

# Engineering Properties of Poly(vinyl chloride)–Poly (butyl methacrylate) Semi-1 and Semi-2 Interpenetrating Polymer Networks

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Received 27 July 2006; accepted 1 May 2007

DOI 10.1002/app.26872

Published online 28 September 2007 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(butyl methacrylate) (PBMA) have been synthesized using diallyl phthalate and ethylene glycol dimethacrylate as the crosslinkers of PVC and PBMA, respectively. These were then characterized with reference to their mechanical, thermal, and morphological properties. The mechanical and thermal characteristics revealed modification over the unmodified polymeric systems in relation to their phase morphologies. The semi-1 IPNs displayed a decrease in their mechanical parameters of modulus and UTS while semi-2 IPNs exhibited a marginal increase in these two values. The semi-1 IPNs, however, also revealed

a decrease in the elongation and toughness values away from the normal behavior. The thermomechanical behavior of both the systems is in conformity with their mechanicals in displaying the softening characteristics of the system and stabilization over unmodified PVC. The DSC thermograms are also correlated to these observations along with the heterogeneous phase morphology which is displayed by both the systems especially at higher concentration of PBMA incorporation. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 966–975, 2008

**Key words:** interpenetrating network; mechanical properties; thermal properties; morphology; poly(vinyl chloride)

## INTRODUCTION

A semi-interpenetrating polymer network (IPN) consists of linear polymer chains threaded through a crosslinked polymer network, characterized by their bicontinuous structure without any chemical linkage between them. The present system focuses on the formation of sequential IPNs in which a monomer (butylmethacrylate) is polymerized and crosslinked in the immediate presence of another polymer poly(vinyl chloride) (PVC). In semi-1 IPNs, only the major polymer is crosslinked (here the major matrix PVC) and in semi-2 IPN, the second polymer synthesized is crosslinked (polybutylmethacrylate, PBMA).<sup>1–4</sup> The introduction of crosslinks into the system influences the mechanical, thermal, and morphological aspects of the ultimate IPNs, thus controlling the factors like resistance to degradation and phase separation. The engineered crosslink formation also restricts the domain size and enhances molecular mixing. However, with proper selection of polymers and composition, an appreciably high

extent of mixing can be obtained.<sup>5</sup> The methacrylate monomer polymerized *in situ* within the major matrix PVC, exerts its modifying influences in promoting mechanical and thermal stability. The phase morphology also exhibits change over the entire composition ranges of the semi-1 and semi-2 IPN systems under study.<sup>6</sup> Polymerization and crosslinking lead to a reduction in the entropy of mixing and tend to induce phase separation. In IPNs, this tendency is counterbalanced by the physical constraint imposed on diffusion by the development of interlocking networks, so that phase separation is limited. This limitation results in structures that are usually much finer than those of the mechanically blended polymers.<sup>7,8</sup>

Crosslinking PVC can improve its heat resistance, solvent resistance, and mechanical properties.<sup>9,10</sup> This, along with the presence of PBMA ester enhances the thermal stability further and facilitates processing.<sup>11</sup>

## EXPERIMENTAL PROCEDURES

### 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

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Burgoyne (India) and tribasic lead sulphate (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.

Butylmethacrylate (BMA) 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 ( $\text{CaCl}_2$ ). It was finally vacuum distilled. Benzoyl peroxide from Loba Chemie (India) was purified by repeated crystallization from chloroform and was used as initiator for acrylic polymerization. Ethylene glycol dimethacrylate (EGDM) from Aldrich Chemical Company, USA, was used as the crosslinker for PBMA.

### Synthesis of semi-1 and semi-2 IPN's

A weighed amount of purified BMA was taken in a test tube and thoroughly mixed with 2% by weight (based on BMA) of recrystallized  $\text{Bz}_2\text{O}_2$ . 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 two 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 semi-1 IPN. The monomer containing initiator was then added to the premix of PVC. EGDM in the ratio of 2% by weight of BMA taken was initially added to the monomer mix in case of semi-2 IPN. Dry mixing was further continued until a thoroughly mixed powder is obtained. The mix was then compression moulded into sheet by subjecting a three piece mould under pressure and heat in two stages.

### Conditions of moulding

Initially, the mould was compressed under a pressure of 15 tons/cm<sup>2</sup> 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 in order to ensure complete sintering of PVC and acrylic polymerization. The whole combination was kept in an oven at 100°C for further 20 min in order to ensure complete polymerization and crosslinking of residual MMA or PVC or both as the cases may be. The mould was then allowed to cool down at room temperature and the moulded 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 was 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.<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 done 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 eq. (2)

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

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

In the subsequent plots of  $Q$  versus  $\delta$  values for different solvents, the solubility parameter corresponding to the maximum value of  $Q$  was noted

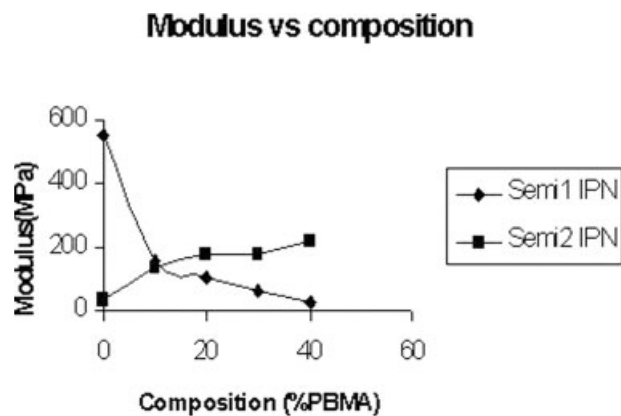


Figure 1 Variation of modulus with IPN composition.

