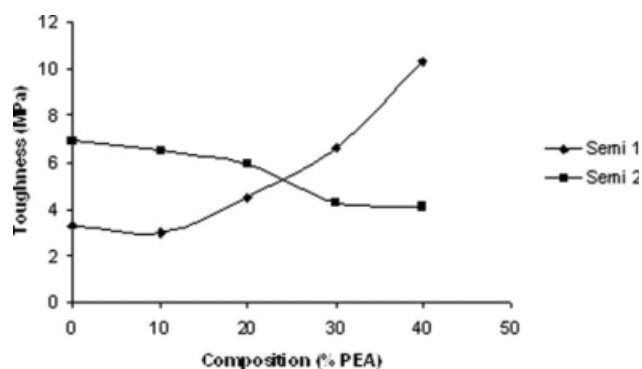
**Scheme 1** Crosslinking of PVC by diallyl phthalate.



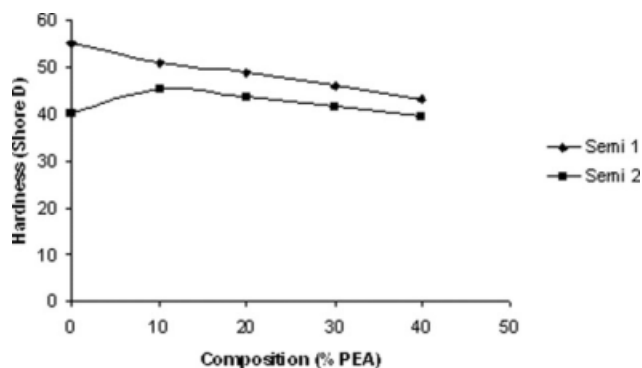
**Figure 3** Variation of percent elongation at break of PVC-PEA semi-IPNs with variation of PVC-PEA blend ratio (w/w).

ing of the minor dispersed PEA domains on the various properties of linear PVC matrix is not so pronounced as that was found with the semi-1 IPNs. The increase in the mechanical parameters might be expected as a result of development of some chain stiffness and rigidity imparted by the dispersed crosslinked PEA domains over the entire range of PVC matrix that is also evident from the morphological characteristics of the system. It is obvious that the crosslinked PEA increases the strength; however, the presence of PEA can also disrupt the dipole-dipole interaction of PVC chains and thus decreases the strength when compared with semi-1 IPN. This might have led to a substantial decrease in modulus values with respect to the semi-1 IPN. Within itself also, although there is a tendency of the UTS to increase with increasing proportion of PEA, the modulus shows marginal increase within the range of concentration studied.

The percent elongation at break and toughness values in case of semi-1 IPNs as shown in Figures 3 and 4 conform to our expectation. The long crosslinks (which may be considered as consisting of two flexible chain moieties pivoted around a rigid aromatic ring) coupled with the soft flexible PEA domains occupying the interchain spaces allow chain slippage



**Figure 4** Variation of toughness of PVC-PEA semi-IPNs with variation of PVC-PEA blend ratio (w/w).



**Figure 5** Variation of hardness of PVC-PEA semi-IPNs with variation of PVC-PEA blend ratio (w/w).

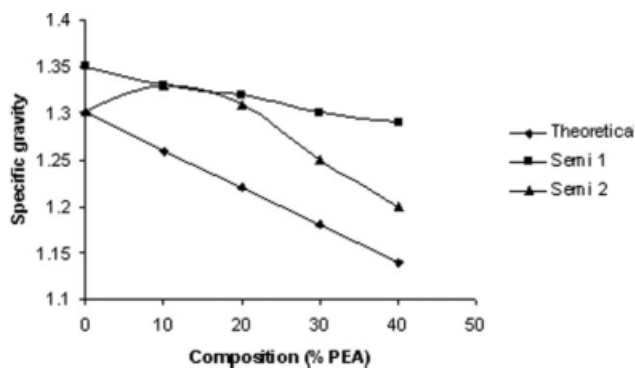
and account for an increased elongation at break and toughness of the system under study.<sup>15</sup>

