

Sequential Interpenetrating Polymer Networks of Novolac Resin and Poly(2-ethyl hexyl acrylate)—Thermal, Mechanical, and Morphological Study

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ABSTRACT: Interpenetrating polymer networks (IPN) of novolac/poly (2-ethyl hexyl acrylate) (PEHA) have been prepared via *in situ* sequential technique of IPN formation. Full and semi-IPNs were prepared with different blend ratios (w/w) e.g., 90 : 10, 80 : 20, and 70 : 30 in which the major constituent was novolac resin. A gradual decrease in specific gravity and hardness values was observed with increase in PEHA incorporation. A steady decrease in crosslink density with increase in PEHA fraction in the IPNs was quite evident. The IPNs were characterized with respect to their mechanical properties, e.g., ultimate tensile strength, percentage elongation at break, modulus, and

toughness. Thermal behavior was studied by differential scanning calorimetry and thermogravimetric analysis. A plasticizing influence of PEHA on the rigid, brittle, and hard matrix of crosslinked phenolic resin is evidenced from the mechanical and thermal properties. The two-phase surface morphology is revealed by scanning electron microscope. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 3007–3016, 2012

Key words: interpenetrating polymer networks; scanning electron microscope; crosslink density; compatibility; toughness

INTRODUCTION

One of the possible methods for reducing the degree of phase separation in multiphase polymer system is the formation of interpenetrating networks of them.^{1,2} Formation of IPNs is one of the best ways of intimately combining crosslinked polymers particularly involving thermosetting resins. In IPNs, the forming polymer chains are subjected to diffusion through an increasingly viscous medium to form phase domains followed by permanent interlocking of entangled chains due to crosslinking.³ Phase separation in IPNs depends primarily on the miscibility of the constituent polymers, crosslink density in both polymer networks and internetwork grafting, reaction temperature, pressure applied during molding, medium viscosity, and relative rate of reaction for the network formation.^{4,5} Due to the interlocking configuration, properties of IPNs are not influenced by subsequent aging rather these are frozen-in.⁶ Generally, the component present in higher concentration and with lower viscosity, is supposed to form the continuous phase, which dictates the ultimate properties.⁷ Moreover, systems with both com-

ponents crosslinked (full IPNs) tend to develop two continuous phases. Despite the extensive technological relevance of IPNs, the characterization of the material in the bulk state is mainly restricted to thermal and mechanical properties. However, IPNs can offer a wide spectrum of properties ranging from toughened elastomers to high impact plastics by judicious selection of the constituents.

Phenol-formaldehyde is a widely known thermosetting resin for its high temperature resistance and insulation characteristics, but its mechanical properties are rather poor, even after crosslinking. The present work is an attempt to improve the toughness of phenolic resin to be applicable in insulation purpose.

In this study, novolac resin, uncrosslinked form of brittle and rigid thermosetting polymer, phenol-formaldehyde (PF), is basically a low viscous and easy flowing material at its fusion temperature. In contrast, the other component of the IPN system, elastomeric chains of poly(2-ethyl hexyl acrylate), being formed by rapid chain growth polymerization, is highly viscous at the same temperature. The relatively high molecular weight rubbery poly(2-ethyl hexyl acrylate) 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 crack through the rubbery phase is expected somewhat restricted as it elongates more under load than the plastomeric phenolic. Thus, toughening of the

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phenolic resin was expected for such systems in both ways. The influence of acrylic resin on the phenolic matrix is investigated as a function of PEHA content (weight %).

EXPERIMENTAL

Materials

Novolac, the precursor of the crosslinked phenolic resin mixed with 10% (of the novolac resin weight) HEXA, (hexamethylene tetramine), was procured from Hindustan Adhesives' (Kolkata, India) and used without further purification. 2-Ethyl hexyl acrylate, EHA, monomer from SRL, Mumbai, India was purified first by washing with a 2% aqueous potassium hydroxide (KOH) 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; then it was finally vacuum distilled. Benzoyl peroxide (Bz_2O_2), from BDH Mumbai, India, was purified by repeated crystallization from chloroform. Ethylene glycol dimethacrylate (EGDMA) (Aldrich Chemical, Germany), without any purification, was used as the comonomer and crosslinker for PEHA.