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<sup>13</sup> as follows:

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

where  $\beta$ , lattice constant = 0.34;  $R$ , Universal gas constant;  $T$ , absolute temperature;  $\delta_S$  and  $\delta_P$  are solubility parameters of the solvent and the prepared samples, respectively.

#### Thermal properties

The thermomechanical analysis of the various samples was 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 8 g throughout the experiment using a compressive mode of probe up to 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 up to 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.

#### Morphology

SEM studies were carried out in a scanning electron microscope (Hitachi model S415A) after suitable gold coating on the samples. 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×.

An optical microscope from Krüss (optromic) (Germany) was used to study the surface morphology of the undeformed samples having thickness <0.5 mm to get a relative idea of the mode of distribution of domains, sizes of the domains, physical state of the domains, and mode of their growth as dictated by the method of synthesis, compatibility, etc. The scale of magnification used was 200×.

## RESULTS AND DISCUSSION

### Mechanical 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 PBMA although there is an initial sharp reduction in modulus in going from pure crosslinked PVC to PVC-PBMA (10%).

The semi-2 IPNs, however, shows steady increasing tendency in modulus and ultimate tensile strength values with increasing proportion of PBMA incorporation. It is worth notifying that the sharp initial drop in modulus as encountered with semi-1 IPN is, however, absent in semi-2 IPN.

The initial sharp drop in the modulus of semi-1 IPN can be attributed to the presence of linear bulky PBMA domains which not only disrupts the regular chain structure of PVC but also does not allow complete crosslinking of the matrix. 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 plasticization of PVC by the already incorporated DOP in the base formula is found to be augmented steadily with the *in-situ* formation of PBMA which occupies the interstices of

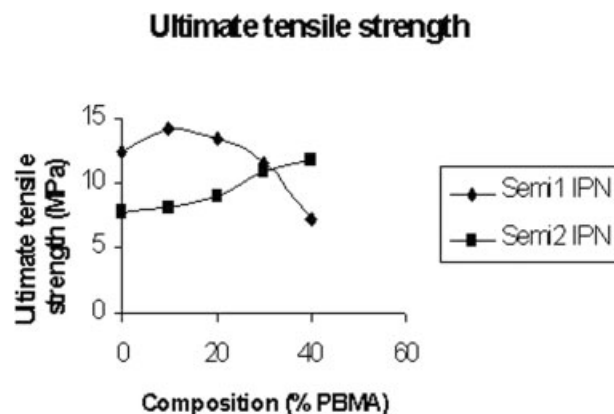
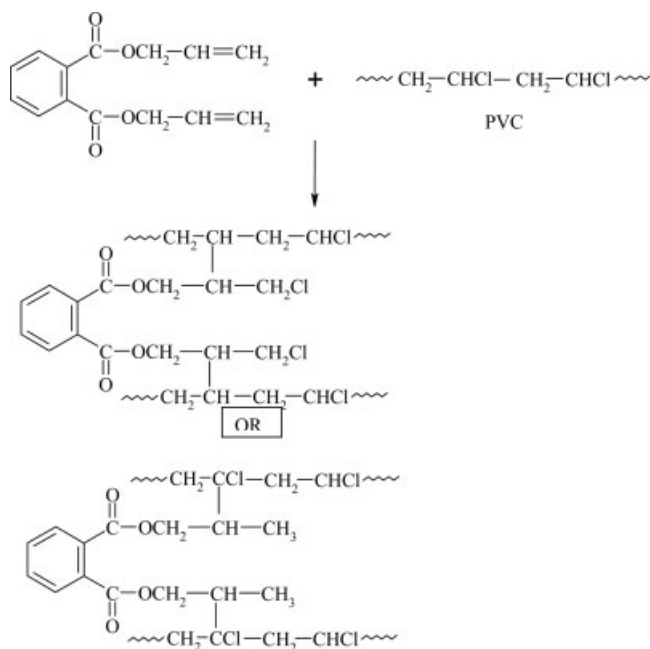


Figure 2 Variation of ultimate tensile strength with IPN composition.

the PVC chains, thus nullifying any antiplasticization effect of DOP because of its presence. Thus, the overall plasticization effect due to the presence of the conventional plasticizer DOP and relatively elastomeric PBMA gets a boost. The flexibility imparted by the long chain crosslinks by DAP is predicted from the following postulated structure



The sluggish decreasing trend of modulus beyond 10% envisages very little influence of the increasing proportion of linear PBMA on this particular mechanical parameter. This can possibly be attributed to the more and more heterogeneous phase separation of the dispersed PBMA phase with increase in its percentage that appears to culminate in almost a catastrophic phase separation at the 60:40 PVC:PBMA composition which gets apparent from the scanning electron micrographs.

