

Modification of Novolac Resin by Interpenetrating Network Formation with Poly(butyl acrylate)

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ABSTRACT: Interpenetrating networks (IPNs) of novolac (phenol formaldehyde) resin and poly(butyl acrylate) (PBA) were prepared by a sequential mode of polymerization. Both full IPNs and semi-IPNs of different compositions were synthesized and characterized with respect to their mechanical properties, that is, their modulus, ultimate tensile strength (UTS), elongation-at-break percentage, and toughness. Their thermal properties were examined with differential scanning calorimetry and thermogravimetric analysis (TGA). A morphological study was performed with an optical microscope. The effects of the variation of the blend ratios on the aforementioned properties were studied. There was a gradual decrease in the modulus and UTS with a simultaneous increase in the elongation-at-break percentage and toughness for both types of IPNs as the proportions of PBA were increased. With increasing proportions of PBA,

the glass-transition temperatures of the different IPNs underwent shifts toward a lower temperature region. This showed a plasticizing influence of PBA on the rigid and brittle phenolic matrix. TGA thermograms depicted the classical two-step degradation for the phenolic resin. Although there was an apparent increase in the thermal stability at the initial stage (up to 350°C), particularly at lower temperatures, a substantial decrease in the thermal stability was observed at higher temperatures under study. In all the micrographs of full IPNs and semi-IPNs, two-phase structures were observed, regardless of the PBA content. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 2407–2417, 2005

Key words: compatibility; crosslinking; interpenetrating networks (IPN); mechanical properties

INTRODUCTION

It is widely accepted that most polymer pairs are immiscible as a result of a small entropy of mixing.¹ One possibility for reducing the degree of phase separation in such circumstances is the formation of interpenetrating polymer networks.^{2,3} Swelling a polymer network of component A in a monomer of component B and then polymerizing the second network forms a sequential interpenetrating network (IPN). The ultimate properties of such IPNs can be varied to a greater extent by the suitable control of the morphologies of the concerned components. The phase morphology in sequential IPNs is affected by the miscibility of the polymer components, composition, crosslink density, polymerization sequence, kinetics of polymerization, and phase separation.^{4–6} Because of their interlocking configuration, the extent of phase separation is frozen in, so the properties are not influenced by subsequent aging.⁷ The properties are dependent on the two-phase morphology that develops during IPN formation. For IPNs, the component present in a

higher concentration and with a lower viscosity is supposed to form the continuous phase, which dictates the properties.⁸ Moreover, crosslinking either polymer I or polymer II tends to promote phase continuity. Materials with both polymers crosslinked (IPNs) tend to develop two continuous phases. Phase separation of the forming polymer chains proceeds by diffusion through an increasingly viscous medium to form phase domains. The formation of crosslinks restricts diffusion and gelation.

The novolac resin in our study, being an uncrosslinked form of a thermosetting resin, possesses very low viscosity and is supposed to flow very quickly inside the mold at its fusion temperature in comparison with the fast growing chains of rubbery poly(butyl acrylate) (PBA) at the start.

In this study, toughening of the hard and brittle phenol formaldehyde (PF) resin was carried out by the involvement of elastomeric PBA in IPN formation with it. The relatively high-molecular-weight rubbery PBA was expected to keep the comparatively low-molecular-weight novolac chains apart from each other and thereby reduce the crosslink density of the latter. Also, the propagation of a crack through the rubbery phase was somewhat restricted as it elongated more under load than the plastomeric phenolic resin and thereby absorbed the propagation energy of

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the crack. Therefore, toughening of the phenolic resin was expected for such systems in both ways. The influence of elastomeric PBA on the continuous matrix of the novolac resin was investigated as a function of the acrylic content.

EXPERIMENTAL

Materials

Novolac, the precursor of the crosslinked phenolic resin mixed with 10% (of the novolac resin weight) hexamethylene tetramine (HEXA), was procured from Hindustan Adhesives (Kolkata, India) and used without further modification. Butyl acrylate (BA), from Burgoyne Burbidges & Co. (Mumbai, India), was purified first by washing with a 2% aqueous sodium hydroxide (NaOH) solution and then by thorough and repeated washing with distilled water (to make it alkali-free, as tested by litmus paper) and dried over fused calcium chloride (CaCl_2); then, it was finally vacuum-distilled. Benzoyl peroxide (Bz_2O_2) from B.D.H., Mumbai, 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 the comonomer and crosslinker for PBA.

IPN synthesis

A weighed amount of purified BA monomer was placed in a test tube and thoroughly mixed with 2 wt % (based on the monomer) recrystallized Bz_2O_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 into a paste. With an increase in the acrylic monomer content, the consistency of the paste, however, became diluted. The resulting mass was then allowed to mature for about 2 h. The paste was then transferred into a positive-type compression sheet mold, which was preheated to 80°C. The mold was then closed and placed on the lower platen of the hydraulic press. The press was then closed with mild pressure to keep the mold airtight and to ensure that no air was entrapped in 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°C with a simultaneous increase in pressure to about 5 tons/ 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 under hot conditions 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 addition of the novolac resin. All other steps remained unaltered.

