

# Synthesis and Characterization of Sequential Interpenetrating Polymer Networks of Novolac Resin and Poly(ethyl acrylate)

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**ABSTRACT:** Interpenetrating polymer networks (IPN) of Novolac/poly(ethyl acrylate) have been prepared via *in situ* sequential technique of IPN formation. Both full and semi IPNs were characterized with respect to their mechanical properties that is, ultimate tensile strength (UTS), percentage elongation at break, modulus, and toughness. Physical properties of these were evaluated in terms of hardness, specific gravity, and crosslink density. Thermal behavior was studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The morphological features were observed by an optical microscope. There was a gradual decrease in modulus and UTS, with consequent increases in elongation at break and toughness for both types of IPNs with increasing proportions of PEA. An inward shift and lowering (with respect to pure phenolic resin) of the glass transition temperatures of the IPNs with increasing proportions of PEA were observed, thus, indicating

a plasticizing influence of PEA on the rigid, brittle, and hard matrix of crosslinked phenolic resin. The TGA thermograms exhibit two-step degradation patterns. An apparent increase in thermal stability at the initial stages, particularly, at lower temperature regions, was followed by a substantial decrease in thermal stability at the higher temperature region under study. As expected, a gradual decrease in specific gravity and hardness values was observed with increase in PEA incorporation in the IPNs. A steady decrease in crosslink densities with increase in PEA incorporation was quite evident. The surface morphology as revealed by optical microscope clearly indicates two-phase structures in all the full and semi IPNs, irrespective of acrylic content. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 2857–2867, 2006

**Key words:** compatibility; interpenetrating polymer networks; differential scanning calorimetry

## INTRODUCTION

Interpenetrating polymer networks are relatively novel types of polymer alloys consisting of two or more crosslinked polymers held together by permanent entanglements with only accidental covalent bonds between themselves, *i.e.*, they are polymeric catenanes.<sup>1–13</sup> Formation of IPNs is the only way of intimately combining crosslinked polymers. The resulting mixture exhibits only limited phase separation as the forming polymer chains are subjected to diffusion through an increasingly viscous medium to form phase domains because of permanent interlocking of entangled chains through crosslinking.<sup>14</sup>

Swelling a polymer network of component A in the monomer of component B and then polymerizing the second one forms a sequential interpenetrating network.<sup>15</sup> The phase morphology of IPNs is particularly complicated and has been subject to many studies.<sup>16–21</sup> Phase separation in IPNs depends primarily

on: (i) the miscibility of the constituent polymers, (ii) the crosslink density in both polymer networks and internetwork grafting, (iii) the reaction conditions (temperature, pressure) and reaction mixture viscosity, and (iv) the relative reaction rates of network formation.<sup>18,19</sup>

Despite the extensive technological relevance of IPNs, the characterization of the material in the bulk state is mainly restricted to thermal and mechanical properties.<sup>22,23</sup> IPNs can offer a wide spectrum of properties ranging from toughened elastomers to high impact plastics by judicious selection of the constituent polymers.

Phenol–formaldehyde resin is basically a hard, brittle, and rigid thermosetting polymer. Various toughening agents are incorporated into phenolics to reduce their brittleness.<sup>24–27</sup> In the present study, toughening of novolac resin was accomplished by the formation of interpenetrating networks with poly(ethyl acrylate). Both semi (only novolac was crosslinked) and full IPNs (where both PEA and the matrix resin were crosslinked) were prepared. The rubbery nature of the polyacrylate is expected to be responsible for the effective dissipation of the applied load, thereby, increasing the toughness without much decrease in elastic modulus.

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## EXPERIMENTAL

### Materials

Novolac, the precursor of the crosslinked phenolic resin mixed with 10% (of the Novolac resin weight) of hexamethylene tetramine (HEXA), was procured from Hindustan Adhesives (Kolkata, India) and used without further modification. Ethyl acrylate (EA) (FLUKA, Germany) was purified by washing first with a 2% aqueous sodium hydroxide (NaOH) solution and then by thorough and repeated washings with distilled water (to make alkali free, as tested by litmus paper) and dried over fused calcium chloride ( $\text{CaCl}_2$ ), after which it was finally vacuum distilled. Benzoyl peroxide ( $\text{Bz}_2\text{O}_2$ ) from B.D.H., India, was purified by repeated crystallization from chloroform. 2-Ethyl-2-(hydroxymethyl)-1,3-propanediol trimethacrylate (Aldrich Chemical, Milwaukee, WI), without any modification, was used as comonomer and crosslinker for PEA.

### IPN synthesis

A weighed amount of purified ethyl acrylate monomer was placed in a test tube and thoroughly mixed with 2% by weight (based on the monomer) of recrystallized  $\text{Bz}_2\text{O}_2$ . The Novolac resin (premixed with HEXA in the proportion required for its complete curing) was weighed in a glass jar to maintain a suitable ratio with the acrylic monomer as weighed earlier. The contents of the test tube were then poured into the jar and mixed thoroughly and uniformly until the mixture turned almost to a paste. With an increase in acrylic monomer content, the consistency of the paste, however, became diluted. The resulting mass was allowed to mature for about 2 h. The paste was then transferred into a positive type compression sheet mold, which was preheated to  $80^\circ\text{C}$ . The mold was then closed and placed on the lower platen of the hydraulic press. The press was then closed with a mild pressure to keep the mold airtight and to ensure that no air was entrapped into the sheet. This condition was maintained for 30 min to allow the acrylic polymerization to initiate and propagate to a certain extent. Once the stipulated time period for the acrylic polymerization was over, the temperature of the mold was increased to  $150^\circ\text{C}$ , with simultaneous increase in pressure to about  $5 \text{ tons}/\text{cm}^2$ , and the mold was kept under such conditions for 30 min to ensure complete crosslinking of the phenolic resin and complete polymerization of acrylic as well. The mold was then removed from the press in hot condition and opened cautiously so that there was no distortion and warpage of the sheet. Samples for testing were cut from the sheet after maturing for 7 days. In the case of full IPNs, the comonomer crosslinker was added (2% w/w with respect to the acrylic monomer taken) before the ad-

dition of Novolac resin. All other steps remained unaltered.

### Measurements

#### Mechanical properties

*Stress-strain behavior.* An Instron Universal Testing Machine (Model 4204) was used for measuring the tensile properties like ultimate tensile strength (UTS), percent elongation at break (% E.B.), modulus, and toughness. ASTM D 638 method was followed. A crosshead speed of 5 mm/min was maintained. All the testing was conducted under ambient conditions, in an environmentally controlled room. Toughness of the IPN samples was determined from the area under load versus elongation plots. The samples were visually inspected before measurements and were found to be free from pores or nicks. The data reported are averages of at least six measurements.