The gradual increase in modulus and UTS values of semi-2 IPNs can be attributed to the rigidity and stiffness of the crosslinked chains of PBMA molecules. The dispersed PBMA domains exert their modifying influences over the entire range of PVC matrix (as can be observed from the optical micrographs and this appears to outweigh even the inter-chain attraction imposed by ordinary dipole-dipole interaction of the uncrosslinked PVC phase).

The percent elongation at break and toughness of the semi-1 and semi-2 IPN systems are shown in Figures 3 and 4. The semi-1 IPNs, however, display a general decrease in these two parameters after an initial increase up to a level of 10% PBMA incorporation. In this system, as the continuous PVC matrix itself is crosslinked, the flexibility imparted by the disruption of the polar PVC chains due to the incor-

### Elongation at break vs composition

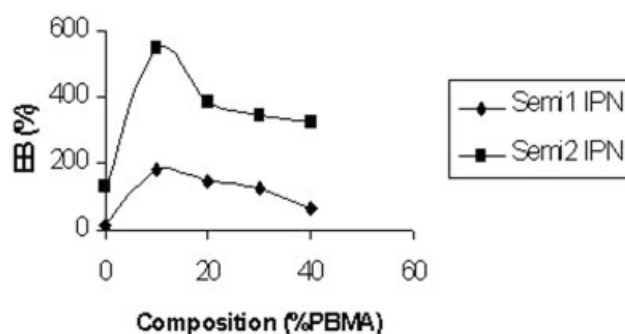


Figure 3 Variation of percent elongation at break with IPN composition.

poration of linear PBMA molecules, is somewhat restricted. The dispersed linear PBMA domains inhibit the complete crosslinking of PVC and furthermore allow chain slippage across the interfaces of the respective phases. The disruption of the regular chain structure of PVC, the distribution of somewhat flexible PBMA domains into the major matrix and the consequent long flexible crosslinks formed within the system all contribute together to the increase in initial percent elongation at break.

The variation of toughness with composition reinforces our earlier observation on the changes in EB% with composition. The toughness of the semi-1 IPNs exhibits somewhat abnormal behavior beyond 10% of linear PBMA incorporation, as a slow decrease with increasing PBMA concentration is observed although there is a steady decrease in modulus in this range. The initial rise in toughness (up to the level of 10–12% of PBMA incorporation) may be attributed to:

1. The heterogeneity brought about by the incorporated linear PBMA molecules which in turn cause a rupture in the regular chain structure of

### Toughness vs composition

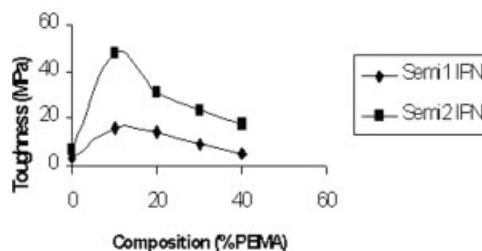


Figure 4 Variation of toughness with IPN composition.

PVC which can be expected to develop an inherent stiffness because of the dipole–dipole interaction and the formation of crosslinks by DAP.

2. The crosslinker although forms a covalent bond between two neighboring PVC chains imparts some plasticizing effect by virtue of its bulky and spacious configuration which allows the chains to undergo a limited deformation (reversible in nature) and leads to some flexibilization.

The reduction in toughness at the later stages may be ascribed to the following:

1. The appreciable difference in solubility parameters of the two participating polymers causes a steady and increasing phase separation with increasing concentration of PBMA.
2. The effectiveness of PBMA in influencing the flexibility of the semi-IPN is reduced somewhat as it gets entrapped within the crosslinks of PVC and does not contribute to chain slippage.

In contrast to the observation with the semi-1 IPN system, the semi-2 IPNs exhibit an initial sharp increase in elongation at break and toughness values followed by a gradual and steady decrease. The effect of crosslinking of the PVC chains being absent in this case, the influence of the crosslinked PBMA domains in occupying the interspaces of PVC chains and imparting flexibility appears to be pronounced. The increased ductility of the semi-2 IPNs over the semi-1 IPNs is evidenced from the scanning electron micrographs where we can find the PBMA microfibrils to pervade throughout the sample. Contrast to the semi-1 IPNs where the fibrils appear to be somewhat broken, kinked, and having lower aspect ratio (because of increased diameter), the semi-2 IPNs possess fibrils with higher aspect ratio having a much higher continuity. This enables a better chain

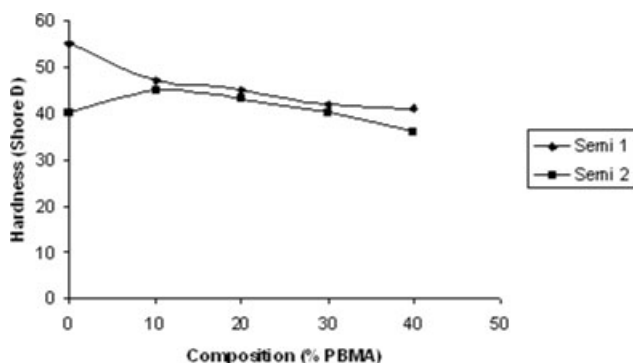


Figure 5 Variation of hardness with IPN composition.