In case of semi-2 IPNs there is a progressive, slow and steady decrease in %EB that can possibly be inferred from the pattern of changes with modulus and UTS. The fast rate of decrease in %EB as is encountered at the later stages may be attributed to the gross-phase separation. The toughness in conformity with %EB decreases progressively with increasing proportions of crosslinked PEA possibly because of its more and more inability to dissipate or absorb fracture growth energy, because of links in the rubbery PEA phase.<sup>16</sup>

The hardness of PVC-PEA semi-1 systems as exhibited in Figure 5 progressively decreases along with increasing PEA concentration, which is in consistency with the reduction in modulus and UTS values. The two opposing effects, which are operative in controlling the effective hardness values, lie so close in various composition that the reduction of hardness occurs over a narrow range.

The semi-2 IPNs also display a marginal decreasing tendency in their hardness values because of the increasing contents of polyacrylate into the system. The influence of the crosslinked PEA seems to be quite marginal over the hardness of pure linear PVC-based compound, although at the later stages the incorporation of crosslinked PEA seems to enhance the hardness a little because of agglomeration of crosslinked rubbery PEA phase.

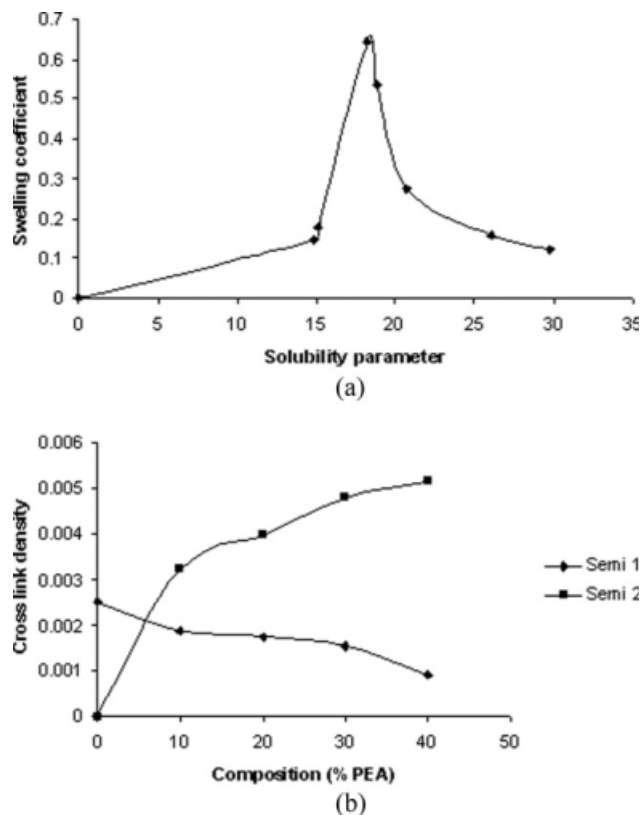
The specific gravities of different semi-IPN samples of PVC-PEA system are shown in Figure 6. They found to differ little in their specific gravities over the entire range of composition under study. It might be expected that in semi-1 IPNs, the decrease in proportion of crosslinked network of PVC is possibly mitigated to some extent by the presence of linear PEA moieties at the initial stages by the way of IPN formation, whereas at the later stages the marginal decrease in specific gravity is attributed to increased proportion of lighter PEA. The positive deviation in both cases from the theoretically pre-