Measurements

Mechanical properties

Stress-strain behavior. An Instron model 4204 universal testing machine (Instron, Norwood, MA) was used for measuring the tensile properties, such as the ultimate tensile strength (UTS), elongation-at-break percentage (% EB), modulus, and toughness. The ASTM D 638 method was followed. A crosshead speed of 5 mm/min was maintained. All testing was conducted under ambient conditions in an environmentally controlled room. The toughness of the IPN samples was determined from plots of the area under load versus the elongation. The samples were visually inspected before the measurements and were found to be free from pores or nicks. The reported data are averages of at least six measurements, and the typical scattering range of the results was $\pm 5\%$.

Hardness. The Shore D hardness of various IPNs was evaluated according to ASTM specifications after the conditioning of the samples in a humidity-controlled cabinet, in which 50% relative humidity was maintained by the adjustment of an ammonium nitrate salt mixture at 30°C.

Physical properties

Specific gravity. The specific gravity was determined with Archimedes' principle.

Gel time. The gel points of the pure novolac resin and its various blends with PBA were determined according to ASTM D 2471.

About 8–10 g of a sample was placed 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 sample attained the temperature of the bath, the stopwatch was started, and a wooden probe was brought in contact with the sample surface to check whether any powdery sample stuck to the probe or it met any resistance to penetration into the sample. The time was noted when no sample adhered to the probe or it could not penetrate the sample.

Crosslink density. This was determined for various IPN samples with the classical Flory–Rehner method.^{9,10}

For each sample, the percentage of equilibrium swelling was determined with acetone as the solvent.

The polymer–solvent interaction parameter (χ) was calculated as follows:

$$\chi = \beta + V_s/RT(\delta_s - \delta_p)^2 \quad (1)$$

where β is the lattice constant (0.34); V_s is the molar volume of the solvent; R is the universal gas constant; T is the absolute temperature (°K); and δ_s and δ_p are the solubility parameters of the solvent and the IPN samples, respectively.

After the swelling of all the samples with nine different liquids with solubility parameters in the range of 14.1–25.2 MPa^{1/2}, the swelling coefficient (Q) was calculated as follows:

$$Q = [(m - m_o)/m_o] \times (d_r/d_s) \quad (2)$$

where m is the weight of the swollen sample, m_o is the original weight of the sample, d_r is the density of the polymer, and d_s is the density of the solvent

The volume fraction of the polymer in the swollen mass (V_p) was determined as follows:

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

Then, with the following Flory–Rehner equation, the molecular weight between successive crosslinks (M_c) for each IPN was calculated:

$$1/M_c = [V_p + \chi V_p^2 + \ln(1 - V_p)]/[d_r V_s (V_p^{1/3} - V_p/2)] \quad (4),$$

where $1/M_c$ is equal to the degree of crosslinking.

Thermal properties

Thermogravimetric analysis (tga). TGA thermograms were obtained with a PerkinElmer Delta series thermogravimetric analyzer (PerkinElmer Corp., Norwalk, CT) under a nitrogen atmosphere at a heating rate of 20°C/min. The samples, ranging between 6 and 10 g, were used for TGA.

Differential scanning calorimetry (dsc). A DuPont 2100 instrument (Wilmington, DE) was used for DSC studies. DSC scans were taken at a heating rate of 10°C/min under a continuous flow of nitrogen. The DSC baseline was calibrated by the DSC apparatus being run without any sample within the container (pan and lid) and then with standard indium sample enclosed in the container. Once the baseline of indium was found to be satisfactory, a standard polystyrene sample was run, and the glass-transition temperature (T_g) was checked.

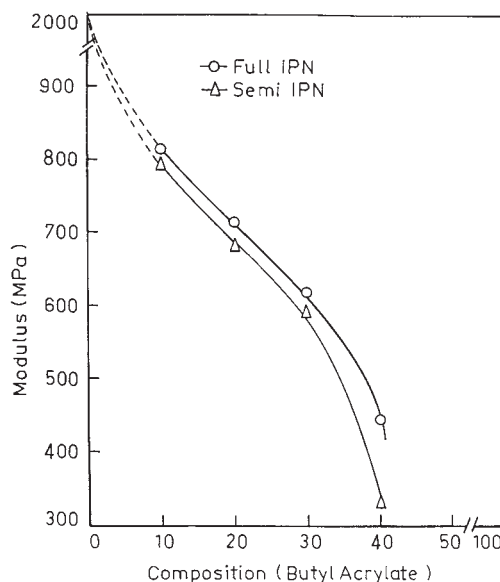


Figure 1 Variation of the modulus with the IPN composition (as the percentage of BA) for semi-IPN and full IPN systems.

Morphology

The phase morphology was examined with an Optronic optical microscope from Krüss (Köln, Germany) with a scale of magnification of 400×.

RESULTS AND DISCUSSION

Mechanical properties

Stress–strain behavior

The patterns of the curves (Figs. 1 and 2, respectively) exhibiting changes in the modulus and UTS, for both full and semi-IPNs of novolac resin with *in situ* formed PBA, as a function of the concentration of acrylate in the novolac resin matrix causes an abrupt fall in the modulus and UTS values at the initial level of PBA incorporation in comparison with those of the corresponding mechanical parameters of the pure novolac resin. On the other hand, % EB and toughness values, as shown in Figures 3 and 4, display an increasing trend with increases in the PBA content.

Thus, it might be concluded that the rigid and brittle novolac resin has been toughened by the formation of an IPN with the rubbery PBA, regardless of whether it is a semi-IPN or full IPN.