*Hardness.* Shore D hardness values of various IPNs were evaluated according to the ASTM specification, in humidity controlled room at  $30^\circ\text{C}$ .

#### Physical properties

*Specific gravity.* Specific gravity was determined by following the Archimedes' principle.

*Gel time.* Gel points of pure novolac resins and its various blends with PBA were determined as per ASTM D 2471.

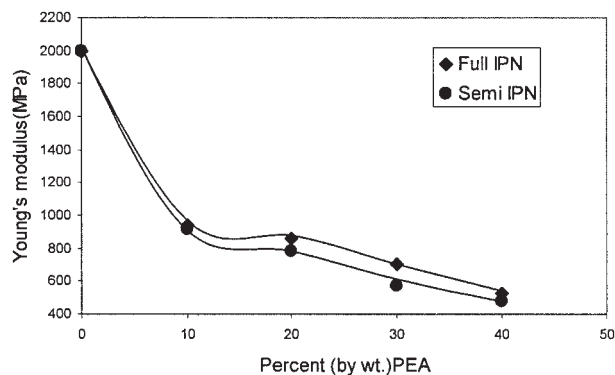
About 8–10 g of the sample was taken in a small aluminum pan. The empty pan was kept in a thermostatic bath maintained at a constant temperature of  $(150 \pm 5)^\circ\text{C}$ . Once the samples attained the temperature of the bath, the stop-watch was started and a wooden probe was brought in contact with the sample surface to check whether any powdery sample sticks to the probe or it gets any resistance to penetration into the sample. The time is noted when no sample adheres to the probe or it cannot penetrate into the sample.

*Crosslink density.* This was determined for various IPN samples by following the classical Flory–Rehner method,<sup>28,29</sup> as follows:

$$\gamma = \frac{V_p + \chi V_p^2 + \ln(1 - V_p)}{V_s d_r (V_p^{1/3} - V_p/2)} \quad (1)$$

Where,  $\gamma$ , crosslink density ( $=M_c^{-1}$ );  $V_p$ , volume fraction of polymer in the swollen mass;  $V_s$ , molar volume of the solvent;  $d_r$ , density of the polymer;  $c$ , polymer solvent interaction parameter.

For each sample, equilibrium swelling was carried out using acetone as the solvent, at a temperature of  $27^\circ\text{C}$



**Figure 1** Variation of Young's modulus of novolac-PEA semi and full IPNs with variation of novolac-PEA blend ratios (w/w).

Equilibrium swelling was done at 27°C using nine different liquids ranging in their solubility parameter from 14.1 (cal/cc)<sup>1/2</sup> to 25.2 (cal/cc)<sup>1/2</sup>. Molded specimens of the IPNs of different compositions, cut in small pieces, were weighed in dry state and then were dipped in different liquids, e.g., acetone, aniline, benzene, benzaldehyde, chloroform, diethylene glycol, ethylene diamine, and *n*-hexane etc. The increase in weight of each of these samples due to swelling by the different liquids were noted in regular intervals of time till the equilibrium swelling was reached.

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

$$Q = (m - m_0) / m_0 \times d_r / d_s \quad (2)$$

Where  $m$ , weight of the swollen sample;  $m_0$ , original weight of the sample,  $d_s$ , density of the solvent.

In the subsequent plots of  $Q$  versus  $\delta_s$  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 ( $\delta_p$ ) of the concerned blend system.

The parameter  $V_p$  was found out by using eq. (3).

$$V_p = 1 / 1 + Q \quad (3)$$

The polymer-solvent interaction parameter was then calculated from Bristow and Watson equation as given in eq. (4):

$$\chi = \beta + (V_s / RT) \times (\delta_s - \delta_p)^2 \quad (4)$$

where  $\beta$  = lattice constant = 0.34;  $R$ , universal gas constant (cal/K/mol);  $T$ , absolute temperature (K);  $\delta_s$  and  $\delta_p$  are solubility parameters (cal/cc)<sup>1/2</sup> of the solvent and the IPN sample, respectively.

## Thermal properties

**Differential scanning calorimetry.** A Du-Pont 2100 instrument was used for differential scanning calorimetry (DSC) studies. DSC scans were taken at the heating rate of 10°C/min under a continuous flow of nitrogen. **Thermogravimetric analysis.** TGA thermograms were obtained by a Perkin-Elmer Delta Series TGA7 (Thermogravimetric Analyzer) under nitrogen atmosphere at a heating rate of 20°C/min. The samples ranging between 6 and 10 g in weight were used for the TGA.

## Morphology

Phase morphology was examined by an Optical Microscope from Krüss (Optronic), Germany, and a scanning electron microscope from JEOL, Tokyo, Japan, of model number JSM-5200. Scale of magnification used in OM and SEM were 400× and 750 μm, respectively.

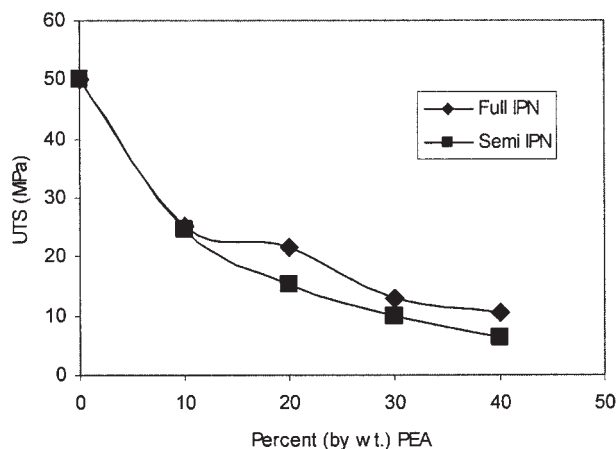
## RESULTS AND DISCUSSION

### Mechanical properties

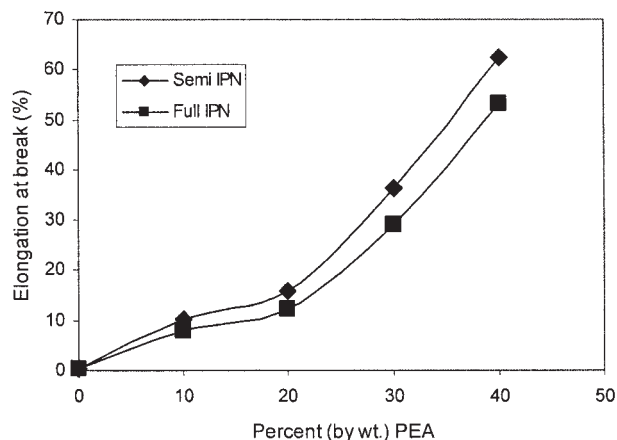
#### Stress-strain behavior

The various mechanical properties of the semi and full IPNs of the Novolac-PEA system have been compared as a function of PEA content in Figures 1–5. Figures 1 and 2 show that the moduli and UTS of different IPNs decrease with increase in PEA content in the IPNs (for both full and semi types). On the other hand, Figures 3 and 4 depict that, with increase in acrylate percentage in the IPNs, both E.B.% and toughness values increase gradually within the concentration of PEA studied; irrespective of whether it is semi or full IPN.