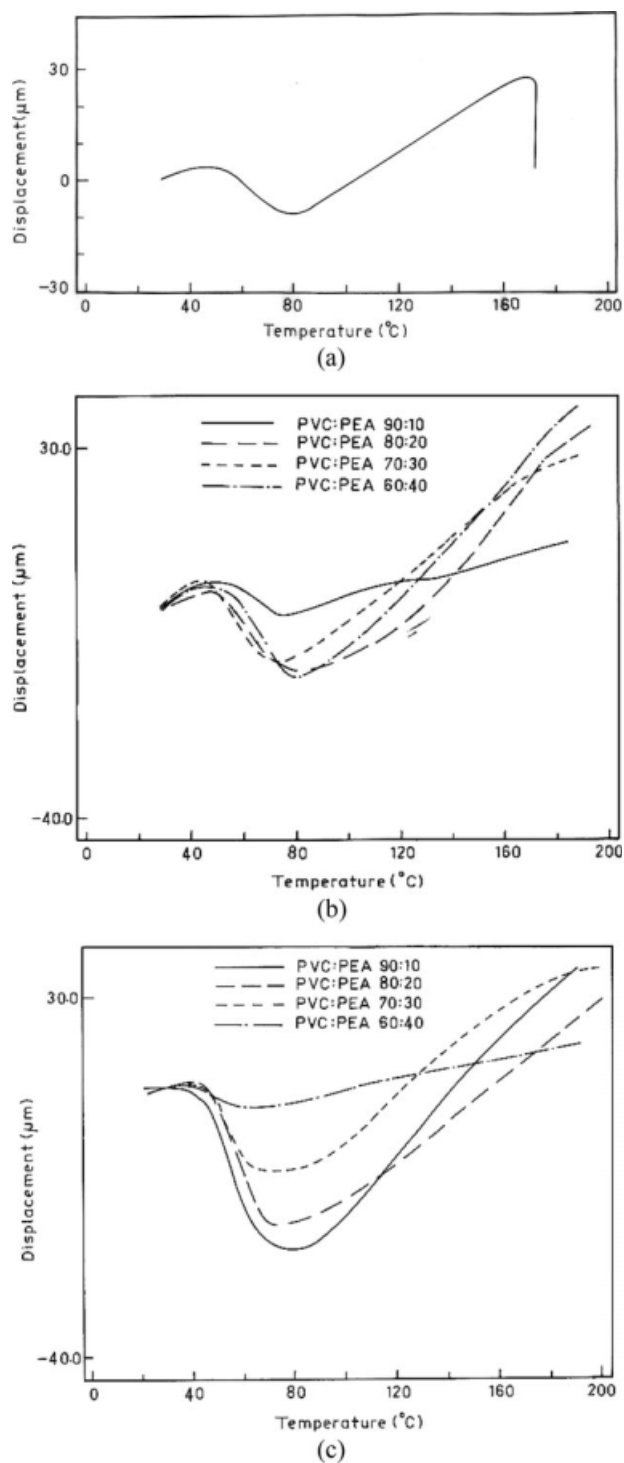
**Figure 6** Variation of specific gravity of PVC-PEA semi-IPNs with variation of PVC-PEA blend ratio (w/w).

dicted curve (obtained by the addition principle) indicates a very good extent of interpenetration.<sup>17</sup>

It is well known that the higher is  $M_c$  (*i.e.*, average molecular weight of the polymer segments between two successive crosslinks) for a system, the lower is the crosslink density. In this study, with an increase in the PEA content in the semi-1 IPNs, there is a gradual decrease and in case of semi-2 IPNs, there is an increase in the crosslink density.<sup>18</sup> The curve of swelling coefficient *vs.* solubility parameter of crosslinked PVC is shown in Figure 7(a).

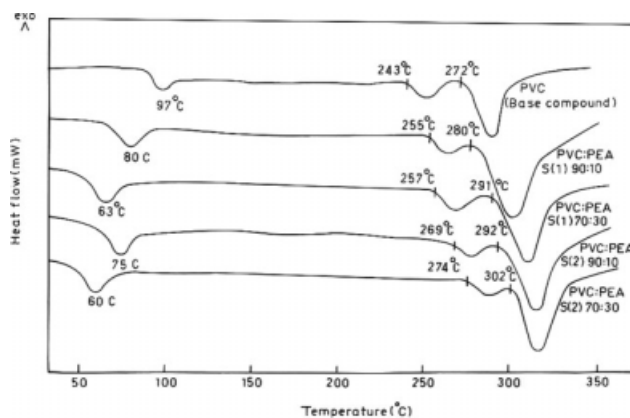


**Figure 7** (a) Swelling coefficient *vs.* solubility parameter for crosslinked PVC. (b) Variation of crosslink density of PVC-PEA semi-IPNs with variation of PVC-PEA blend ratio (w/w).