Full IPNs always have higher values of moduli and UTS in comparison with those for semi-IPNs over the entire range of concentrations of acrylate studied. However, the difference in the values of the moduli and UTS for the full IPNs and semi-IPNs of identical compositions, particularly at the lower concentration

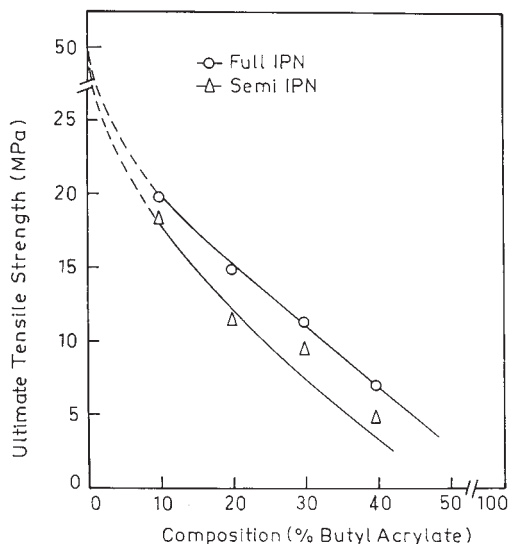


Figure 2 Variation of UTS with the IPN composition (as the percentage of BA) for semi-IPN and full IPN systems.

of PBA, are not so much pronounced in relation to what has been observed at the higher percentages of PBA.

The least differences in the mechanical parameters of the full IPNs and semi-IPNs may possibly be due to the drastic reduction in the crosslink density of the

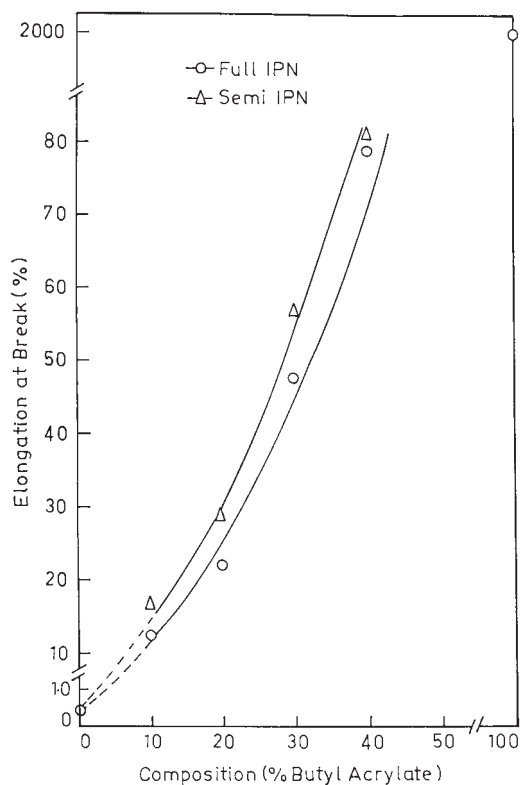


Figure 3 Variation of % EB with the IPN composition (as the percentage of BA) for semi-IPN and full IPN systems.

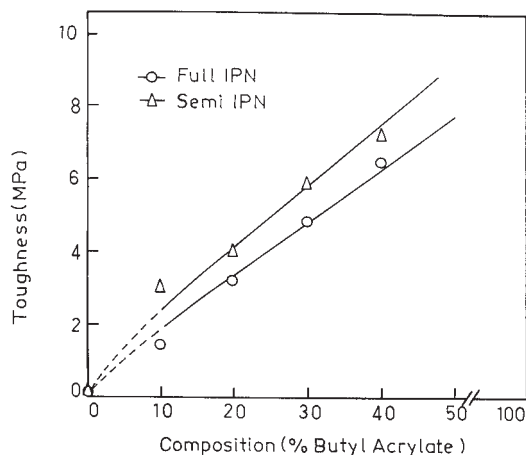


Figure 4 Variation of the toughness with the IPN composition (as the percentage of BA) for semi-IPN and full IPN systems.

novolac resin caused by the presence of the dispersed PBA domains, which might not allow the reactive sites of the resin to react—a possibility arising out of sequential IPN formation. The influence of this reduction is far to be set off even by the crosslinks of PBA itself in the case of full IPNs. This might have exerted a plasticizing action on the ultimate network system, increasing the number of relatively weaker stress concentrators offered by the PBA moieties and thus gradually reducing the effective cross-sectional area that bears the load.¹¹

It may also be argued that the highly extended chains of linear PBA for semi-IPNs may lead to coiling, resulting in an overall increase in the 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 PBA moieties in the case of full IPNs.

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

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

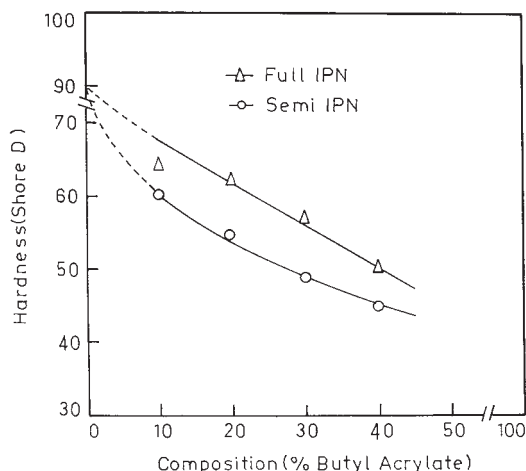


Figure 5 Variation of the hardness with the IPN composition (as the percentage of BA) for semi-IPN and full IPN systems.