It is also evident from the figures that full IPNs have always higher moduli and UTS but lower E.B.% and toughness values compared with the corresponding semi IPNs. At lower ranges of PEA concentration



**Figure 2** Variation of UTS of novolac-PEA semi and full IPNs with variation of novolac-PEA blend ratios (w/w).

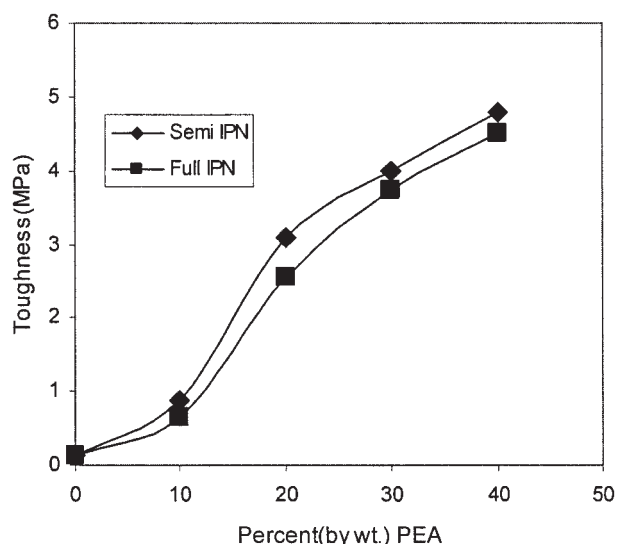


**Figure 3** Variation of %E.B. of novolac-PEA semi and full IPNs with variation of novolac-PEA blend ratios (w/w).

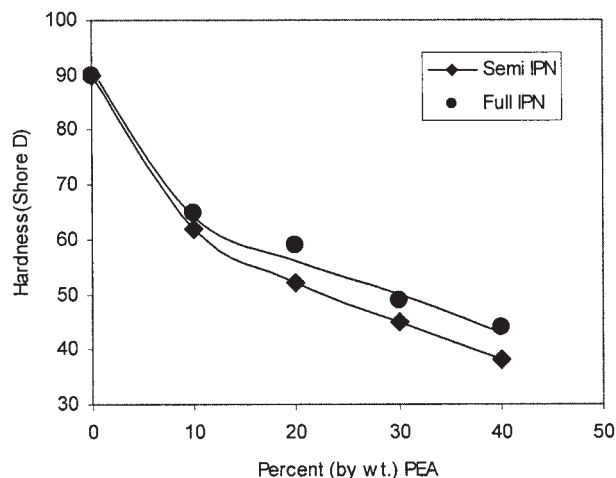
(upto 10–15%), a marked drop in moduli and UTS values for both types of IPNs has been exhibited with respect to that of pure phenolic resin. However, at higher acrylate content, a steady and gradual decrease in these parameters is demonstrated.

The difference in the values of moduli and UTS for full and semi IPNs of identical compositions at lower concentration region of PEA is not so pronounced as it is observed at the higher concentration ranges within the concentration of PEA studied.

Crosslinking of the dispersed PEA domains in full IPNs cause the strengthening of the system in comparison to the semi IPNs so far as the moduli and UTS values are concerned. The least difference in moduli and UTS values of full and semi IPNs at the lower concentration region (upto 10–15%) may be due to the following possibilities:



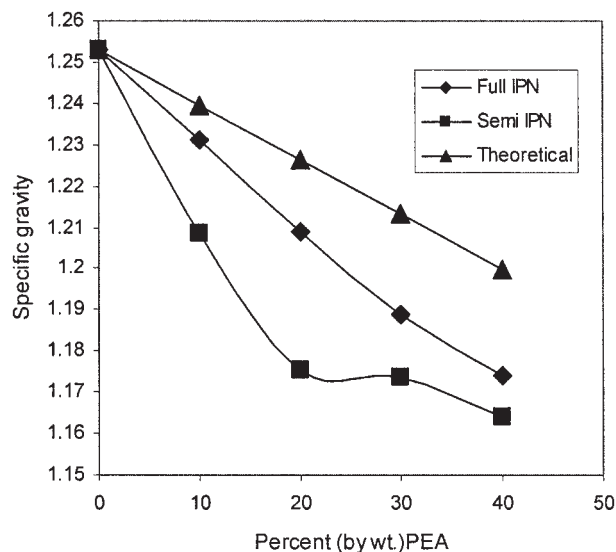
**Figure 4** Variation of toughness of novolac-PEA semi and full IPNs with variation of novolac-PEA blend ratios (w/w).