**Figure 8** (a) Thermomechanical curve of unmodified base reference compound PVC. (b) Thermomechanical curves of PVC-PEA semi-1 IPNs. (c) Thermomechanical curves of PVC-PEA semi-2 IPNs.

In case of semi-1 IPNs [Fig. 7(b)], a probability of an increase in the interchain distances of the PVC chain molecules due to the inclusion of more and more linear PEA phase may be attributed to (i) decreasing proportion of PVC and (ii) the statistically distributed long-chain crosslinks of DAP not favoring the forma-

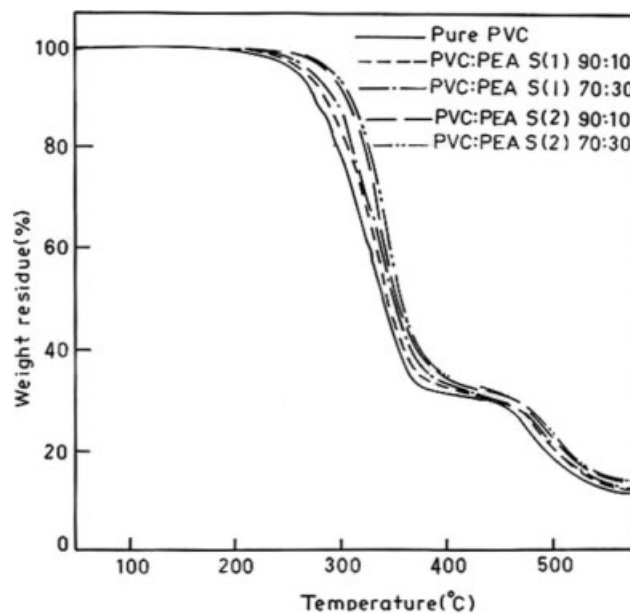


**Figure 9** DSC curves of PVC-PEA semi-IPNs; S(1) refers to semi-1 IPNs and S(2) for semi-2 IPNs.

tion of physical crosslinks through dipole-dipole interaction between the neighboring chains. This results in a gradual decrease in cumulative crosslink density of the semi-1 IPN system.

With the semi-2 IPNs, the crosslinked dispersed compact domains of PEA phase enables the linear PVC chains to come closer in comparison with the semi-1 ones and increases the probability of formation of hydrogen bonding among the neighboring PVC chains and acrylate moieties. This consequently increases the effective crosslink density.

The effect of crosslink density is also a reflection of the mechanical properties of the systems under study. The fall in modulus and UTS in case of semi-1 IPNs is to some extent an effect of the reduced crosslink density. On the other hand, the rise in modulus and UTS in case of semi-2 IPNs bears a



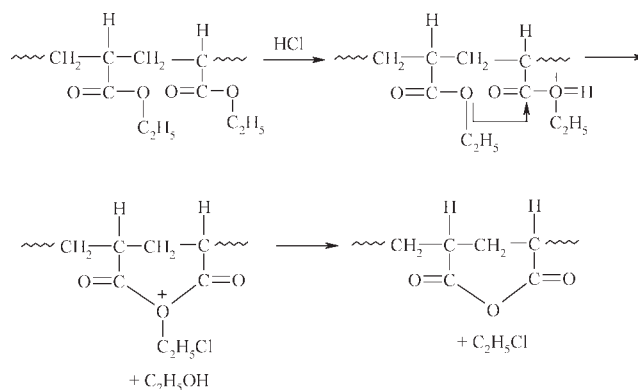
**Figure 10** TGA thermograms of PVC-PEA semi-IPNs.



the pattern as expected. The slopes of the curves beyond maximum softening indicate the maximum coefficient of thermal expansion for the 90 : 10 composition of the semi-2 IPN, whereas the same is found to own with 60 : 40 sample of semi-1 IPN. The IPNs, however, also exhibit stabilization over unmodified PVC, which is exhibited at the upper limiting test temperature where the molten samples undergo tendency of expansion while PVC shows breakdown and exhibits a sharp fall.<sup>14,19</sup>

The DSC thermograms of the system under study as shown in Figure 9 reveal a shift of the baseline at the region where the glass transition temperature of the interpenetrating networks of PVC-PEA is expected. The glass transition temperatures indicate relative increasing plasticisation with increasing concentration of the dispersed PEA moieties into the system. However, the crosslinking of the major matrix in semi-1 IPN or the minor phase in semi-2 IPN seems to influence the glass transition and degradation very little.<sup>20</sup> The two-stage degradation characteristics as observed at the higher temperature ranges reveal increased stability of the IPNs over unmodified PVC compound.