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

The widening gap in the curves, particularly at higher ranges of PBA incorporation, may possibly be explained by the fact that crosslinked PBA offers much higher resistance than linear PBA as present in semi-IPNs. The linear PBA 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 from coming closer for the curing reaction. Although for full IPNs the PBA moieties are still present in the interstitial spaces, they are tighter and 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 an increase in the proportion of PBA in the IPNs, both the toughness and % EB increase steadily. This is due to the increase in the 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 PBA domains, are superior to full IPNs in this aspect as they elongate relatively easily and supposedly by increases in the path length of fracture propagation through the interfaces between the linear PBA and crosslinked phenolic resin. Also, the energy required for causing rupture in a semi-IPN is more than that required for the corresponding full IPN because more energy is expected to overcome a longer fracture path.¹²

Hardness

Figure 5 shows the hardness of different IPN samples as a function of the PBA content. Hardness values for both full IPNs and semi-IPNs show decreasing trends as the concentration of the acrylate is increased. However, full IPNs always have higher hardness values than the corresponding semi-IPNs within the PBA concentration range studied. This may be attributed to the crosslinked acrylate phase present in the full IPN system.^{13,14}

Physical properties

Specific gravity

Figure 6 elucidates the mode of variation in the specific gravity values for both full and semi-IPNs as a function of the compositions of the respective systems. Full IPNs always have higher values than semi-IPNs of identical compositions, whereas the theoretically predicted figures (calculated on the basis of the rule of additivity) are much higher than the experimentally observed values.

The *in situ* formed rubbery PBA molecules, having a very high molecular weight as expected, occupy spaces between the uncrosslinked novolac chains. The subsequent crosslinking of the novolac chains according to the mode of IPN synthesis in this work cannot lead to the compactness that would be obtained with only pure novolac. The somewhat small increase in mass due to the presence of light PBA within the novolac chain and due to threading with the same is

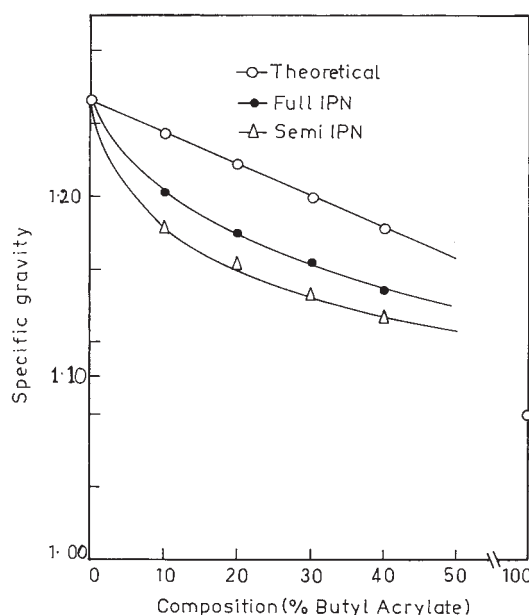


Figure 6 Variation of the specific gravity with the IPN composition (as the percentage of BA) for semi-IPN and full IPN systems.

more than compensated by the large increases in the free volume originating from entangled chains of PBA. The observed trend in the specific gravities for both semi-IPN and full IPN systems with an increase in the PBA content might explain this. Again, for full IPNs, crosslinking of the PBA phase may cause a higher specific gravity for the systems within the range of concentrations of acrylate studied because of an increase in compactness.

The two methods of polymerization for BA and novolac proceed via noninterfering mechanisms, and there appears to be no possibility of interaction between the acrylate and the phenolic precursor.

However, this being a sequential technique, the first formed polymer (PBA), either linear or crosslinked, seems to be swelled by the very low molecular weight novolac chains; although at later stages the novolac undergoes hardening, it cannot give as tight a network as it would generate in the absence of dispersed PBA. Therefore, the effective volume in every case is presumably more than what is dictated by the rule of additivity.

Gelling behavior

In this study, the growth of the two polymeric components occurs by two different noninterfering mechanisms: PBA by a fast chain-growth process and novolac resin by a slower step-growth process. The acrylic polymerization occurs quickly, and with an increase in the acrylic monomer concentration, both the rate of polymerization (R_p) and the kinetic chain length (hence the molecular weight) increase, as suggested by the following equations:^{15,16}

$$R_p = k_p(k_d/k_t)^{1/2}[I]^{1/2}[BA] \quad (5)$$

$$DP = R_p/R_t = k_p[BA]/2(k_d)^{1/2}(k_t)^{1/2}[I]^{1/2} \quad (6)$$

where k_d , k_p , and k_t are the rate constants of initiator decomposition, chain propagation, and termination, respectively; $[I]$ and $[BA]$ represent the molar concentrations of the initiator and BA, respectively; R_t is the rate of termination of acrylic polymerization; and DP is the degree of polymerization.