IPN synthesis

A weighed amount of purified ethyl hexyl acrylate (EHA) monomer was placed in a test tube and thoroughly mixed with 2% by weight (based on the monomer) recrystallized Bz_2O_2 . The novolac resin (premixed with crosslinker) was weighed in a glass jar to maintain suitable ratio (e.g., 90 : 10, 80 : 20, and 70 : 30 w/w) with 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 4 h. The paste was then transferred into a positive type compression sheet mold (12 cm \times 6 cm \times 2 cm), which was preheated to 80°C. The mold was then closed and placed on the lower platen of the hydraulic press and it was closed with a mild pressure to ensure that no air was entrapped into the sheet. This condition was maintained for half an hour to allow the acrylic polymerization to initiate and propagate to a certain extent. Once the stipulated time period for the acrylic polymerization (as estimated earlier from homopolymerization) was over, the temperature of the mold was increased to 160°C, with simultaneous increase in pressure to about 5 tons/cm², and the mold was kept under such conditions for half an hour to ensure complete

polymerization of acrylic as well. The mold was then removed from the press in hot condition and sample was taken out carefully. In case of full IPNs, the comonomer crosslinker was added (2% w/w with respect to the acrylic content) to the liquid monomer before mixing with novolac powder. All other steps were kept unaltered. Specimens for testing were cut from these sheets after maturing for 7 days.

Measurements

Physical properties

Specific gravity. Specific gravity of the samples was determined by following Archimedes' principle and using the following relation:

$$\text{Specific gravity} = \frac{A}{A - B},$$

where A and B are weight of the sample in air and water, respectively.

Gel time. Gel points of pure novolac resin and its various blends with PEHA were determined as per ASTM D 2471. About 8–10 g of sample was taken in a small aluminum pan. The empty pan was kept in a thermostatic bath maintained at a constant temperature of 160°C \pm 5°C. Once the samples attained the temperature of the bath, 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 equation⁸ as follows:

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

where, γ crosslink density is equal to M_c^{-1} , molecular weight of polymer in between two successive crosslink points. V_p , volume fraction of polymer in the swollen mass; V_s , molar volume of the solvent; d_r , density of the polymer; χ , polymer solvent interaction parameter. For each sample, equilibrium swelling was carried out using acetone as the solvent, at a temperature of 27°C. This was done using different liquids ranging in their solubility parameter (δ_s) from 7.3 cal/cm³ to 12.1 cal/cm³ e.g., *n*-hexane, benzene, chloroform, acetone, benzaldehyde, aniline, and diethylene glycol. Molded specimens of the IPNs of different compositions, cut in small pieces, were weighed in dry state and then were dipped in these different liquids. The increase in weight of

each of these samples due to swelling by the different liquids was noted in regular intervals of time till the equilibrium swelling was reached. The swelling coefficient Q was calculated using equation,⁹

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

where, m_o is original weight of sample, m is weight of the swollen sample, and d_s , density of the solvent. In the subsequent plots of Q versus δ_s values for different liquids, the solubility parameter corresponding to the maximum value of Q was noted and this value was taken as the solubility parameter (δ_p) of the corresponding IPN composition. The parameter V_p was found out by using equation,

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

The polymer–solvent interaction parameter (χ) was then calculated from Bristow and Watson¹⁰ equation,

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

where β = lattice constant (0.34); R , universal gas constant (cal/K/mol); T , absolute temperature (K);

Mechanical properties

Stress–strain behavior. An Instron Universal Testing Machine (model-3366) was used for measuring the tensile properties like ultimate tensile strength (UTS), percent elongation at break (% E.B.), Young's modulus and toughness. ASTM D 638 method was followed. A crosshead speed of 5 mm/min was maintained. The testing was carried out at 25°C and in an environmentally controlled room (40% humidity). The samples were visually checked before the experiments and were found to be free from pores and nicks. The data reported are averages of at least six measurements.

Thermal properties

Differential scanning calorimetry. An instrument from Shimadzu, Japan (model-DSCQ-10) carried out DSC studies of various IPNs. Scans were taken at the heating rate of 10°C/min under continuous flow of nitrogen. The glass transition temperature (T_g) of a particular IPN was found out at the minimum of the corresponding endotherm.^{11,12} Indium was used as standard to calibrate the temperature and heat flow.