**Figure 5** Variation of hardness of novolac-PEA semi and full IPNs with variation of novolac-PEA blend ratios (w/w).

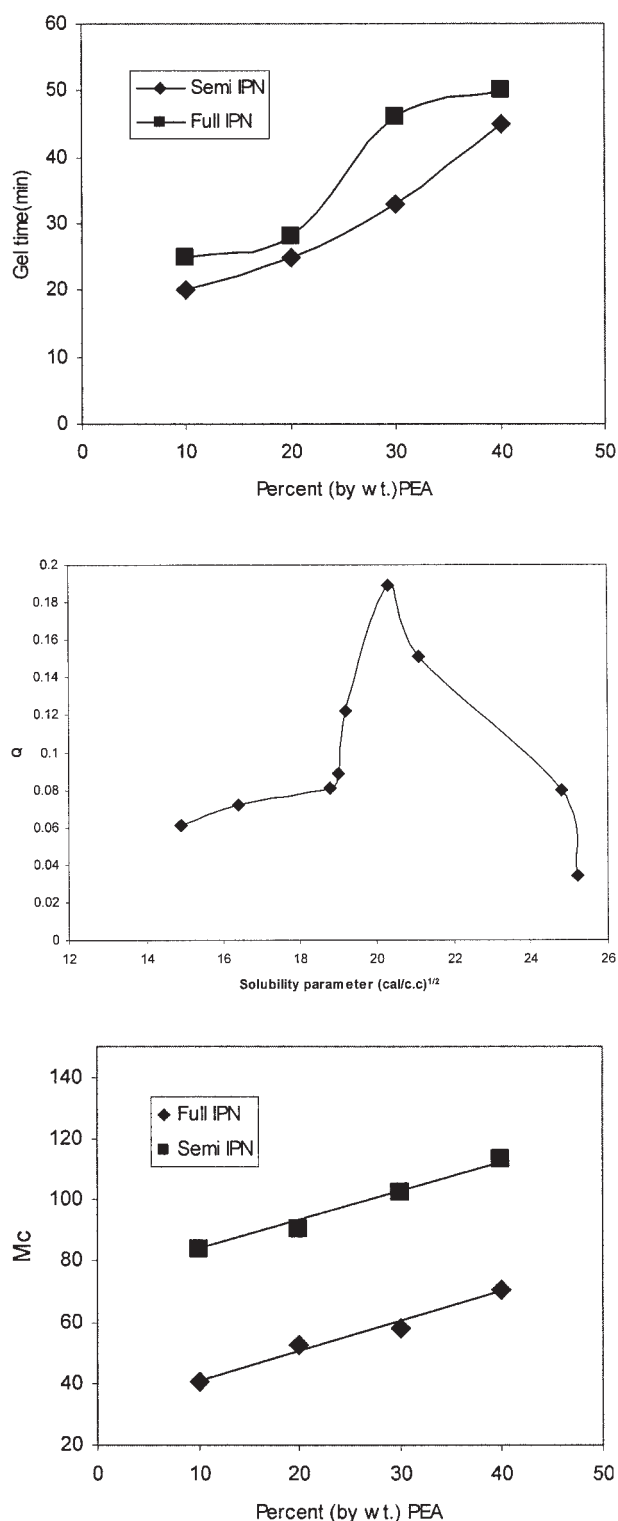
(1) The drastic reduction in the crosslink density of the novolac resin caused by the presence of the dispersed PEA phase, which might not allow the reactive sites (methylol groups) of the resin to react—a statistical probability arising out of sequential IPN formation. The influence of this reduction is far to be compensated by the crosslinks of PEA itself in case of full IPNs. (2) This might have exerted a plasticizing action upon the ultimate network system. (3) Increasing number of relatively weaker stress concentrators offered by the rubbery PEA domain and, thus, gradually decreasing the effective cross-sectional area that bears the load.<sup>29</sup>

It may also be argued that the highly extended chains of linear PEA in case of semi IPNs may lead to



**Figure 6** Variation of specific gravity of novolac-PEA semi and full IPNs with variation of novolac-PEA blend ratios (w/w).





**Figure 7** (a) Variation of gel time of novolac-PEA semi and full IPNs with variation of novolac-PEA blend ratios (w/w). (b) Variation of swelling co-efficient of novolac-PEA full IPN having novolac-PEA blend ratio of 80:20 (w/w) versus solubility parameter of solvents. (c) Variation of  $M_c$  of novolac-PEA semi and full IPNs with variation of novolac-PEA blend ratios (w/w).

coiling, resulting in an overall increase in strength of the somewhat loosely crosslinked novolac matrix. This increase in strength of the semi IPNs is, however, almost counterbalanced by the incorporation of crosslinks in PEA moieties in case of full IPNs.

The influence of crosslinking of the dispersed PEA domains on these two strength properties is quite reflected in the mechanical curves of the full IPNs as they always lie above those for the semi IPNs.

The sharp initial drop (upto an acrylic concentration of ~15%) is, however, followed by a slow and steady decrease in going from 15 to 40% of PEA incorporation. At higher concentrations of PEA, it may be expected that the relatively higher free volume of randomly coiled long chains of PEA (which are being expected to have very high molecular weight also) in a semi IPN enable it to be interpenetrated or threaded more with the subsequently formed crosslinked network of phenolic resin than what would have been possible in a corresponding full IPN, where the mobility of the chains is restricted more because of the presence of crosslinks in PEA itself. Thus, crosslinking in the dispersed phase of PEA may lead to a lowering in the degree of interpenetration in full IPNs.

It may thus be possibly inferred that the increased extent of interpenetration in case of semi-IPNs has nullified to some extent the influence of crosslinking in case of full IPNs that still predominate over the semi- ones in these aspects.

The widening gap in the curves, particularly, at higher ranges of PEA incorporation may possibly be accounted for by the fact that the crosslinked PEA offers much higher resistance compared with that of the linear PEA as present in semi-IPNs. The linear PEA phase in semi-IPNs not only offers very little resistance to deformation, but also may be expected to interrupt the complete crosslinking in the Novolac matrix by occupying the interchain spaces, and thus, preventing the necessary reactive sites to come closer for the curing reaction. Although in case of full IPN the PEA moieties are still present in the interstitial spaces, they are tighter, smaller, and possess a restricted capacity by virtue of lower mobility to inhibit the Novolac molecules getting crosslinked. This can be visualized to some extent from the corresponding micrographs.

With increase in proportion of PEA in the IPNs, both the toughness and % E. B. increased steadily. This is due to the increase in rubbery dispersed phase in the novolac network systems. As mentioned earlier, the rubbery domains undergo extension under the application of load rather than allowing any fracture to grow. Semi IPNs by virtue of having linear PEA domains are superior to full IPNs in this aspect as it elongates relatively easily and supposedly by increases in path length of fracture propagation through the interfaces between the linear PEA and crosslinked

phenolic resin. Also, the energy required for causing rupture in a semi IPN is more compared with that required for the corresponding full IPN, because more energy is to be expected to overcome a longer fracture path.<sup>30</sup>

#### Hardness

Figure 5 depicts the variation of hardness (shore D) values for different IPNs with their compositions. Hardness values for full IPNs are higher than the corresponding semi IPNs of equivalent compositions, as the chain rigidity of the polymers involved increases because of crosslinking.<sup>30</sup> As expected, both the semi and full IPNs exhibit a decreasing trend in their respective hardness values with increasing PEA concentration within the range of percentage studied. This is due to the increasing rubbery content dispersed in the crosslinked Novolac resin matrix.

#### Physical properties

##### Specific gravity

Figure 6 shows the variation of specific gravity values for both full and semi IPNs with the composition of the respective systems. It is seen that full IPNs have always higher values compared with that of the semi IPNs of identical compositions while the theoretically predicted figures (calculated on the basis of rule of additivity) are much higher than the experimentally observed ones.

