

Modification of the Mechanical and Thermal Properties of PVC by Semi IPN Formation with Poly(butyl acrylate)

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ABSTRACT: Semi1 and semi2 interpenetrating polymer networks of poly(vinyl chloride) PVC and *in situ* formed poly(butyl acrylate) (PBA) have been synthesized and characterized using diallyl phthalate (DAP) and ethylene glycol dimethacrylate (EGDM) as the crosslinkers of PVC and PBA, respectively. These two types of IPNs have been compared with respect to their mechanical and thermal properties. The semi1 IPNs displayed a decrease in their mechanical parameters and the physical properties as well, while in contrast, the semi2 IPNs exhibited a marginal increase in the corresponding values when compared to the crosslinked PVC in the case of semi1 IPN and linear

PVC in case of semi2 IPN. The representative samples of semi1 and semi2 IPNs revealed a two-stage-degradation typical of PVC while confirming the increased stability of the samples with higher onset temperature of degradation. The softening characteristics as detected by thermomechanical analysis are in conformity with their mechanicals. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 170–176, 2008

Key words: poly(vinyl chloride); poly(butyl acrylate); interpenetrating networks; mechanical properties; thermo-mechanical properties

INTRODUCTION

Poly(vinyl chloride) (PVC) has been widely used as an important general plastic because of its excellent corrosion resistance, electrical properties, self extinguishing characteristics, low cost, and recoverability. But its sensitivity to notched impact, high temperature and poor processibility limits its applications. PVC products are restricted to environments not exceeding 80°C and to non structural applications because of low strength.¹ Hence the polymer is often mixed with other polymers to improve its properties. In this study, toughening of PVC is carried out by the involvement of relatively elastomeric poly(butyl acrylate) (PBA) through IPN formation in the form of semi1 IPN (in which the major matrix PVC is crosslinked) and semi2 IPN (in which the minor matrix PBA is crosslinked).^{2,3} Paul and Barlow⁴ have suggested that the α hydrogen of PVC can interact with the ester carboxylate group (H bond acceptor of the acrylic polymer) to form hydrogen bond and is also a key factor in achieving miscibility.⁵ Also, there is a probability of interaction between the C–Cl dipole of PVC and the α hydrogen of the acrylate ester.⁶ These two phenomena can account for

increased strength of the IPNs and thus interpenetrating networks of PVC and PBA can be expected to display improved tensile as well as toughness behavior. The degree of network interlocking between the components hence has a measurable effect on the various mechanical properties such as modulus, hardness, and ultimate tensile strength (UTS) which in turn depends on whether either component of the network is crosslinked or both of them are crosslinked.^{7,8} Increased network interlocking is expected to improve compatibility.⁹

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 plasticizers and stabilizers, respectively. Diallyl phthalate (DAP) from M/s Burgoyne (India) was used as a crosslinker for PVC.

Butyl acrylate (BA) from M/s Burgoyne (India) 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 (CaCl₂). It was finally

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vacuum-distilled. Benzoyl peroxide from Loba Chemie (India) was purified by repeated crystallization from chloroform and was used as initiator for acrylic polymerization. Ethylene glycol dimethacrylate (EGDM) from Aldrich Chemical Company, USA, was used as the crosslinker for PBA.

Synthesis of semi1 and semi2 IPN's

A weighed amount of purified BA was taken in a test tube and thoroughly mixed with 2% by weight (based on BA) of recrystallised Bz_2O_2 . PVC resin was weighed such that a predetermined ratio with respect to the monomer as weighed earlier was just made. The resin was taken in an air tight warm dry blender and mixed with 30 parts of DOP and 2 parts of TBLS with respect to the amount of PVC resin taken. Five parts by weight of DAP w.r.t PVC was then added in case of synthesis of semi1 IPN. The monomer containing initiator was then added to the premix of PVC. EGDM in the ratio of 2% by weight of BA taken was initially added to the monomer mix in case of semi2 IPN. Dry mixing was further continued unless a thoroughly mixed powder is obtained. The mix was then compression molded into sheet by subjecting a three piece mold under pressure and heat in two stages.