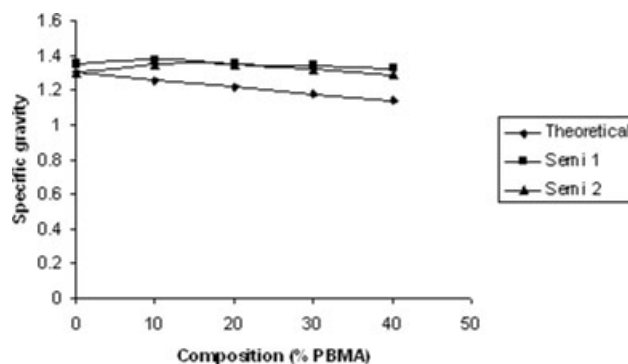


Figure 6 Variation of specific gravity with IPN composition.

slippage and hence increased percentage elongation at break and toughness at the initial stages.

## Physical properties

### Hardness

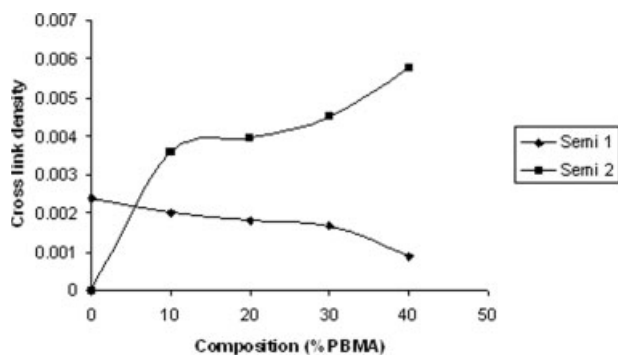
The gradual and steady decrease of hardness with increasing proportion of PBMA of the semi IPN systems as depicted in Figure 5 are in conformity with the other mechanical parameters like modulus, UTS, etc. The semi-1 IPNs with PVC crosslinked appears to be relatively harder than the semi-2 IPNs. In semi-1 IPNs, the rigidity due to dipole–dipole interaction and the deliberately introduced crosslinks offers hardness superior to semi-2 IPNs. The relatively soft PBMA domains whether it is in linear form or cross-linked state appears to make marginal differences in hardness in semi-1 and semi-2 IPNs, respectively.

### Specific gravity

The experimentally observed specific gravity curves as exhibited in Figure 6 show a rise above the theoretically predicted values for both the semi-1 and semi-2 IPNs which is definitely a positive pointer towards interpenetration.<sup>14</sup> In case of semi-1 IPNs, the formation of long flexible crosslinks between the PVC chains and the threading of the bulky PBMA moieties within these long crosslinks renders it more compact and hence increase in the specific gravities. In case of semi-2 IPNs, the increase in the concentration of crosslinked bulky PBMA moieties into the linear matrix, as also the enhanced scope of interwinding with the linear PVC molecules helps to develop higher specific gravities.

### Crosslink density

It is well known that the higher  $M_c$  (i.e average molecular weight of the polymer segments between two



**Figure 7** Variation of crosslink density with IPN composition.

successive crosslinks) is for a system, the lower is the crosslink density. In this study, with an increase in the PBMA 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.

In case of semi-1 IPNs (Fig. 7) a probability of an increase in the interchain distances of the PVC chain molecules due to the inclusion of more and more linear PBMA phase may be attributed to (i) decreasing proportion of PVC and (ii) the statistically distributed long chain crosslinks of DAP not favoring the formation 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 PBMA phase enables the linear PVC chains to come closer in comparison to the semi-1 ones and increases the probability of formation of physical crosslinking through dipole–dipole interaction amongst the neighboring PVC chains and 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 ultimate tensile strength 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 ultimate tensile strength in case of semi-2 IPNs bears a direct correlation with the increasing crosslink density with increasing PBMA content.

## Thermal properties

### Thermomechanical analysis

The thermomechanical curves of the two IPN systems are depicted in Figure 8(a,b). In all the cases, the probe is slightly pushed up by the expansion of the samples up to a temperature around 50°C. The onset of softening is followed by the penetration of