Thermogravimetric analysis. TGA was obtained by a TA instrument, USA (model-DTG-60), under nitrogen atmosphere at a heating rate of 10°C/min. The

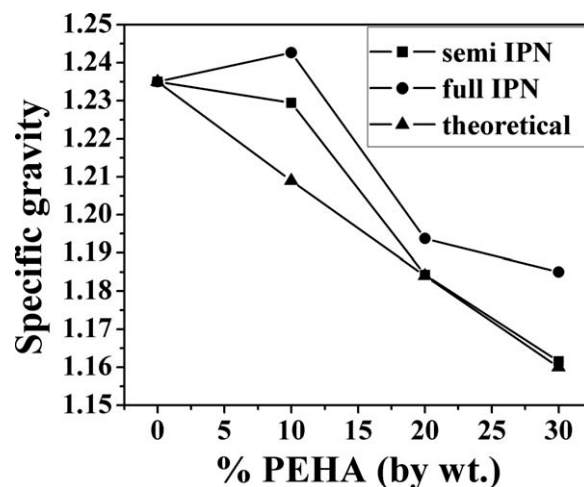


Figure 1 Variation of specific gravity of novolac-PEHA semi- and full IPNs with variation of novolac-PEHA blend ratio(w/w).

samples ranging between 6 and 10 mg in weight were used.

Morphology

Phase morphology was examined by a scanning electron microscope from JEOL, Tokyo, Japan, (JSM-6390LV). Scale of magnification was 500× μm .

RESULTS AND DISCUSSION

Physical properties

Specific gravity

Figure 1 shows the variation of specific gravity values for both full and semi-IPNs with the composition of the respective systems. Specific gravity values of semi-IPNs are marginally higher than the theoretically expected values for the blends as calculated by using rule of additivity.¹³ This is a typical characteristic of IPNs compared with that of the simple blends of corresponding polymer constituents as the free volume of the polymers has decreased here due to the interlocked network formation.

Increase in PEHA content in the IPNs has decreased the specific gravity values for both semi and full types. This may be due to the inclusion of *in situ* formed rubbery PEHA chains of larger free volume occupying the spaces in between the phenolic chains leading to decrease in degree of crosslinking of the latter. Moreover, the full IPNs have higher specific gravity values compared with that of semi-IPNs of similar compositions. Crosslinked and compact PEHA domains in the full IPNs and entrapment of these in between the phenolic chains may have increased the statistical probability of phenolic crosslinking compared with that in case of semi-IPNs; hence the increase in mass per unit volume for them.

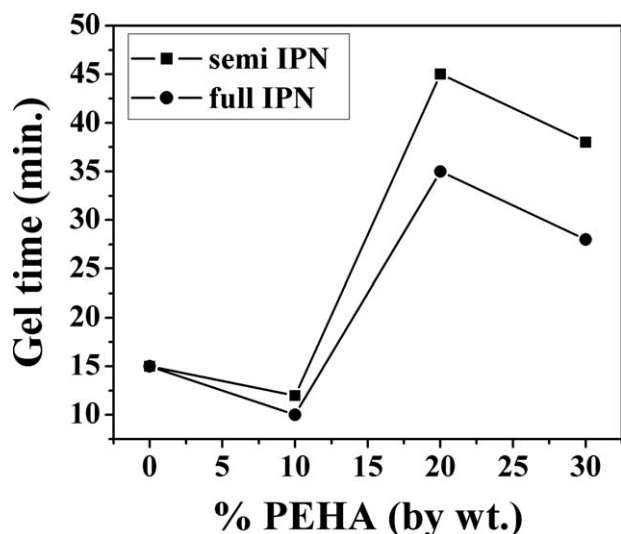


Figure 2 Variation of gel time of novolac-PEHA semi- and full IPNs with variation of novolac-PEHA blend ratios(w/w).