Conditions of molding

Initially, the mold was compressed under a pressure of 15 tons/cm² at a temperature of 80°C to initiate and propagate acrylic polymerization. This was allowed to continue for 30 min. Subsequently, the temperature was raised to 160°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°C for further 20 min to ensure complete polymerization and crosslinking of residual BA 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

Mechanical properties

An Instron Universal Testing Machine (Model 4204) was used for measuring the tensile properties like ultimate tensile strength (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. Toughness of the samples were determined from the area under the load versus 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 $\pm 5\%$.

Physical properties

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.

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 equilibrium swelling of such polymer system by a good solvent.¹⁰

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

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, d_r = density of the polymer, χ = polymer-solvent interaction parameter.

The polymer-solvent interaction parameter (χ) was calculated as follows. Equilibrium swelling was done at 27°C using seven different liquids ranging in their solubility parameter (δ) from 14.9 to 29.7.

The swelling coefficient Q was calculated using the following eq. (2)

$$Q = \left(\frac{m - m_o}{m_o} \right) \times \frac{d_r}{d_s} \quad (2)$$

where m = weight of the swollen samples, m_o = original weight of the sample, d_s = density of the solvent.

In the subsequent plots of Q versus δ 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:

$$\chi = \beta + (V_s/RT) \times (\delta_s - \delta_p)^2 \quad (3)$$

where β = lattice constant = 0.34, R = Universal gas constant, T = absolute temperature, δ_s and δ_p are solubility parameters of the solvent and the prepared samples, respectively.

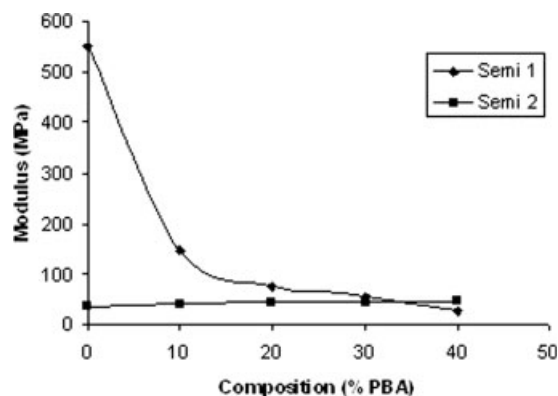


Figure 1 Variation of Young's modulus of PVC-PBA semi IPNs with variation of PVC-PBA blend ratio (w/w).

Thermal properties

The thermomechanical analysis of the various samples were carried out in a TMA apparatus from Shimadzu (model TMA 50) in presence of oxygen. The thermo-oxidative characteristics were studied under a constant load of 0.008 kg 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 5×10^{-6} to 8×10^{-6} kg.

RESULTS AND DISCUSSION

Physicomechanical properties

The modulus and UTS of semi1 IPN (PVC cross-linked) as depicted in Figures 1 and 2 show a decreasing trend with increasing proportion of PBA. The reduction in modulus is quite sharp initially (with respect to pure crosslinked PVC), but gradually slows down and becomes almost invariant with composition beyond 25–30% of linear PBA incorporation, the UTS however exhibiting a steady and sluggish decrease. The semi2 IPNs, however, shows steady increasing tendency in modulus and ultimate tensile strength values with increasing proportion of PBA incorporation. It is worth notifying that the sharp initial drop in modulus as encountered with semi1 IPN is however absent in semi2 IPN.

The reduction in tensile characteristics can possibly be explained by the introduction of the flexible rubbery bulky polybutylacrylates into the cross-

linked PVC matrix which creates a breakdown in the molecular alignment. This is further accentuated by the increasing hindrance to the crosslinking process of PVC, which goes on simultaneously with the *in situ* generation of PBA and thus promotes flexibility.¹¹ Thus it appears that the fast rate of acrylic polymerization predominates over the rate of crosslink formation between the PVC chains as otherwise the reverse would have taken place. 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 PBA which occupies the interstices of the PVC chains, thus nullifying any antiplasticization effect of DOP due to its presence. Thus the overall plasticization effect due to the presence of the conventional plasticizer DOP and relatively elastomeric PBA gets a boost. The flexibility imparted by the long chain crosslinks is predicted from the following postulated structure in Scheme 1.

The crosslinking of PVC taking place by a thermally initiated free radical process, which is assumed to take place after *in situ* formation of PBA, might occupy the interchain spaces and inhibit the complete crosslinking process of PVC.