The gel time of the novolac resin is supposed to be affected by an increase in *in situ* formed PBA. Equation (6) gives an idea of DP of the PBA formed, which, in turn, is dependent on the rate of propagation, as given in eq. (5), both being dependent on the BA monomer concentration. Other parameters remaining constant, the molecular weight of PBA increases with increasing BA concentration. Thus, at a higher dosage of BA, the condensation of the methylol groups of the novolac chains may be expected to be retarded as the

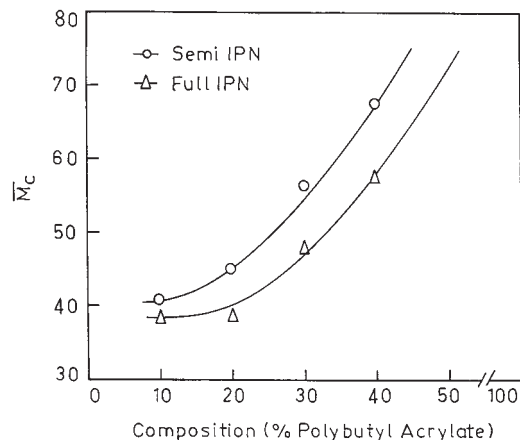


Figure 7 Variation of the average molecular weight of the polymer chain between two successive crosslinks (M_c) with the IPN composition (as the percentage of BA) for semi-IPN and full IPN systems.

long chains of PBA might not allow the two methylol groups to come in close proximity and condense.

However, the polymerization of the acrylic monomer starts at a lower temperature (80°C) than the crosslinking temperature (160°C) of the novolac resin. The growing chains of PBA thus formed initially appear to be associated at the reactive sites of the short linear novolac chains. In other words, shielding of the methylol side groups of the phenolic resin occurs. Also, the movement of macroradicals of PBA is somewhat restricted by the presence of the short chains of the other resin in the system. Therefore, propagation of the PBA chains occurs more predominantly than termination, and this results in an autoacceleration effect. This causes a reduction in the overall gelation time as the content of BA increases in the medium.

On the contrary, crosslinking of the phenolic resin, which is supposed to start during the later stages inside the mold, is somewhat suppressed because of the availability of an insufficient number of methylol side groups for the reaction. However, at higher PBA concentrations (30–40%), there is a possibility of phase separation before gelation, and as a result, no substantial improvement in the physical properties of the IPNs occurs, as observed at a lower BA content.¹⁷

Crosslink density

Figure 7 displays the variation of the M_c (i.e., average molecular weight of the polymer segments between two successive crosslinks) values of both the full IPNs and semi-IPNs with respect to the variation in the PBA concentration in various IPN systems. It is well known that the higher M_c is for a system, the lower the crosslink density is.¹⁰ In this study, with an increase in the PBA content in the IPNs, there is a gradual decrease in the crosslink density.

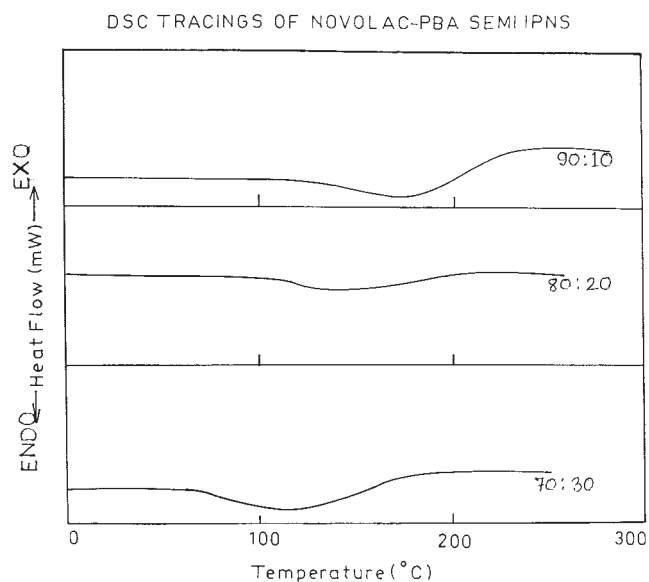


Figure 8 DSC plots for full IPN systems.

This may possibly be explained as follows. There is a probability of an increase in the interchain distances of the novolac molecules due to the inclusion of more and more high-molecular-weight rubbery PBA molecules formed *in situ*, which 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 an increase in the PBA concentration, the availability of the reactive groups on the novolac chains is reduced, and this causes a lowering of the overall crosslink density of the IPN.

Also, the full IPNs always have higher crosslink densities than the corresponding semi-IPNs over the entire range of PBA concentrations studied. This may be attributed to the crosslinking of both the matrix resin and the dispersed domains of the elastomeric PBA molecules in the case of full IPNs in comparison with the semi-IPNs, in which only the novolac resin is crosslinked and PBA is present as linear chains.

Thermal properties

DSC

The DSC tracings of the representative samples of both the semi-IPN and full IPN systems are shown in Figures 8 and 9, respectively. The plasticizing influence of the PBA phase formed *in situ* in the presence of the phenolic resin precursor on the ultimately crosslinked three-dimensional network of the phenolic resin is quite evident from the figures. This holds true, regardless of whether the samples belong to the semi-IPN or full IPN varieties. In a manner similar to

the trend of reduction in the mechanical properties of the phenolic resin, the temperature at the secondary transition (T_g) is diminished remarkably in comparison with that of the pure phenolic resin, even when rubbery PBA is present to an extent as low as 10 phr.

The subsequent reduction in the glass transition is slow and gradual.

The full IPNs, as expected, demonstrate higher T_g values than those exhibited by the corresponding compositions of semi-IPNs.

Furthermore, in the case of semi-IPNs, the inward shift of the glass-transition point is attended by a concomitant wide and deep endotherm that progressively increases with increasing PBA content. Thus, the enthalpy change involved in such an endothermic process increases steadily and gradually with increasing proportions of PBA within the range of PBA concentrations studied (from 17.78 to 42.86 J/gm).