Gelling behavior

Figure 2 depicts the variation of gel time for different IPNs (both semi- and full IPNs) with their compositions. As the concentration of acrylate increases in the blend, the overall gel time, which is practically cumulative effect of two opposing facts, increases, within the range of acrylate content studied. The gel time of the novolac resin is supposed to be affected by an increase in *in situ* formed poly (2-ethyl hexyl acrylate). According to the equation,¹⁴

$$R_p = k_p \left\{ \frac{\sqrt{k_d}}{\sqrt{k_c}} \right\} \sqrt{[I]} \times [M], \quad (5)$$

$$DP = \frac{R_p}{R_t} = \frac{k_p [M]}{2\sqrt{k_d} \times k_t \times [I]}, \quad (6)$$

rate of polymerization of acrylics (R_p) is dependent on monomer concentration, $[M]$. In the above equation initiator concentration is $[I]$, rate constants of initiator decomposition, termination reaction, and propagation step are designated as k_d , k_t , k_p respectively, and rate of termination is R_t . "DP" represents degree of polymerization. Other parameters remaining constant, the molecular weight of PEHA increases with EHA monomer concentration. Thus, at a higher dosage of EHA, the condensation of methylol groups of the novolac chains may be expected to be retarded as the long chains of PEHA formed at lower temperature (80°C) might not allow the two methylol groups to come close proximity and condense at the crosslinking temperature of novolac. On the other hand, mobility of comparatively longer chain radicals of acrylics, formed at higher concentration of monomer, becomes retarded due to the increased viscosity as

well as due to the presence of novolac chains in the medium. This results chain propagation preferably over termination (auto acceleration effect) and causes a reduction in the crosslinking of novolac and lengthen overall gelation time as the content of EHA increases in the medium up to the value studied. Gelation of full IPNs occurred faster than that of the corresponding semi-IPNs. This may be due to the faster polymerization and simultaneous crosslinking of the acrylate at lower temperature to form the first network through which the growth of the phenolic network in the later stage has been allowed.

Crosslink density

Variation of M_c values, i.e., average molecular weight of the polymer segments in between two successive crosslinks, of the IPNs with increasing PEHA content is shown in Figure 3. To our knowledge, that the higher values of M_c for a system is lowering the corresponding crosslink density.¹⁵ In this study, it is found that the IPNs possess lower crosslink density compared with that of pure PF and also with increase in PEHA content in the IPNs, there is a gradual decrease in the crosslink density. This may be attributed to the probability of increase in the interchain distances of the novolac molecules because of gradual inclusion of *in situ* formed high molecular weight rubbery PEHA molecules thereby reducing the statistical probability of crosslinking, which is known as plasticization effect.

Mechanical properties

Stress-strain behavior

Mechanical properties of novolac-PEHA IPNs have been compared as a function of PEHA content

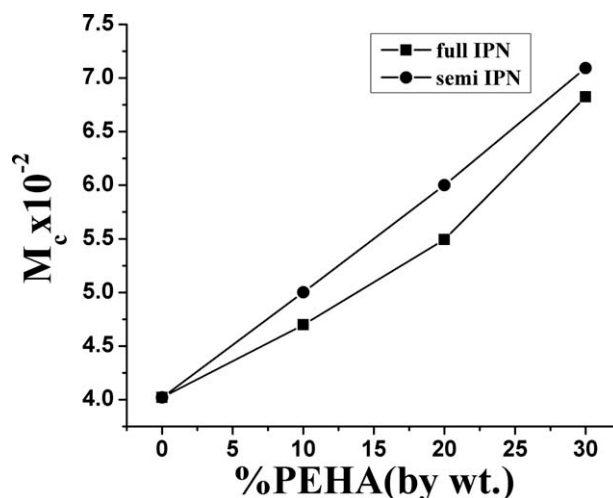


Figure 3 Variation of M_c of novolac-PEHA semi- and full IPNs with variation of novolac-PEHA blend ratios(w/w).

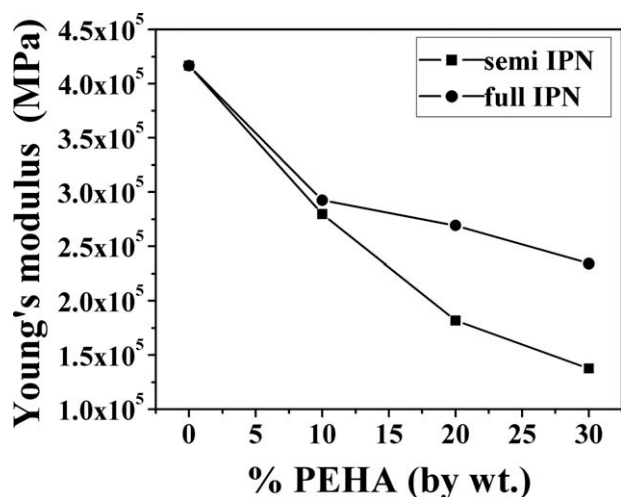


Figure 4 Variation of Young's modulus of novolac-PEHA semi- and full IPNs with variation of novolac-PEHA blend ratios (w/w).