In contrast to the observation of semi1 IPN systems the semi2 IPNs of PVC-PBA of different composition display a marginal increasing behavior of modulus and UTS with increasing proportions of crosslinked PBA in a linear matrix of PVC. A very slow and gradual increase of modulus over the unmodified linear PVC matrix indicates the little influence of crosslinks in the dispersed rubbery domains of PBA on the modulus and UTS of linear PVC in particular. The minor phase itself being rubbery in nature, the effect of strength modification through formation of crosslinks within itself remains somewhat subdued and the modulus values near to that of pure plasticized PVC (without any modifying resin) results. Here it is interesting to note that the

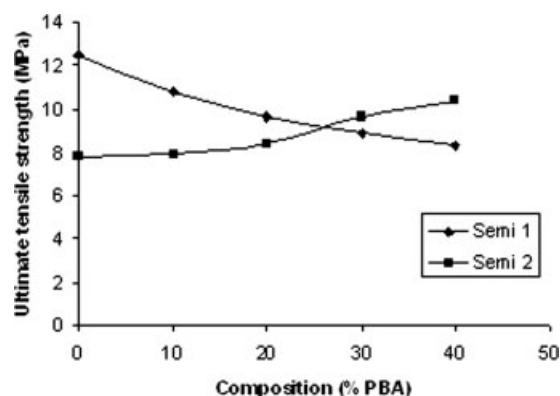
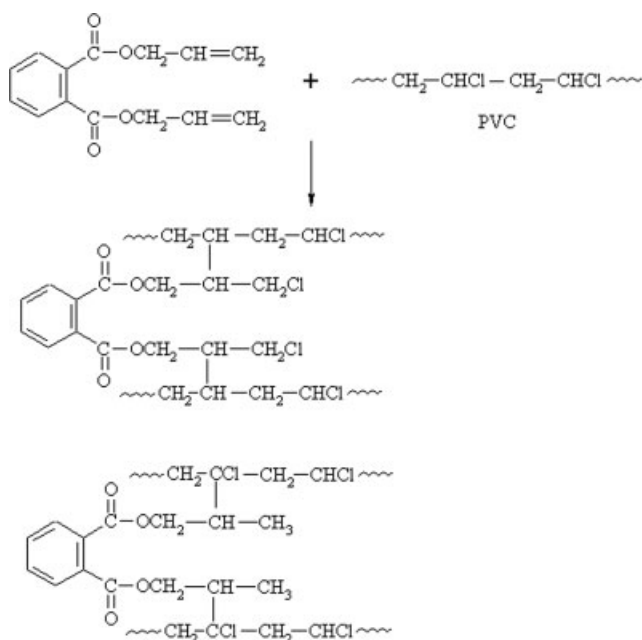


Figure 2 Variation of ultimate tensile strength of PVC-PBA semi IPNs with variation of PVC-PBA blend ratio (w/w).



Scheme 1 Cross linking of PVC by diallyl phthalate.

decrease in modulus of unmodified base PVC compound due to breakdown in regular chain structure and in dipole-dipole interaction between the chains due to the incorporation of linear PBA molecules is compensated to a small extent by the crosslinking within the dispersed PBA phase.

A simultaneous increase in elongation at break and toughness of the semi1 IPN systems under study as depicted in Figures 3 and 4 are supportive of the previous observations of decreasing modulus and UTS as the PBA content increases in composition. In analogy to the mechanism of rubber toughening (rubber being stretchable and absorbing the energy for crack propagation),^{12,13} the *in situ* generated PBA domains provide not only a greater path length for the cracks to cover before rupture but also

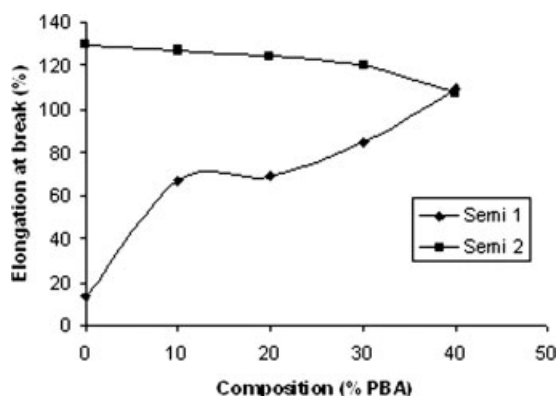


Figure 3 Variation of percent elongation at break of PVC-PBA semi IPNs with variation of PVC-PBA blend ratio (w/w).