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 an increase in the PBA content. It might be expected that with an increase in the PBA content, there would be a wide range of mixing of phases with different compositions of the constituents, particularly in the IPN formation.

The phase mixing for full IPNs appears to be limited, as it is constrained by the restricted mobility of the crosslinked rubbery phase, which is formed before the formation of the phenolic network. This is why the span of the endothermic changes as encountered in full IPNs is narrow. The enthalpy changes involved at T_g increase progressively, and this has been exemplified in the DSC endotherms. However, BA and novolac, being two immiscible components in IPN for-

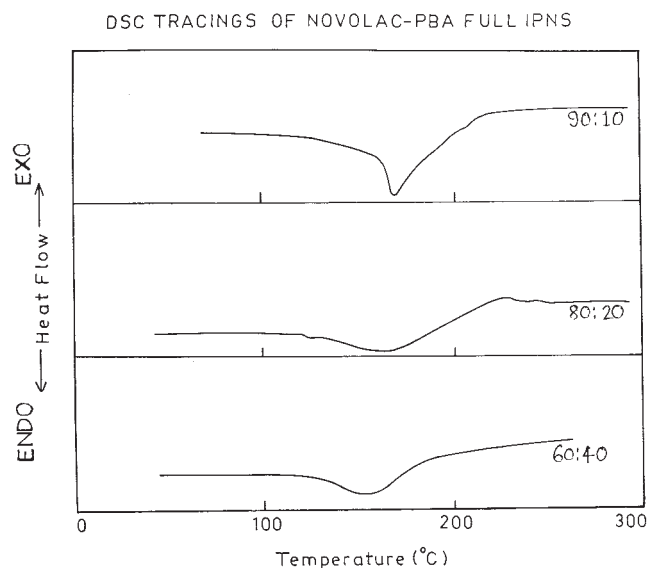


Figure 9 DSC plots for semi-IPN systems.

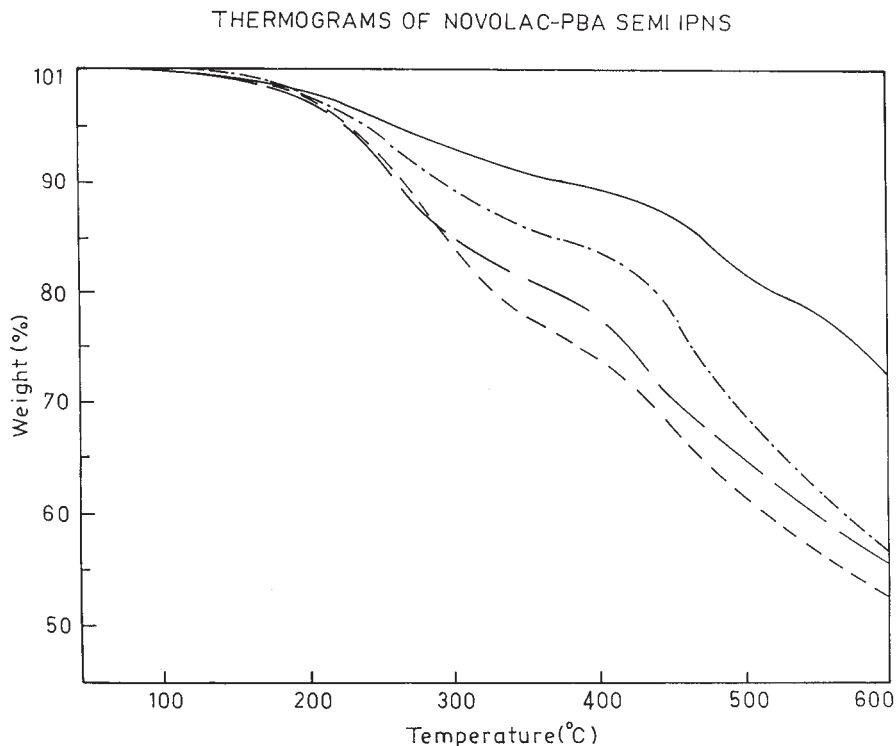


Figure 10 TGA plots for full IPN systems: (—) pure PF, (---) 90:10 PF/PBA, (- - -) 80:20 PF/PBA, and (— — —) 70:30 PF/PBA.

mation in this case, show a window of miscibility (presumably they are partially miscible) within certain ranges of composition formed *in situ* from the given weight ratio of IPN. This range of composition is reflected in the respective DSC thermograms.

TGA

Thermograms of both semi-IPNs and full IPNs of the novolac resin and PBA system (Figs. 10 and 11, respectively) demonstrate typical characteristic of pure phenolic resin, that is, a two-step degradation process.¹⁷

The onset temperature of degradation of different IPNs appears to vary with their composition. However, semi-IPNs show a lowering of the onset temperature with respect to the pure phenolic resin. On the other hand, full IPNs display a higher onset temperature, and this clearly indicates an initial resistance to thermal degradation, particularly in its first phase (i.e., up to a temperature of 350°C).

Although the initiation of degradation for full IPNs is delayed, the subsequent degradation occurs at a much faster rate than that of the pure phenolic resin, and the ultimate percentage of residue left behind is far less than that with pure phenolic within the range of temperatures under study.