(% weight) and shown in Figures 4–7. Figures 4 and 5 have shown that the Young's modulus and UTS of different IPNs decrease with increase in PEHA content in the IPNs (for both full and semi-types). On the other hand, Figures 6 and 7 depict that, with increase in acrylate % in the blends, both E.B. % and toughness values increase gradually within the concentration of PEHA studied; irrespective of whether it is semi- or full IPN.

Again full IPNs have shown higher Young's modulus and UTS but lower E.B. % and toughness than the semi-IPNs of corresponding compositions. A marked drop in the moduli and UTS values has been observed with both full and semi-IPNs with minimum PEHA content (10%), with respect to that of pure phenol-formaldehyde though the decrease

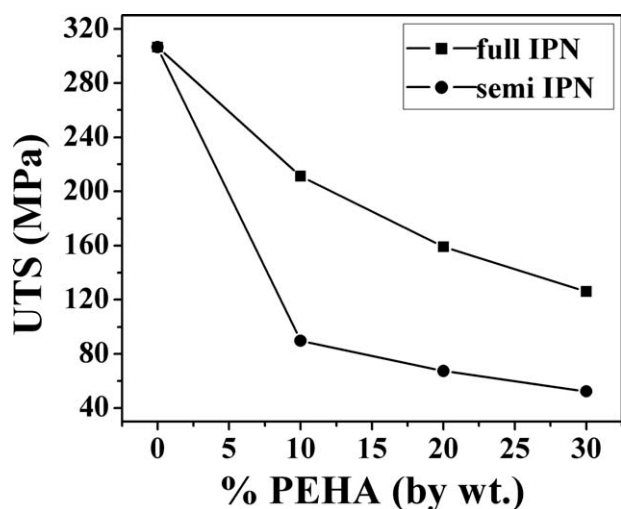


Figure 5 Variation of UTS of novolac-PEHA semi- and full IPNs with variation of novolac-PEHA blend ratios (w/w).

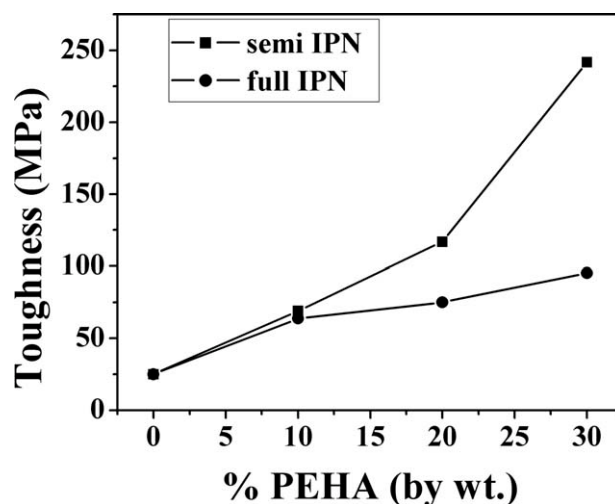


Figure 6 Variation of toughness of novolac-PEHA semi- and full IPNs with variation of novolac-PEHA blend ratios (w/w).

has been found to be more gradual in case of the IPNs containing higher level of PEHA.