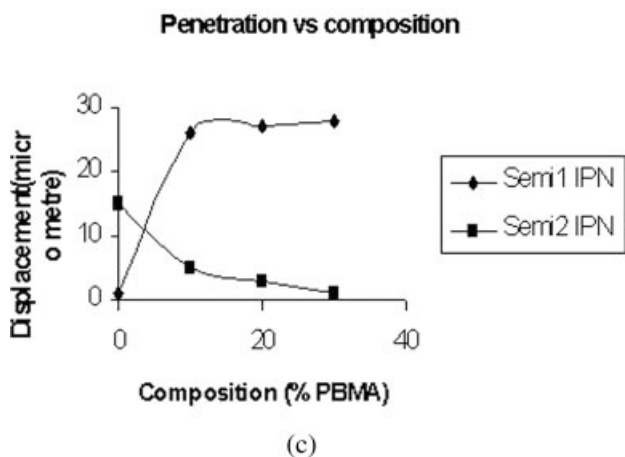
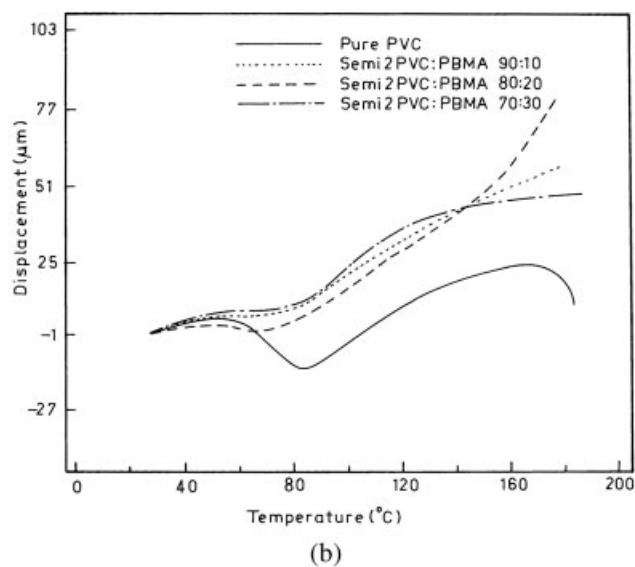
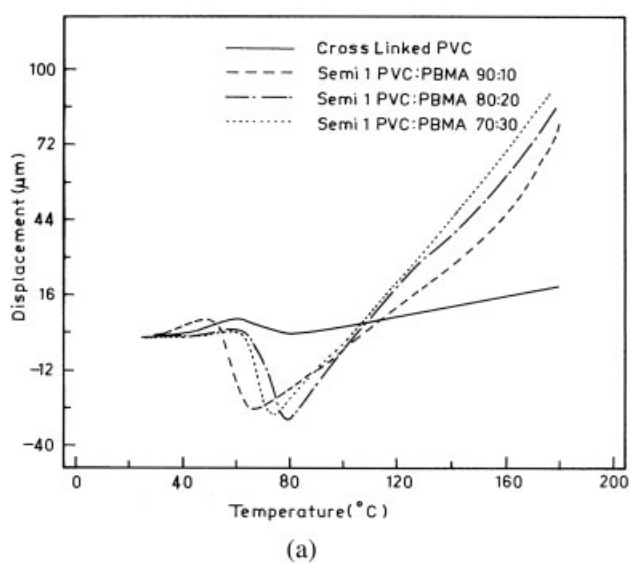
the probe into the samples at a rate inversely related to their moduli.<sup>11</sup> The extent of penetration versus composition as shown in Figure 8(c) reveals that in case of semi-1 IPNs, at the initial stages of PBMA incorporation, the lowering of rigidity due to breakdown in the regular chain structure of PVC has led to softness which in effect causes some plasticization. This softness has further been augmented by the entrapment of methacrylate molecules within the already soft PVC matrix whereas at the later stages, the slow and gradual association of the phase separated PBMA particles probably accounts for the slow and steady increase in penetration of the probe and thus offering little extent of plasticization within the range of PBMA incorporation studied.

The extent of penetration in case of semi-2 IPNs where the matrix PVC is linear however displays somewhat reverse behavior. The effect of crosslinking of the minor constituent PBMA in case of semi-2 IPNs, however, appears to be more predominating in influencing the resistance towards penetration within the linear PVC matrix. The increased crosslink frequency with increasing proportion of incorporated PBMA accounts for the decreased penetration of the probe into the samples as observed.

The higher softening temperature range with increasing proportion of PBMA in case of semi-1 IPN in composition accounts for increased thermal stability of the PVC matrix.<sup>15</sup> The chloride radicals Cl if produced by the degradation of PVC causes the PBMA chains to break and subsequently unzip quite readily at low temperatures. The unzipped monomer is also considered to be a very good radical scavenger, and thus scavenges the chloride radicals immediately as they are formed in the system. The PBMA molecules thus exert a stabilizing action by not allowing the PVC chains to undergo autocatalytic degradation by removing the Cl radicals from the system.<sup>16</sup>

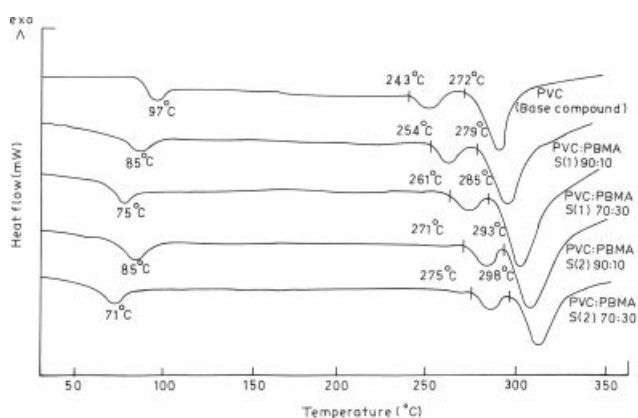
### Differential scanning calorimetry

The DSC curves of two representative samples of different composition of both semi-1 and semi-2 IPN systems vis-à-vis that of pure PVC are shown in Figure 9. Both the IPN varieties indicate the increasing trend of plasticisation of the PVC matrix irrespective of whether it is crosslinked (as in semi 1 IPN) or linear (semi 2 IPN) as the proportion of PBMA increases from 10 parts to 30 parts, which is quite apparent from the inward shifting of their glass transition temperatures w.r.t the  $T_g$  of PVC resin. The influence of crosslinking of either of the networks on the glass transition behavior of the corresponding systems appears to be very much limited as their  $T_g$ s lie within very close ranges. The reduction in span width over which the transition occurs is indic-



**Figure 8** (a) TMA plots for semi-1 IPN systems. (b) TMA plots for semi-2 IPN systems. (c) Variation of penetration with composition.

ative of the possible diminution in phase mixing in case of composition with higher percentages of PBMA irrespective of whether the dispersed phases are crosslinked or not.