The *in situ* formed rubbery poly(ethyl acrylate) molecules being expectedly of very high molecular weight possess large free volume. Therefore, the possible entrapment of such molecules in between the phenolic chains might be causing reduction in mass per unit volume for the IPNs. The observed trend in specific gravity for both semi and full IPN systems with increase in PEA content might be accounted for this. Also the large rubbery chains of PEA may not allow the novolac crosslinking to occur freely. In case of full IPNs, crosslinked, and therefore, compact PEA phase may increase the statistical probability of phenolic crosslinking and hence the higher specific gravity of the systems within the range of concentration of the acrylate studied.

##### Gelling behavior

Figure 7(a) depicts the variation of gel time for different IPNs (both semi and full types) with their compositions. Both the semi and full IPNs exhibit longer gel time compared to that of pure phenolic resin. For the semi IPNs, the gelling of phenolic resin has been delayed due to the shielding of the reactive groups on it by the PEA molecules as it is formed first in the

TABLE I  
Swelling Coefficients of Different Solvents

Solvent	Solubility parameter (cal/cc) <sup>1/2</sup>	Swelling coefficient Q
<i>n</i> -Hexane	14.9	0.0612
Diethyl amine	16.4	0.07231
Benzene	18.8	0.089
Chloroform	19	0.0808
Benzaldehyde	19.2	0.1219
Acetone	20.3	0.1892
Aniline	21.1	0.1511
Di-ethyl glycol	24.8	0.0795
Ethylene diamine	25.2	0.0338

present sequential IPN formation. The polymerization of ethyl acrylate monomers is being expected to be delayed somewhat in presence of novolac chains in the medium because of a slightly arrested mobility of the monomer molecules. As a result, the overall gel time of the semi IPNs is increased with respect to pure phenolic resin.

Again, with increase in acrylate content, the gel time has been increased. This is possibly due to the cumulative effect of two reactions with gelling characteristics opposed to each other. As the acrylate monomer concentration increases, the rate of propagation (*R<sub>p</sub>*) being directly proportional to the concentration of monomer,<sup>31-33</sup> the gel time appears to be shortened because of the auto-acceleration effect. On the contrary, the step growth polymerization technique for the crosslinking of novolac resin is itself a slow process, which is being further, delayed because of the presence of PEA moieties in between the novolac chains. This effect appears to be much more predominant as the concentration of EA increases, resulting in increased gel time even in spite of the earlier gel effect of the PEA.

The gel time for full IPNs is observed to be much more prolonged than the semi IPNs of corresponding composition. This may be due to the presence of the first formed crosslinked PEA molecules along with some fraction of the homopolymer of the comonomer-crosslinker formation.

These two together are being expected to increase the interchain separation of the novolac molecules, thereby, reducing statistical probability of phenolic crosslinking.

##### Crosslink density

The experimental procedure, as mentioned earlier, was repeated for the different IPNs (both semi and full types) separately, and the solubility parameter values for the different compositions were found out. In this study, the values of swelling coefficients of novolac-PEA full IPN of composition 80:20 (w/w) are shown

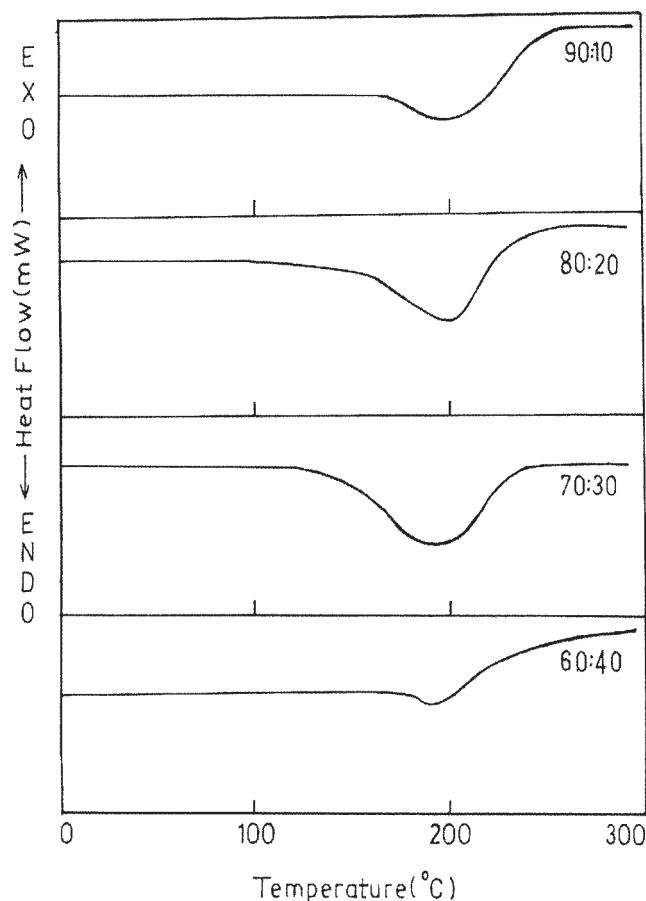


Figure 8 DSC thermograms of novolac-PEA semi IPNs.

in Table I and Figure 7(b) shows the solubility parameter ( $\delta p$ ) of the particular IPN.

The variation of  $M_c$  (i.e., average molecular weight of the polymer segments in between two successive crosslinks) values of both the full and semi IPNs with the PEA concentration in various IPN systems is shown in Figure 7(c). It is well known that higher the value of  $M_c$  for a system, lower is the crosslink density.<sup>29</sup> In the present study, it is observed that with increase in PEA content in the IPNs, there is a gradual decrease in the crosslink density.

This may possibly be attributed to the following:

There is a probability of increase in the interchain distances of the Novolac molecules because of inclusion of more and more high molecular weight rubbery PEA molecules formed in situ that may not allow the reactive sites of the novolac chains to approach each other to form the necessary bridge, the plasticizing effect (as discussed earlier).

Thus, it may be expected that with increase in PEA concentration, the availability of the reactive groups on the Novolac chains gets reduced, which causes decrease in overall crosslink density of the IPN.

Also, the full IPNs are always having higher crosslink densities than the corresponding semionics,

over entire range of PEA concentration studied. This may be accounted for the crosslinking of both the matrix resin and the dispersed domains of the elastomeric PEA molecules in case of full IPNs in comparison to the semi IPNs, where only the novolac resin is crosslinked and PEA is present as linear chains.