The TGA thermograms of both semi-1 and semi-2 IPNs along with PVC-based compound as depicted in Figure 10 clearly indicate thermal stabilization of the semi-IPNs over that of unmodified PVC. It can also be pointed out that the semi-2 IPNs possess marginally higher thermal stability over the corresponding IPNs of the semi-1 type. The presence of crosslinks in the dispersed phase thus seems to influence PVC degradation to a very limited extent, which is supportive of the DSC results obtained previously. The two stages of thermal degradation typical of pure PVC namely the dehydrochlorination and subsequent polyene formation and its consequent degradation are influenced by the *in situ* generated linear and crosslinked PEA in semi-1 and -2 IPNs, respectively.<sup>21</sup> The delayed onset of degradation with increasing percentages of the polyacrylate in both types of IPNs may be ascribed to the scavenging of the chloride radicals by the *in situ* generated PEA groups thus interacting via allylic shift. Also, as the concentration of the dispersed phase increases within the matrix, the chloride radicals become more inaccessible to the  $\alpha$  hydron atoms to form HCl due to the coalescence and occupancy of the bulky PEA molecules within the interspaces of the PVC chains. Even if some HCl is produced, it is consumed in hydrolyzing the ester groups of PEA as depicted in Scheme 2. Thus, the autocatalysis is stopped as is often considered to be the main reason for PVC degradation and the semi-IPNs achieve their stability.<sup>22</sup> In both types of semi-IPNs, the increased stabilities at higher percentages of PEA can be accounted by the more statistical availability



**Scheme 3** Scavenging of HCl formed *in situ*.

of the polyacrylates to interact with the HCl produced in the system (Scheme 3).