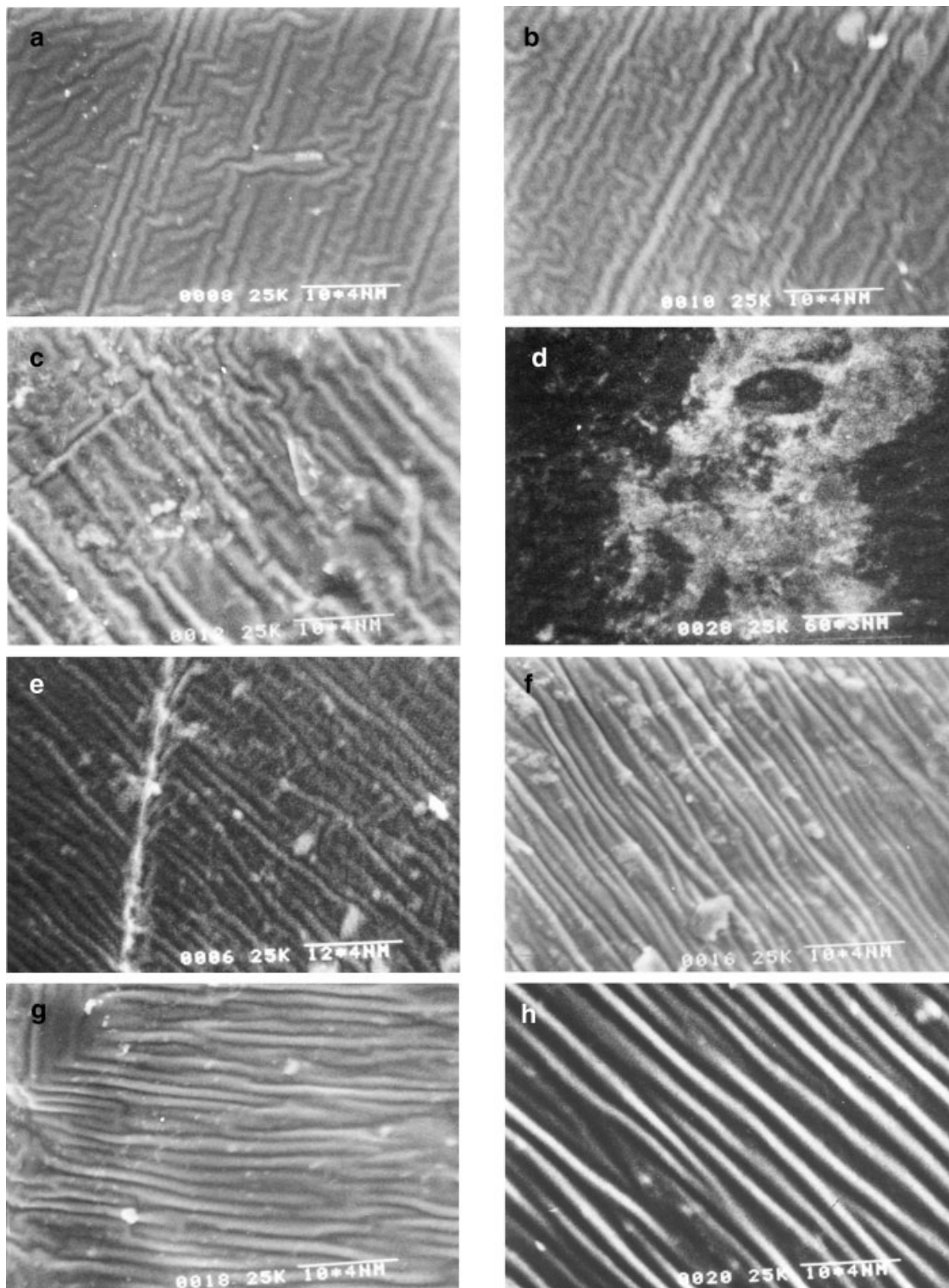
**Figure 9** DSC plots for semi-1 and semi-2 IPN systems.

At the higher temperature region, the sharp endotherms clearly indicate the two stage degradation transitions and it has been observed that the degradation temperature of the IPNs are to some extent higher than that of the unmodified PVC resin matrix. This is clearly an indication of the relative stabilization imparted by introduction of the polyalkylmethacrylate phase domains within PVC attributable by the scavenging of chloride radicals by PBMA molecules thus preventing it to form HCl and proceed the breakdown reaction further.<sup>17</sup> This again increases with increase in the PMA content. The modified PVC matrix thus achieves stabilization.