### Thermal properties

#### Differential scanning calorimetry

The DSC tracings of the representative samples of both the semi and full IPN systems have been shown in Figures 8 and 9, respectively. The plasticizing influence of the PEA phase formed in situ in presence of the phenolic resin precursor on the ultimately crosslinked three dimensional network of phenolic resin is quite evident from the figures. This holds true irrespective of whether the samples belong to the semi or full IPN varieties. In a manner similar to the trend of reduction in mechanical properties of the phenolic resin, the temperature at the secondary transition ( $T_g$ ) is diminished remarkably compared with that of the pure phenolic resin when only the rubbery poly(ethyl acrylate) is present, to the extent of even 10 phr. The subsequent reduction in glass transition is found to be slow and gradual. The full IPNs, as expected, demonstrate higher  $T_g$  in comparison to that exhibited by the corresponding compositions of semi IPN.

Furthermore, in case of semi IPNs, the inward shift of the glass transition point is attended by a wide and deep endotherm that progressively decreases with increasing PEA content. Thus, the enthalpy change involved in such endothermic process is found to decrease steadily and gradually with increasing proportions of PEA within the range of PEA concentration studied.

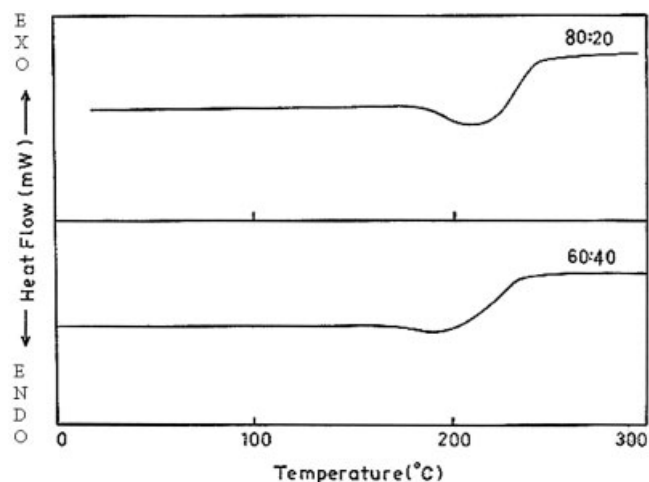


Figure 9 DSC thermograms of novolac-PEA full IPNs.

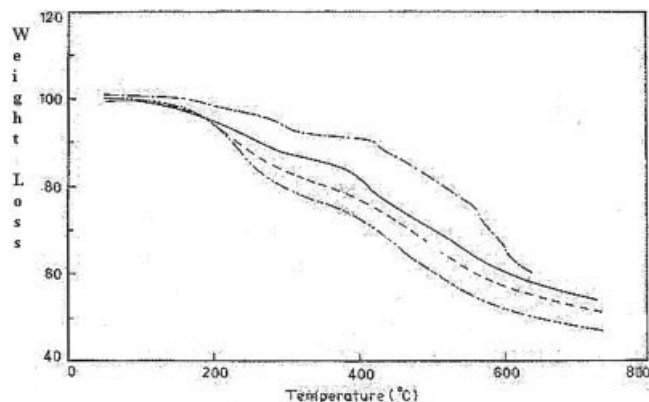


Figure 10 TGA-Thermograms of novolac-PEA semi IPNs.

The extent of phase mixing, as is evident from the width of the span over which the endothermic enthalpy change occurs, appears to develop with increase in PEA content. It might be expected that with increase in PEA content, there is a wide range of mixing of phases having different compositions of the constituents, particularly, in the IPN formation.

The phase mixing, in case of full IPNs, appears more homogeneous, i.e., the discrete particles, as shown in the micrographs, are much more uniform in their composition, such that the width of transition is very narrow.

#### Thermogravimetric analysis

TGA of both the semi and full IPN systems (Figs. 10 and 11, respectively) appear to exhibit results characteristic of pure phenolics. The onset of degradation of the different systems appears to vary with their compositions. However, semi-IPNs show lowering in onset temperature with respect to the pure phenolic resin. On the other hand, full IPNs display higher onset temperature, which clearly indicates an initial resistance to thermal degradation, particularly, in its first phase (i.e., upto a temperature of 350°C).

Although the initiation of degradation in case of full IPNs is delayed, they appear to degrade at much faster rate than that of pure phenolic resin in the subsequent stages (beyond 350°C), and the ultimate percent residue left behind is found to be far less than the pure phenolic resin within the range of temperature under study. In general, both the semi and full IPNs are thermally unstable compared with that of the pure phenolic resin.

However, the rate of degradation increases with increase in proportions of the acrylate within the range of concentrations of PEA studied. The higher stability of the full IPNs compared with that of the semionies might be attributed to the presence of crosslinks in the rubbery PEA domains.

From the low temperature study,<sup>34,35</sup> the course of degradation of a phenolic resin is found to be primarily oxidation at the bridging methylene linkages.

Upon further oxidation, it has been reported that sterically hindered phenols are oxidized to quinonoid type structure.<sup>32</sup> It is quite well known that the poly(ethyl acrylate) undergoes depolymerization through the mechanism shown in Scheme 1.<sup>36-39</sup>

Thus, it is obvious that the two polymers involved in IPN formation undergo degradation by two different noninterfering mechanisms.

However, the statistically small number of quinonoid structure (C) formed during the thermal degradation of phenolic resin within the temperature region of 230–270°C can abstract the  $\alpha$ -H atom more preferentially from the poly(ethyl acrylate) (as shown in Scheme 2).

The higher stabilization energy of the aromatic compound (D) formed in the earlier reaction with respect to the quinonoid structure favors the reaction further, which results in the degradation of the IPNs at further elevated temperature.

However, the reactions involving two macromolecules are somewhat retarded at higher concentrations of PEA beyond the temperature 350°C. Also, the stability of semi IPNs and full IPNs is merging at higher concentrations of PEA because of being highly reactive and known to be as a very good oxidizing agent that gets murkier due to the presence of the substituents, and attains stability by splitting of the labile H-atom of the depolymerized poly(ethyl acrylate) molecule. In this process, the substituted quinone is itself reduced to substituted hydroquinone structure and the depolymerized poly(ethyl acrylate) molecule attains some stability with the formation of a terminal unsaturation.

Following Le chateliers principle of chemical equilibrium, the thermal degradation of the phenolic resin goes on unabated, conferring thermal instability of the matrix resin in the IPNs compared to that in the pure phenolic resin.