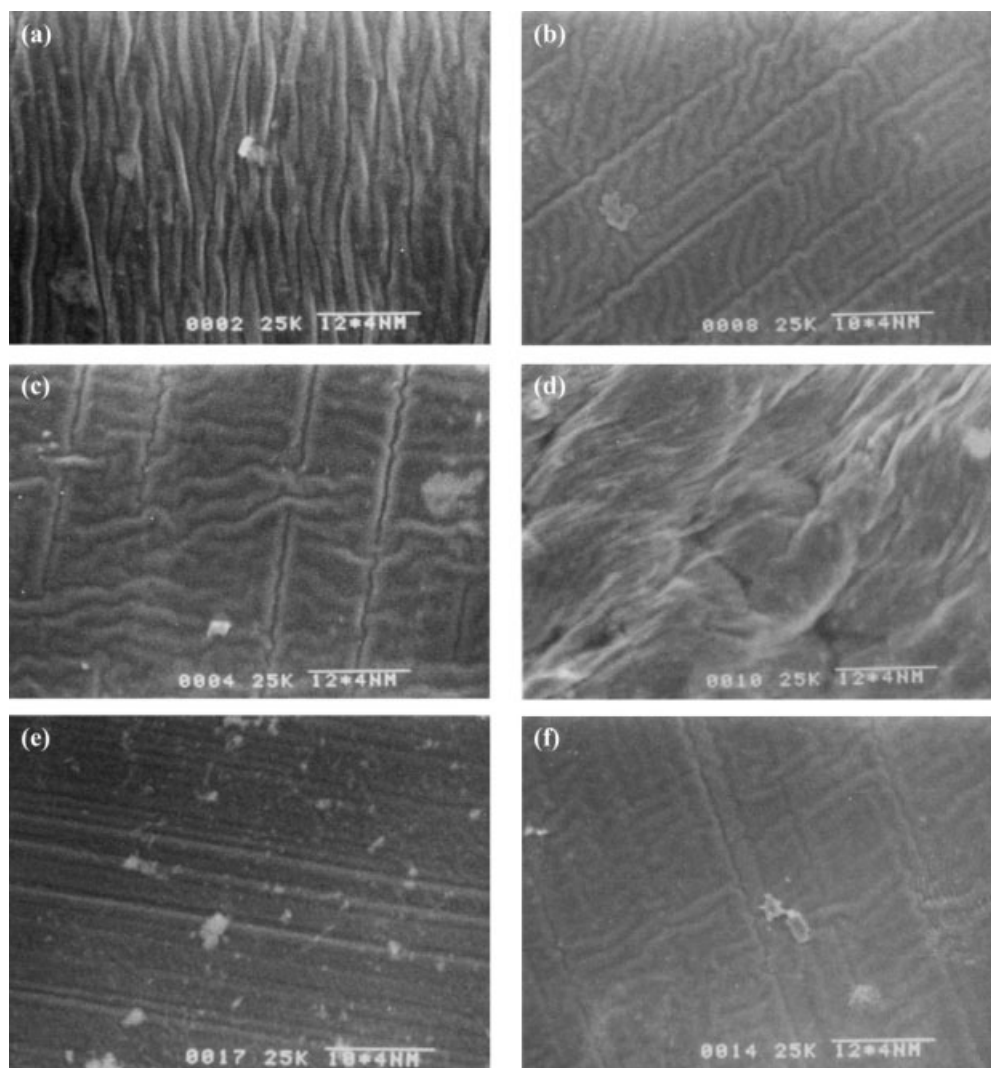
### Morphology

The semi-1 IPNs display a unique fibrillar morphology as demonstrated by the scanning electron micrographs ( Fig. 11). The major PVC matrix being crosslinked, the fibrillar PEA gets very limited room to grow and thereby gets interpenetrated with either the crosslinks or the major PVC chains. This results in a discontinuous array of the fibrillar chains in a continuous matrix.<sup>23</sup> With increasing PEA content, the fibrils of PEA are not only found to grow in thickness, they appear to be entangled and kinked more and more with itself possibly because of the tendency of being accommodated within the PVC whose content also goes on receding. This is in correlation with the rising elongation at break with rise in PEA content. There is no exception to the fibrillar morphology in case of semi-2 IPNs. Here, possibly because of the presence of crosslinks in the PEA phase the fibrils seem to be sharp and compact. The phase domains of PEA moieties in case of semi-2 IPNs are more regular in nature, which can be attributed to the crosslinking of the dispersed phase which makes it much tighter and enables it to adopt a much regular shape.<sup>24</sup> However, the phase heterogeneity observed at the later stages may be attributed to the co-continuous formation of the matrices and increased number of PEA particles that tend to undergo coalescence and agglomeration. The effect of these factors result in deterioration of elongation with rising crosslinked PEA phase.

### CONCLUSION

The systems under study revealed the impact of IPN formation of PVC with the poly(alkyl acrylate) ester. The introduction of PEA moieties within the matrix of PVC produced a rise in the mechanical and





**Figure 11** Scanning electron micrographs of PVC-PEA semi-IPNs with magnification 500 $\times$ ; S(1) refers to semi-1 and S(2) refers to semi-2 IPNs, respectively.

thermal stability compared with base compound PVC. The combination of the two polymers also created a directing influence one over the other which was explicit from the micrographs. The degree of PEA incorporation had a measurable increasing effect on the modulus and UTS and an overall rise in the toughness values in semi-2 and semi-1 IPNs, respectively. Thus interpenetrating networks with increased strength and acceptable toughness have been simultaneously achieved. The toughness values though exhibiting a gradual fall along with composition in case of semi-2 IPNs, always lie above that of unmodified PVC. The thermomechanical properties have also been modified which produces an overall increasing stability. The rise in the onset temperature of degradation as explicit from the TGA and DSC results indicate the influence of the dispersed PEA moieties in producing thermal stability.

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