The full IPNs exhibit increased thermal stability in comparison with the corresponding semi-IPNs. This may possibly be attributed to the fact that the crosslinked rubbery network of PBA is thermally more stable than the linear PBA chains, as present in semi-IPNs.

From a low-temperature study, the course of degradation of a phenolic resin has been found to be primarily oxidation at the bridging methylene linkages. Upon further oxidation, it has been reported that sterically hindered phenols are oxidized to a quinonoid-type structure.¹⁸ This is a slow process and occurs in a stepwise manner.

It is quite well known that PBA undergoes depolymerization through the mechanism shown in Scheme 1.¹⁹⁻²¹

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 the quinonoid structure (C, formed during the thermal degradation of the phenolic resin within the temperature region of 230–270°C)²⁰ may abstract the α -H atom more preferentially from PBA (as shown in Scheme 2).

The higher stabilization energy of the aromatic compound (D) formed in the aforementioned reaction

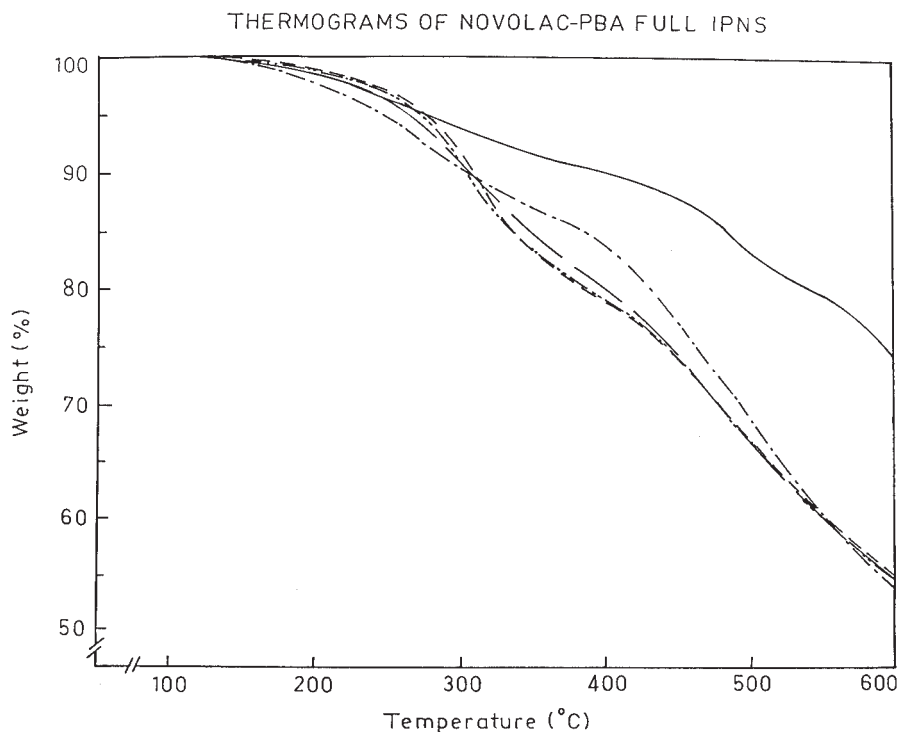
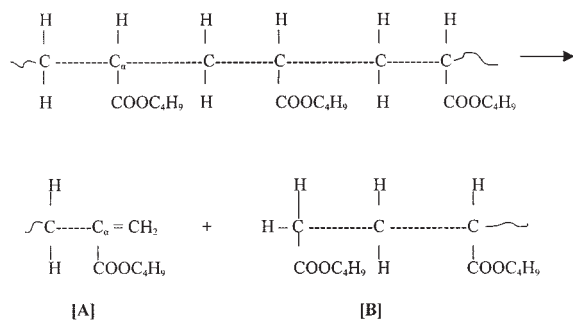


Figure 11 TGA plots for semi-IPN systems: (—) pure PF, (---) 90:10 PF/PBA, (- · - ·) 80:20 PF/PBA, (— — —) 70:30 PF/PBA, and (· · ·) 60:40 PF/PBA.

with respect to the quinonoid structure favors the reaction further, and this results in degradation of the IPNs at further elevated temperatures.

However, the reactions involving two macromolecules are somewhat retarded at higher concentrations of PBA beyond 350°C. Also, the stability of semi-IPNs and full IPNs merges at higher concentrations of PBA because it is highly reactive and is a very good oxidizing agent that gets murkier because of the presence of the substituents; stability is attained by the splitting of the labile H-atom from the depolymerized PBA molecule. In this process, the substituted quinone is itself reduced to a substituted hydroquinone structure, and the depolymerized PBA molecule attains some stability with the formation of a terminal unsaturation.

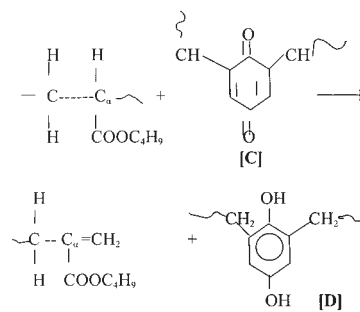


Scheme 1

According to the Le Chateliers principle of chemical equilibrium, the thermal degradation of the phenolic resin continues unabated, conferring thermal instability of the matrix resin in the IPNs in comparison with the pure phenolic resin.