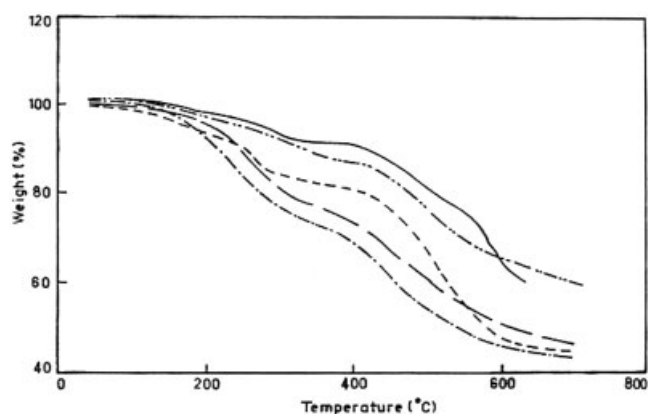
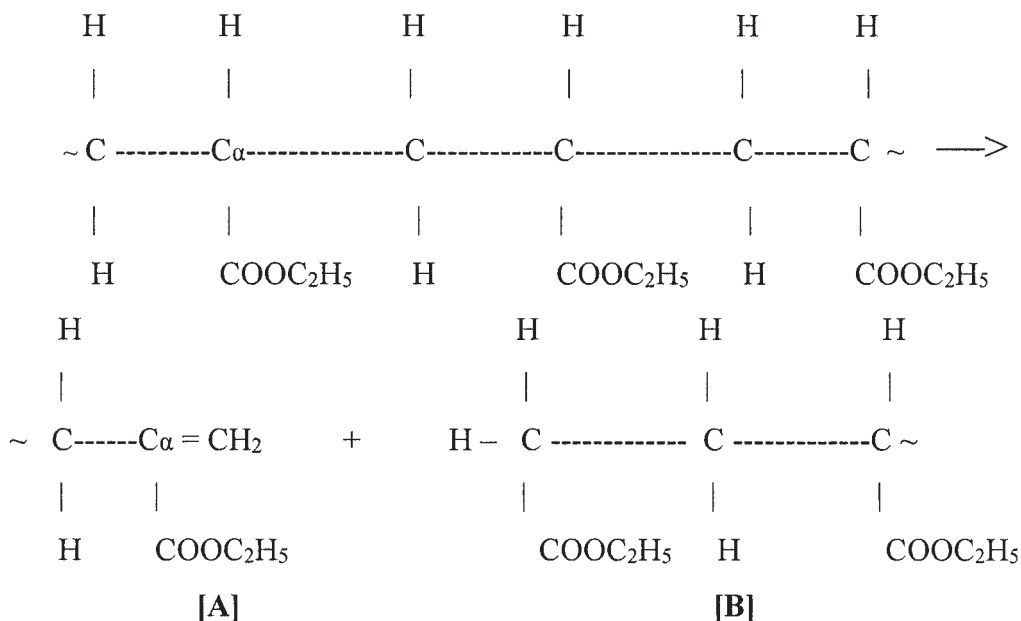


Figure 11 TGA Thermograms of novolac-PEA full IPNs.