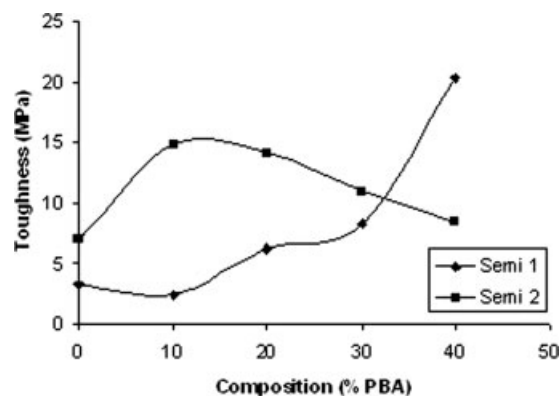


Figure 4 Variation of toughness of PVC-PBA semi IPNs with variation of PVC-PBA blend ratio (w/w).

absorbs high energy of crack propagation leading to a stoppage of the crack growth and substantial increase in toughness of the system under study results.¹⁴ The elongation at break and toughness values of the semi2 IPN systems again reflects the effect of flexible PBA moieties within the linear PVC chains by occupancy of the interspaces. However, the EB % and toughness of the system under study undergoes little increase compared to that of the uncrosslinked PVC matrix and then levels off almost close to the value of unmodified PVC.

The variation in hardness with changes in composition of the semi1 and semi2 IPNs is shown in Figure 5. The trend in both cases is found to be a replica of the changes in modulus versus composition. A gradual, steady and slow decrease in hardness for semi1 IPNs with increasing PBA content is observed while for semi2 IPNs the hardness values level off after an initial increase.

The two IPN systems exhibit almost identical behavior i.e., an initial rise in specific gravity and then a decrease with increasing nPBA content, the semi2 IPNs however lying above the semi1 IPNs, the

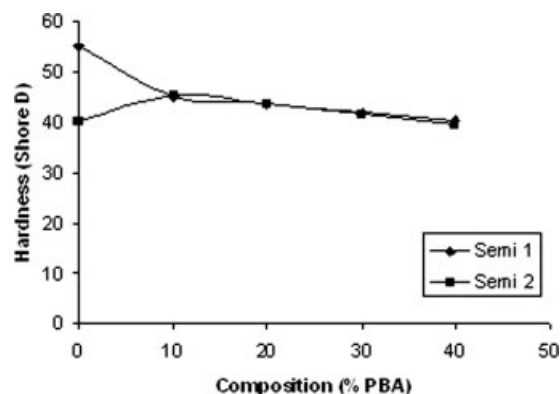


Figure 5 Variation of hardness of PVC-PBA semi IPNs with variation of PVC-PBA blend ratio (w/w).

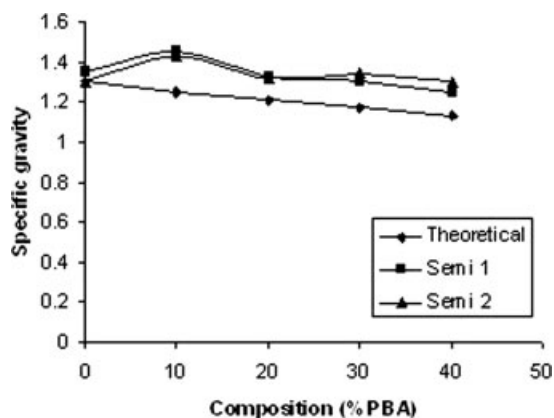


Figure 6 Variation of specific gravity of PVC-PBA semi IPNs with variation of PVC-PBA blend ratio (w/w).

difference being marginal (Fig. 6). As has already been mentioned in case of semi1 IPN, it is the accumulation of linear PBA particles within the confined spaces produced by the long chain crosslinks of PVC and the scope of its interpenetration due to the relatively higher mobility of the linear PBA chains with PVC which might lead to such higher initial values of specific gravity. The specific gravity however gradually decreases as the proportion of crosslinked PVC decreases. With the semi2 IPN systems however, the crosslinked compact domains of PBA occupy the spaces between linear and rigid chains of PVC and increases the density. However, in both the cases, the positive deviation of the experimental values from the theoretical ones indicates a positive pointer towards interpenetration.¹⁵