Morphology

The micrographs, obtained from optical microscopy (Fig. 12), clearly indicate the coexistence of a dual phase, which appear to be cocontinuous as well. An interesting feature of the full IPNs is that most of the domains are compact and are devoid of any occluded novolac. The somewhat irregular compressed and nonspherical linear domains present in semi-IPNs appear to be condensed by the force of shrinkage exerted



Scheme 2

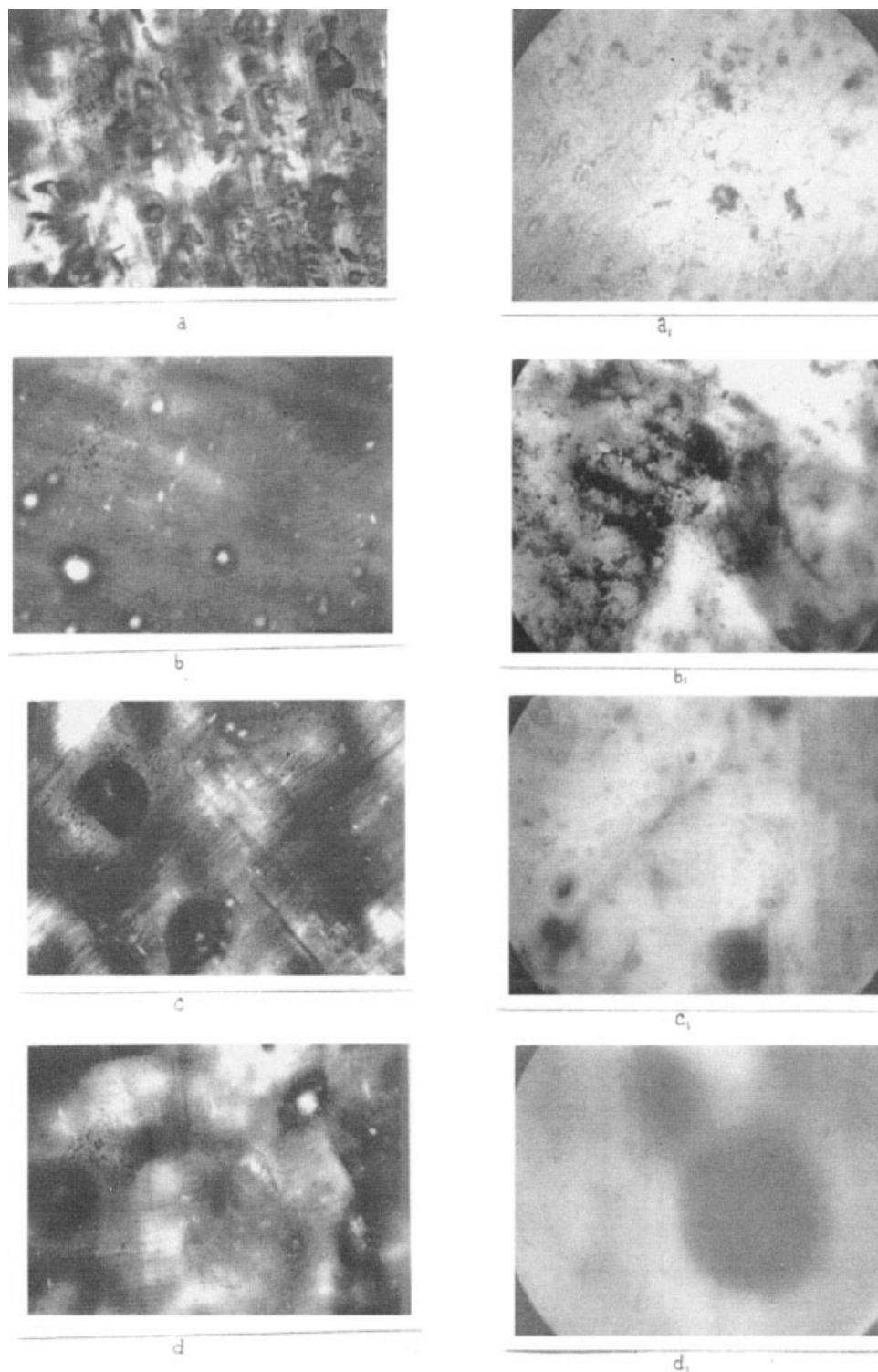


Figure 12 Optical micrographs for semi-IPN and full IPN systems (scale = 400 \times): (a) 90:10 PF/PBA (semi-IPN), (a₁) 90:10 PF/PBA (full IPN), (b) 80:20 PF/PBA (semi-IPN), (b₁) 80:20 PF/PBA (full IPN), (c) 70:30 PF/PBA (semi-IPN), (c₁) 70:30 PF/PBA (full IPN), (d) 60:40 PF/PBA (semi-IPN), and (d₁) 60:40 PF/PBA (full IPN).

by the crosslinked novolac. In both cases, the typical cellular domain, as normally found in IPN systems, appears to grow from the inside of the shell wall and proceeds toward the core; in most instances, the

cells contain some entrapped novolac resin. The domain formation appears to be more and more complete at the higher level of PBA incorporation, whereas at the lower doses of the dispersed PBA

phase, a mixture of different sizes of *in situ* formed domains pervades the novolac matrix. The PBA domains formed first in the presence of linear novolac chains particularly grow in size in an uninterrupted manner and are encapsulated in the novolac matrix formed subsequently, sometimes even under phase-separated conditions.

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