## Morphology

### Scanning electron microscopy

The scanning electron micrographs as depicted in Figure 10 indicate some phase miscibility at the ini-

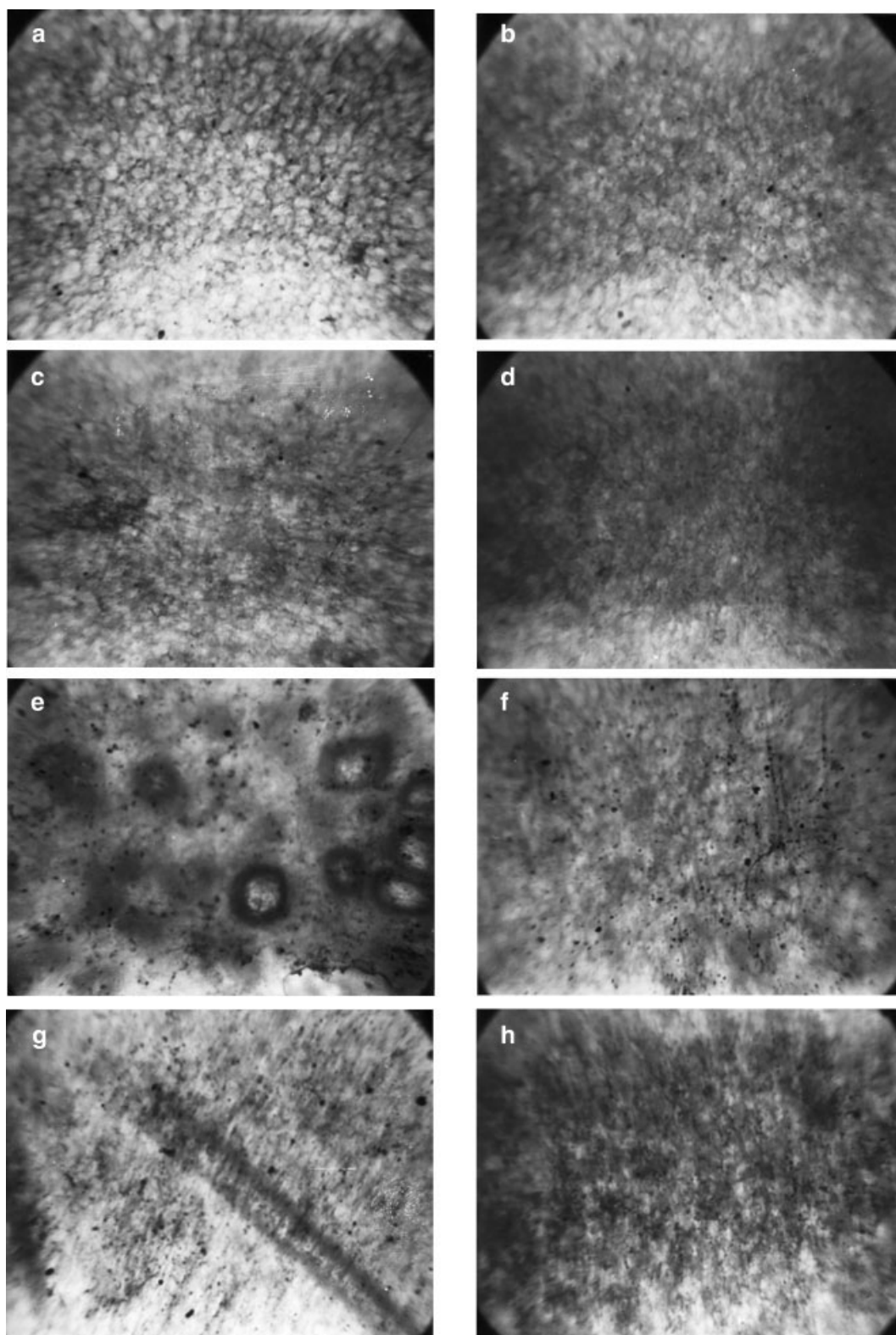


**Figure 10** Scanning electron micrographs of semi-1 and semi-2 IPN systems. (a) Semi-1 PVC:PBMA 90 : 10. (b) Semi-1 PVC:PBMA 80 : 20. (c) Semi-1 PVC:PBMA 70 : 30. (d) Semi-1 PVC:PBMA 60 : 40. (e) Semi-2 PVC:PBMA 90 : 10. (f) Semi-2 PVC:PBMA 80 : 20. (g) Semi-2 PVC:PBMA 70 : 30. (h) Semi-2 PVC:PBMA 60 : 40.

tial stages of semi-1 and semi-2 IPN formation. The fibrillar disposition of the linear PBMA molecules within the crosslinked network of PVC gets interrupted and exhibit a tendency to form kinked micro-

fibrils within the statistically distributed crosslinks of PVC. In case of semi-2 IPNs, the PBMA fibrils do not show such kinked structures or behavior and thus they are capable of being oriented or stretched





**Figure 11** Optical micrographs of the IPN systems. (a) Semi-1 PVC:PBMA 90 : 10. (b) Semi-1 PVC:PBMA 80 : 20. (c) Semi-1 PVC:PBMA 70 : 30. (d) Semi-1 PVC:PBMA 60 : 40. (e) Semi-2 PVC:PBMA 90 : 10. (f) Semi-2 PVC:PBMA 80 : 20. (g) Semi-2 PVC:PBMA 70 : 30. (h) Semi-2 PVC:PBMA 60 : 40.

in a more linear manner. However, a more or less extent of regularity in the chain structure is observed in both cases of semi-1 and semi-2 IPNs. With the

increase in proportion of PBMA in case of semi-1 IPNs, the fibrils are not only thickened and condensed but exhibit a tendency to be thrown out of

the system which is almost complete in the case of 60:40 PVC:PBMA semi-1 IPN system.