It is well known that the higher M_c (i.e., average molecular weight of the polymer segments between two successive crosslinks) is for a system, the lower is the crosslink density. The PVC-Poly(butyl acrylate) semi1 and semi2 IPNs exhibit a fall and rise in crosslink densities respectively, with increase in content of PBA respectively, (Fig. 7). In case of semi-1 IPNs, this may be attributed to the entry of more and more bulky PBA moieties within the interstitial spaces of the PVC phase and thus enhancing the intermolecular distances between them hence diminishing the possibility of crosslink formation within the PVC molecules.¹⁶ As the concentration of PBA increases within the linear major matrix of PVC, the intensity of crosslink density in case of semi2 IPNs increases. The crosslink density of PVC-PBA semi2 IPNs thus indicate an upward swing with rise in concentration of the dispersed PBA phase.

Thermal properties

The thermomechanical curves of the systems [Figs. 8(a–c)] under consideration typically represent the

resistance offered by the respective samples towards penetration of the probe, the depth of penetration of which is dependent upon the mechanical strength of the individual IPNs. The semi1 IPN samples of different composition exhibit the development of relatively more thermally stable systems compared to pure PVC. Not only the softening temperature undergoes a gradual and regular increase with increasing proportion of linear PBA but also the rate of expansion becomes sluggish beyond the maximum softening point as nPBA is present in large amounts. The semi2 IPNs display somewhat opposite behavior to that of semi1 IPNs. The resistance offered by the crosslinked PVC in case of semi1 IPN is absent here and although the minor dispersed phase of PBA is crosslinked, it fails to exert any appreciable influence on softening point as the maximum softening points displayed by the semi2 IPN samples of different composition appear to remain almost unaffected. Furthermore, the rate of expansions increases as the PBA content increases. However, in case of both the systems, once the IPNs have softened completely, the molten samples undergo expansion till the upper test temperature is reached. While at this stage, PVC shows breakdown and sharp fall, the IPNs (both semi1 and semi2) remain stable and exhibit stabilization over PVC.¹⁷

The effect of thermal stabilization is also explicit from the DSC tracings of unmodified PVC and the representative samples of semi1 and semi2 IPNs as shown in Figure 9. The shifting of the glass transition temperature at the lower temperature region is indicative of some effect of plasticization produced by the entry of the somewhat rubbery PBA molecules within the PVC matrix.¹⁸ At the higher temperature region, the characteristic two stage degradation typical of PVC is quite explicit with the IPNs exhibiting a higher onset temperature compared to that of the base compound PVC. Moreover, increasing content of PBA within the system, increases the onset

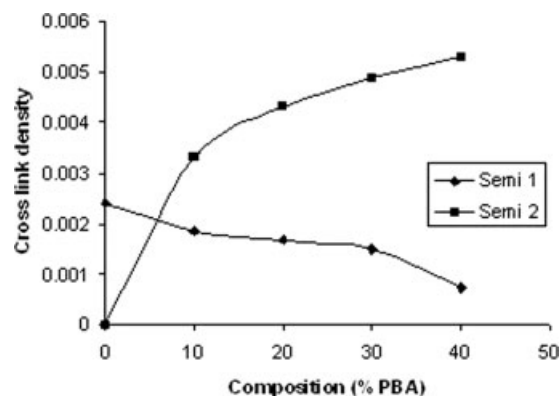


Figure 7 Variation of crosslink density of PVC-PBA semi IPNs with variation of PVC-PBA blend ratio (w/w).