The least difference in Young's modulus and UTS values of full and semi-IPNs of identical composition at the lower concentration region (10–15%) may be explained as below:

The drastic reduction in the crosslink density of novolac resin caused by the inclusion of high molecular weight PEHA molecules in the space between reactive sites (methylol groups) on the novolac chains may be one of the reasons behind the plasticizing action of the ultimate network system in contrast to the unmodified phenolic resin. The influence of this reduction in crosslink density is far to be compensated by the strengthening of the full IPNs

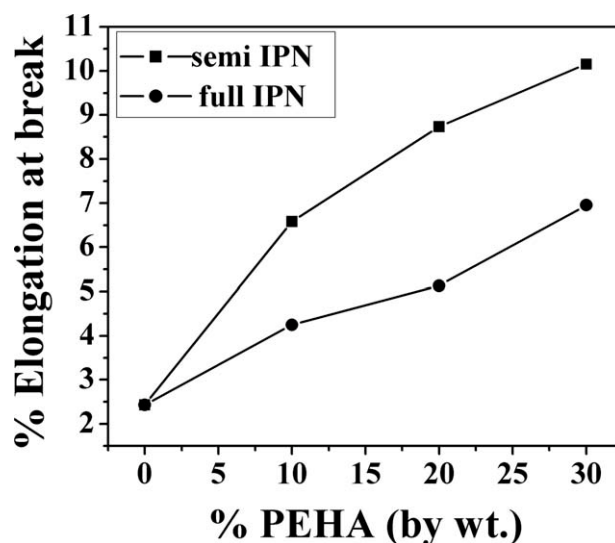


Figure 7 Variation of % E.B. of novolac-PEHA semi- and full IPNs with variation of novolac-PEHA blend ratios (w/w).

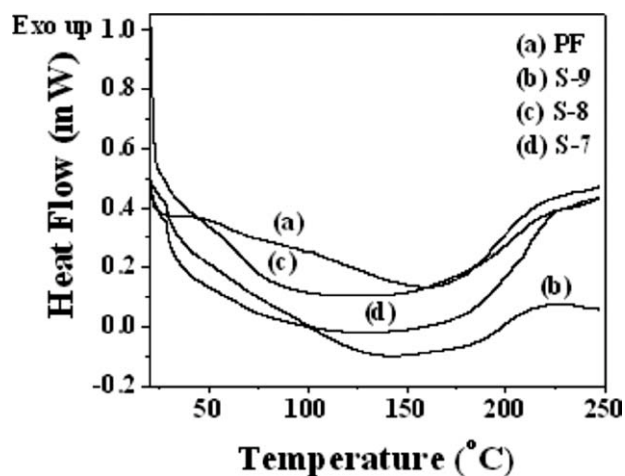


Figure 8 DSC curves for PF/PEHA IPNs: PF, S-9, S-8, and S-7 refer to pure PF, 90 : 10, 80 : 20, and 70 : 30 (w/w) compositions of PF/PEHA semi-IPNs.

having crosslinked domains of PEHA, compared with the corresponding semi-IPNs. Also increasing number of relatively weaker stress concentrators offered by the inclusion of rubbery PEHA domain in the brittle PF gradually decreases the effective cross-sectional area that bears the load.

At higher concentration of PEHA, it may be expected that the relatively higher free volume of randomly coiled longer and higher molecular weight chains of PEHA in semi-IPNs enable it to be interpenetrated or threaded more with the subsequently formed crosslinked network of phenolic resin than what would have possible with the corresponding full IPN. In the later case, the chain mobility is restricted because of the crosslinks present between the PEHA chains resulting in low degree of interpenetration. Earlier studies show toughening of phenolic resin by the formation of novolac-acrylic IPNs involving different homologous polyalkyl methacrylate as well as polyalkyl acrylate.^{12,16} Presence of alkyl group on the same carbon atom on which the ester group is present cause greater degree of chain rigidity to the poly alkyl methacrylate in comparison to that of poly alkyl acrylate; hence, the higher degree of toughening of the novolac acrylic IPNs involving polyalkyl acrylate as minor component in comparison to the IPNs formed with polyalkyl methacrylate.