In case of semi-2 IPNs, the PBMA fibrils getting thickened with increasing proportion of PBMA although are phase separated at higher level of PBMA incorporation, they still exhibit a regular chain structure which is characterized by sharp boundaries.

#### Optical microscopy

Most IPNs exhibit a greater or lesser degree of phase separation. Polymerization and crosslinking lead to a reduction in entropy of mixing and tend to induce phase separation. The phase morphology is affected by the miscibility of the polymeric components, composition, crosslink density, and polymerization sequence.<sup>18</sup>

The figures of optical microscopy (Fig. 11) reveal heterogeneity between the dispersed and the continuous phases with the dispersed PBMA domains being entrapped in the crosslinked network of PVC. Both the types of IPNs display phase mixing at the initial stages of PBMA incorporation followed by the tendency to phase out at higher concentration. The inclination towards agglomeration in case of semi-1 IPN can be accounted from the incompatibility between the crosslinked PVC matrix with the linear PBMA domains which enhances with the increasing content of the latter.<sup>19,20</sup>

On scrutinizing closely, it can be inferred that the phase domains of PBMA in case of semi-2 IPNs are somewhat more regular in nature (showing a tendency to be spherical to elliptical shapes). This can possibly be attributed to the crosslinking of PBMA which makes it much tighter and enabling it to assume a much more defined shape. However, the extent of phase mixing in case of both the systems at the later stages may be attributed to (1) the cocontinuous formation of matrices (2) the greater number of PBMA particles generated at higher concentration intend to undergo coalescence and agglomeration.

#### CONCLUSION

From the systems under consideration, it can be noted that the two semi IPNs of PVC-PBMA display

mechanical behavior which are in contrast to each other as more and more PBMA moieties are incorporated within the system. The crosslinked methacrylate domains present in semi-2 IPNs reinforce the PVC matrix while the same is being found to be toughened by the presence of long chain crosslinks of DAP within the PVC matrix in case of semi-1 IPNs. The thermomechanical data, irrespective of the nature of the IPNs exhibit an increase in thermal stability although differing marginally among them. This is again reflected from the DSC studies particularly at the higher temperatures where the onset of degradation commences. Thus, in this attempt, thermally stable tougher IPNs compared to base reference compound PVC have been estimated.

#### References

1. Nishiyama, Y.; Sperling, L. H. *J Appl Polym Sci* 1986, 32, 6227.
2. Slusznzy, A.; Silverstein, M. S.; Kababya, S.; Schmidt, A.; Narkis, M. *J Appl Polym Sci Part A: Polym Chem* 2001, 39, 8.
3. Sanchez, M. S.; Ferrer, G. G.; Cabanilles, C. T.; Duenas, J. M. M.; Pradas, M. M.; Ribelles, J. L. G. *Polymer* 2001, 42, 10071.
4. Rey, L.; Duchet, J.; Galy, J.; Sautereau, H.; Vouagner, D.; Carrion, L. *Polymer* 2002, 43, 4375.
5. Mathew, A.; Deb, P. C. *J Appl Polym Sci* 1992, 45, 2145.
6. Sperling, L. H. *J Polym Sci: Macromol Rev* 1977, 12, 141.
7. Yeo, J. K.; Sperling, L. H.; Thomas, D. A. *Polymer* 1983, 24, 307.
8. Howston, D. J.; Zian, Y. *J Appl Polym Sci* 1984, 29, 2963.
9. Kelnar, I.; Schatz, M. *J Appl Polym Sci* 1993, 48, 669.
10. Hjertberg, T.; Dahl, R. *J Appl Polym Sci* 1991, 42, 107.
11. Chakrabarti, R.; Das, M.; Chakraborty, D. *J Appl Polym Sci* 2004, 93, 2721.
12. Flory, P. J.; Rehner, J. *J Chem Phys* 1943, 11, 521.
13. Bristow, G. H.; Watson, W. *Trans Faraday Soc* 1958, 54, 1731.
14. Blaga, A.; Feldman, D. *J Appl Polym Sci* 1996, 59, 1803.
15. Santamaria, E.; Edge, M.; Allen, N. S.; Harvey, H. B.; Mellor, M.; Orchison, J. *J Appl Polym Sci* 2004, 93, 2731.
16. Mcneill, I. C. In *Developments in Polymer Degradation-1*; Grassie, N., Ed.; Applied Science Publishers: Essex, UK, 1977; Chapter 6, p 236.
17. Mcneill, I. C.; Nell, D. *Eur Polym J* 1970, 6, 569.
18. Goswami, S.; Bandopadhyay, D.; Mandal, P. K.; Chakraborty, D. *J Appl Polym Sci* 2003, 89, 2764.
19. Yang, Y.; Fujiwara, H.; Chiba, T.; Inoue, T. *Polymer* 1998, 39, 2745.
20. Kim, S.; Chiba, T.; Inoue, T. *Polymer* 1993, 34, 2809.