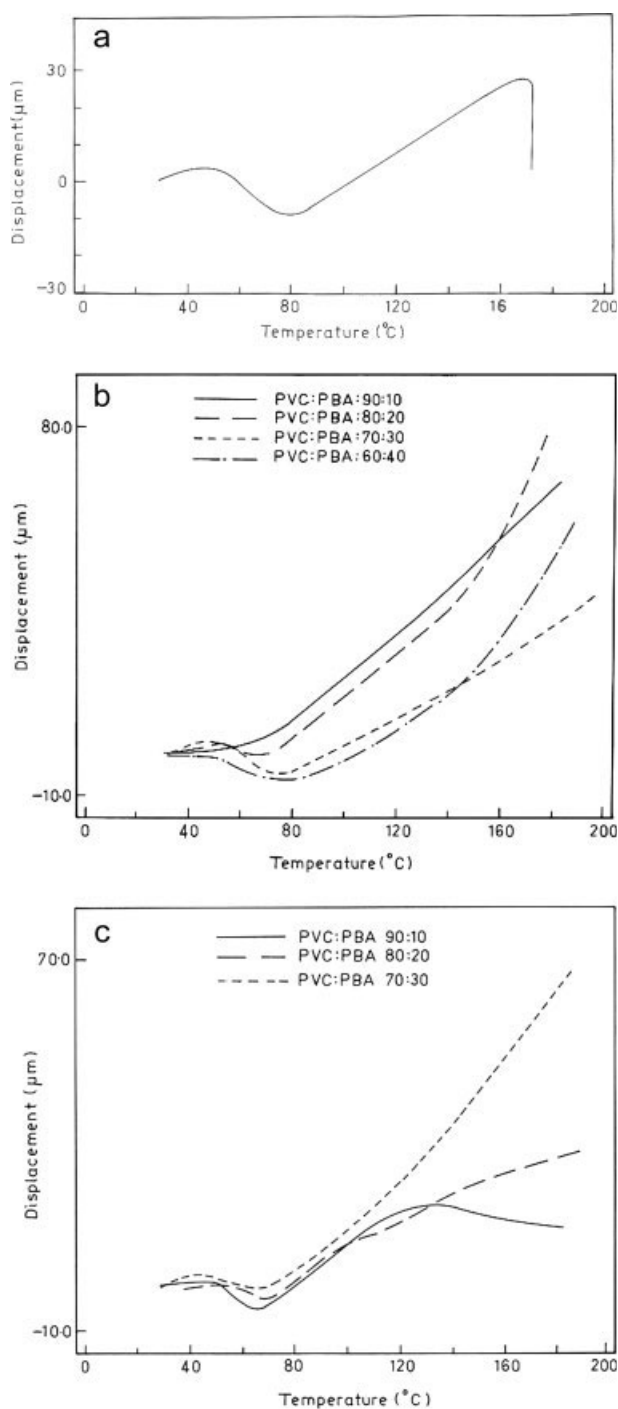


Figure 8 (a) Thermomechanical curve of unmodified base reference compound PVC. (b) Thermomechanical curves of PVC-PBA semi1 IPNs. (c) Thermomechanical curves of PVC-PBA semi2 IPNs.

temperature of degradation. This observation can be well explained as follows:

Dehydrochlorination as considered to be the first stage in thermal degradation of PVC is not random, but proceeds along the chains following the initial loss of hydrogen chloride. This process is assumed

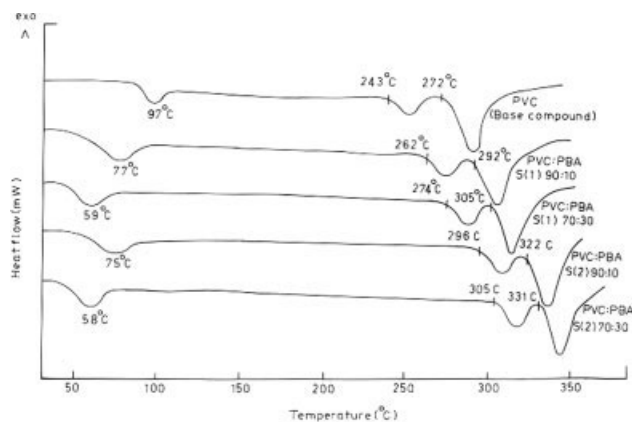
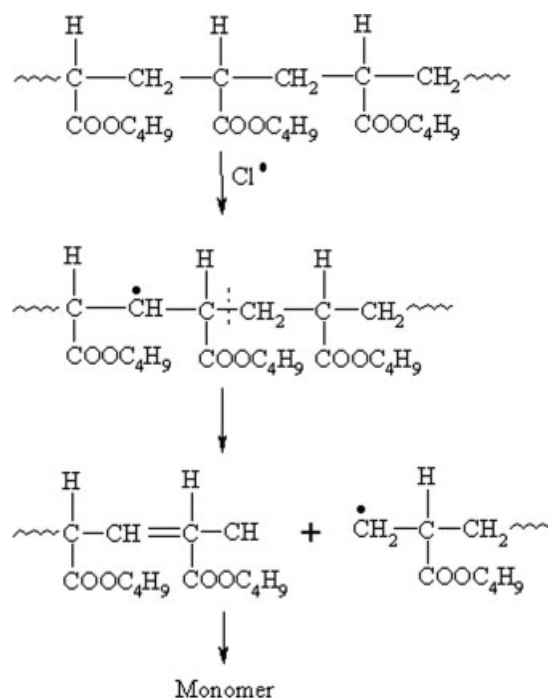


Figure 9 DSC curves of PVC-PBA semi IPNs; S(1) refers to semi1 IPNs and S(2) for semi2 IPNs respectively.