Scheme 1

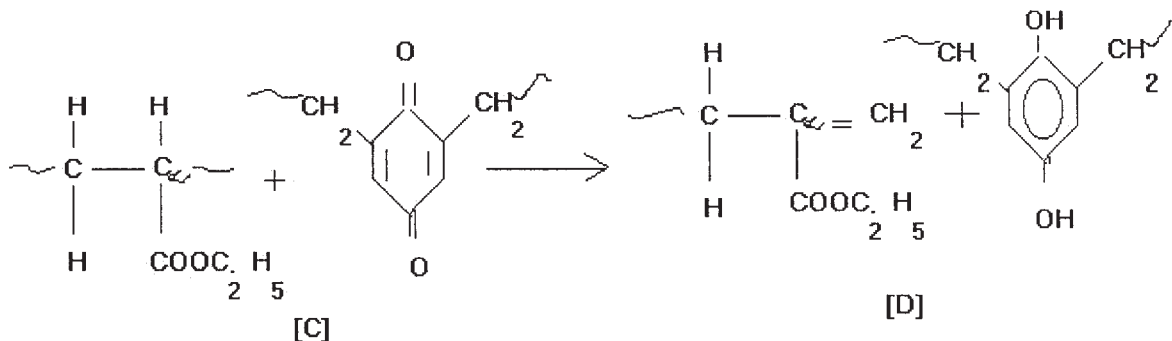
## Morphology

### Optical microscopy

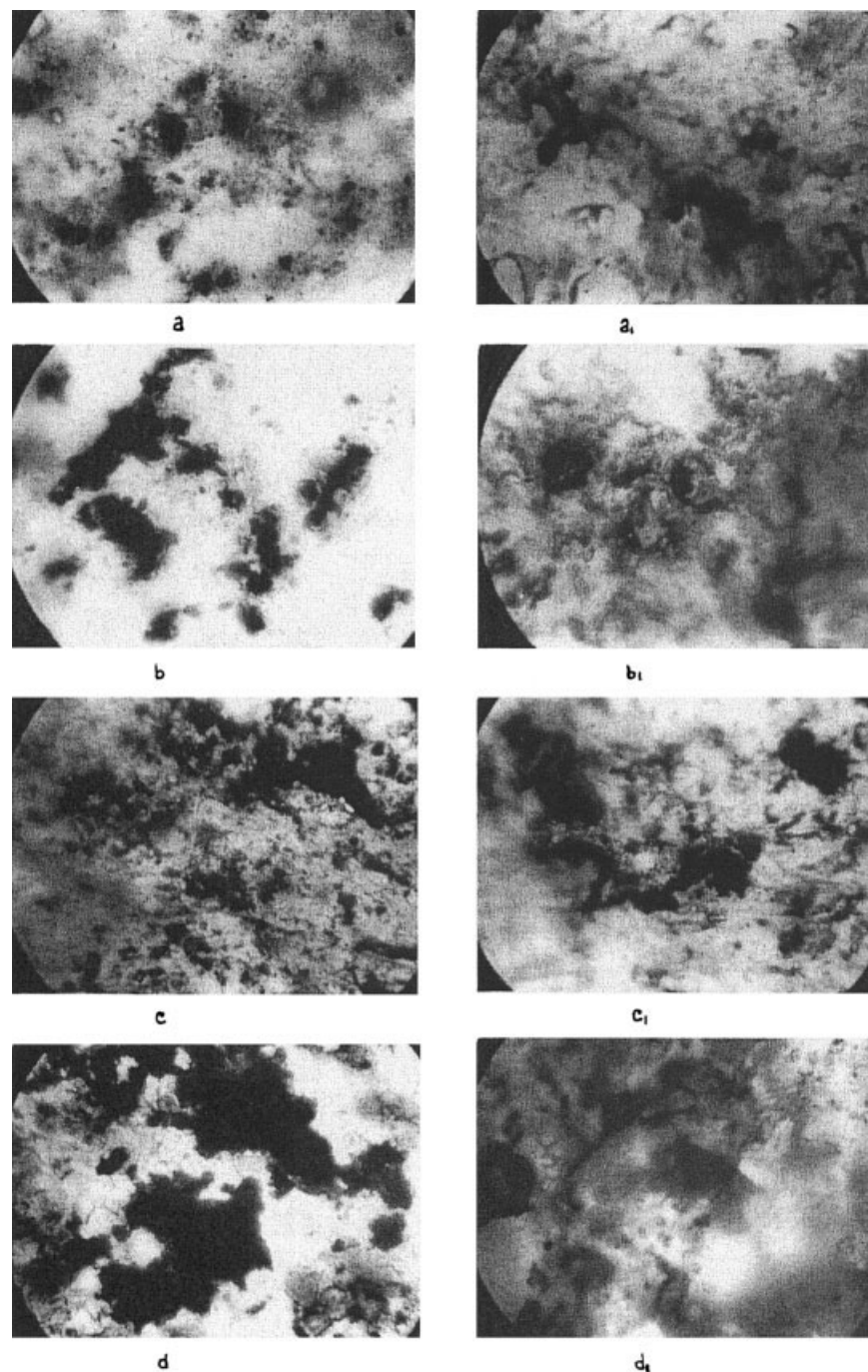
In the micrographs (Fig. 12), the bi-phasic and dual continuity of the different samples of IPN is quite apparent. The minor component in the present case (the PEA moieties) being formed first appears to have the scope of being interwound with the Novolac matrix formed later. The interesting feature of the full IPNs is that most of the domains are compact and are mostly devoid of any occluded novolac. The somewhat irregular, compressed, and elongated linear domains as is present in semi IPNs appear to be condensed by the force of shrinkage exerted by the crosslinked novolac. They are distributed in a random manner throughout the matrix and exhibit a tendency to be pulled out of the system. The statistical variation in particle size distribution

as encountered in case of semi IPNs appears to be somewhat minimized with full ones. Furthermore, the sharp and distinct contrast observed at the phase boundaries in case of semi IPNs, however, appears to be absent with full IPNs, and a diffusing interface develops indicating a better phase mixing that may possibly be attributed to the presence of crosslinker-comonomer.

In both cases, the typical cellular domain, as is normally found in IPN systems, appears to grow from the inside of the shell wall and proceeds toward the core and in most of the instances, the cells contain some entrapped novolac resin. The domain formation appears to be more and more complete at the higher level of PEA incorporation, while at the lower doses of the dispersed PEA phase, a mixture of different sizes of *in situ* formed domains pervade the novolac matrix.



Scheme 2

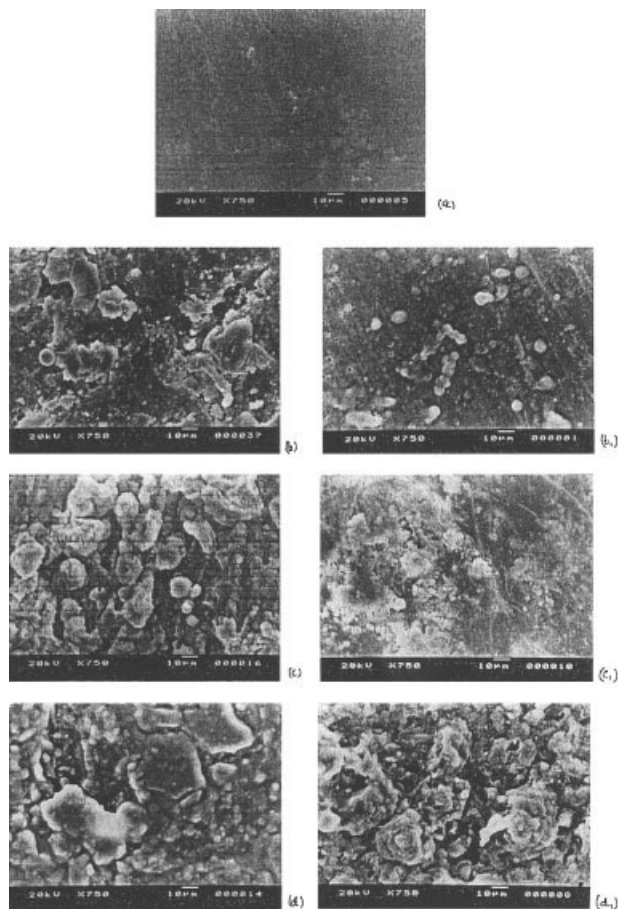


**Figure 12** Optical micrographs of novolac-PEA ( $\times 400$ ): sets of micrographs (a)/(b)/(c)/(d) refer to (90 : 10)/(80 : 20)/(70 : 30)/(60 : 40) semi IPNs and (a<sub>1</sub>)/(b<sub>1</sub>)/(c<sub>1</sub>)/(d<sub>1</sub>) refer to (90 : 10)/(80 : 20)/(70 : 30)/(60 : 40) full IPNs, respectively.

#### Scanning electron microscopy

The random distribution of the linear and crosslinked PEA domains formed in situ in the rigid matrix of phenolics is apparent in the scanning electron micrographs (Fig. 13) of the semi and full IPNs, respectively. Although the dispersed PEA phase in both the cases is mostly irregular in shape and size, those of the full IPNs appear to be somewhat compact and diffused.

Domains of PEA are found to pervade the entire matrix of phenolic although the properties of the diffused domains in case of full IPNs are seen to decrease gradually with increasing proportions of PEA. The relatively compact domains of full IPNs exhibit a tendency to coalesce together and to form linear chain structure that may help in threading or winding with the crosslinked phenolic resin to account for the



**Figure 13** Scanning electron micrographs of novolac-PEA IPNs: micrograph (a) refers to pure phenolic resin; sets of micrographs (b)/(c)/(d) refer to (90 : 10)/(80 : 20)/(70 : 30) semi IPNs and (b1)/(c1)/(d1) refer to (90 : 10)/(80 : 20)/(70 : 30) full IPNs, respectively.

higher mechanicals compared to the semi ones. However, with increase in proportions of PEA, this trend gradually decreases.

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