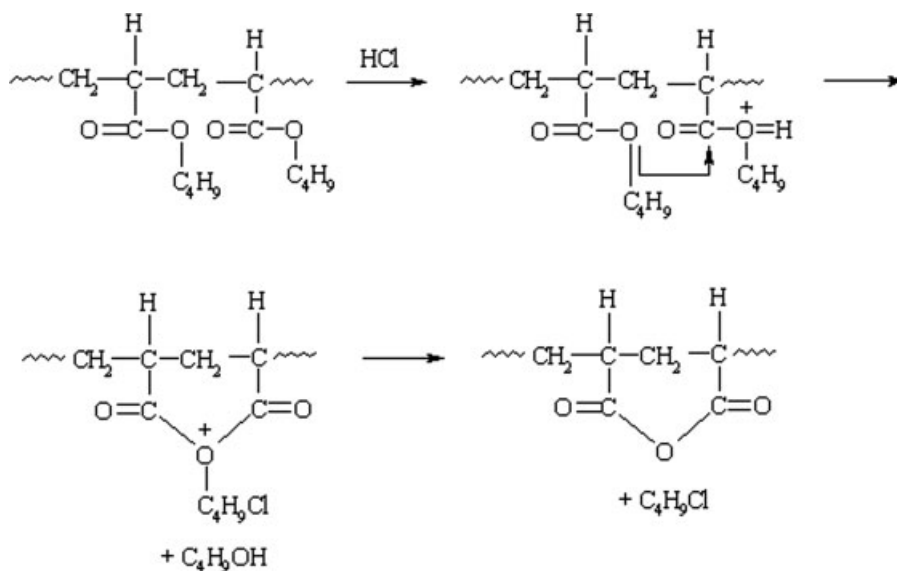
to be free radical process involving the initial formation of chlorine radicals (intermediate in the dehydrochlorination of PVC). This chlorine radical fails to form HCl as it interacts with the PBA (Scheme 2).¹⁹

Second, even if the HCl is produced, it fails to catalyze the process of subsequent degradation as it reacts with the ester group of PBA (Scheme 3).

The chloride radical Cl^\bullet causes the PBA chain to break and subsequently unzip quite readily at low temperatures. Reaction with HCl on the other hand, presumably a slower process gives rise to anhydride rings which acts as locking groups reducing the zip length of depolymerization and thus stabilizing the



Scheme 2 Stabilising mechanism of PVC by PBA.



Scheme 3 Scavenging of HCl formed in situ.

chain. Moreover the unzipped monomers (BA) are considered to be very good radical scavenger and thus scavenges the chloride radicals immediately as they are formed. In this way there is a mutual stabilizing effect whereby PVC is stabilized by PBA in IPNs by not allowing the Cl^\cdot radical to form hydrogen chloride and subsequently not permitting the HCl even if formed by forming an anhydride type of structure.²⁰ The onset gradually rises with increasing proportion of PBA as more moieties are available to absorb the chloride free radicals.

CONCLUSIONS

The systems under study reveal the effect of IPN formation of PVC with the poly(alkyl acrylate) ester, PBA. It can be noted that the two types of IPNs display mechanical behavior contrasting to each other as more and more PBA moieties are incorporated within the system. The introduction of PBA moieties within the matrix of PVC produces a marginal rise in the mechanical and thermal stability compared to base compound PVC. The degree of PBA incorporation has an effect on the modulus and ultimate tensile strength and an overall rise in the toughness values as well in both the cases of semi1 and semi2 IPNs. Thus interpenetrating networks with increased toughness have been simultaneously achieved at as the toughness values always lie above that of unmodified PVC. The thermomechanical and DSC

results indicate the influence of the dispersed phase PBA in achieving thermal stability.

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