Thermal properties

Differential scanning calorimetry

DSC tracings of the representative samples of both semi- and full IPNs have been shown in Figures 8 and 9 respectively. The plasticizing influence¹⁷ of the PEHA phase formed *in situ* in presence of the phenolic resin precursor on the three dimensional network of PF is quite evident from the figures. This

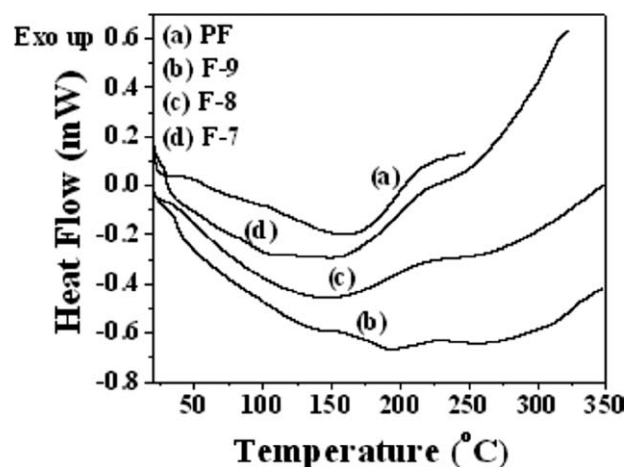


Figure 9 DSC curves for PF/PEHA IPNs: PF, F-9, F-8, and F-7 refer to pure PF, 90 : 10, 80 : 20 and 70 : 30 (w/w) compositions of PF/PEHA full IPNs.

holds true whether the samples belong to the semi-IPN or full IPN varieties. The temperature at the secondary glass transition (T_g) for the IPNs, is diminished remarkably compared with that of the pure phenolic resin, even when the rubbery PEHA is present, to the extent of even 10% by weight. The subsequent decrease in glass transition is found to be slow and gradual in case of IPNs with higher content of PEHA. The full IPNs, as expected, show higher T_g , in comparison to that exhibited by the corresponding compositions of semi-IPNs. Moreover, the enthalpy change, which is proportional to and evident from the extent of heat flow, involved in such endothermic process is found to decrease steadily and gradually with increasing proportions of PEHA concentration studied.

The extent of phase mixing, as is evident from the width of the span over which the endothermic

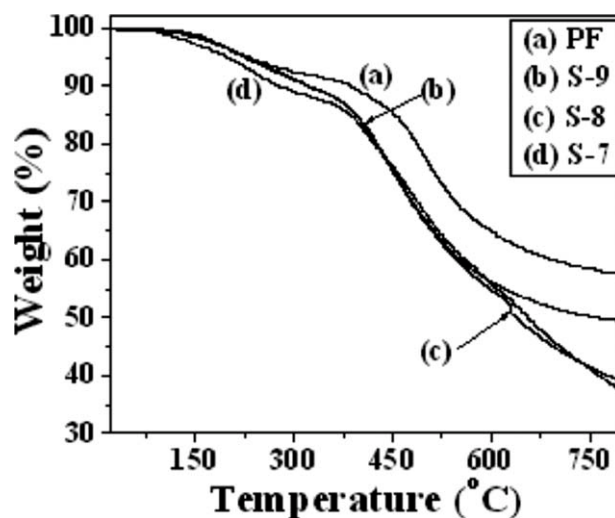


Figure 10 TGA curves for PF/PEHA IPNs: PF, S-9, S-8, and S-7 refer to pure PF, 90 : 10, 80 : 20, and 70 : 30 (w/w) compositions of PF/PEHA semi-IPNs.

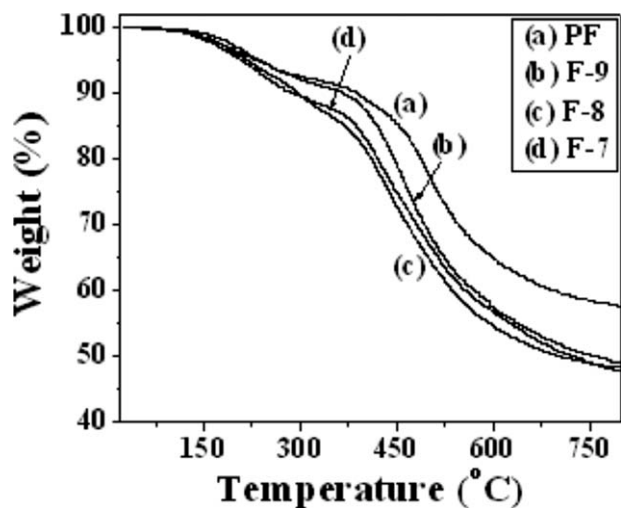


Figure 11 TGA curves for PF/PEHA IPNs: PF, F-9, F-8, and F-7 refer to pure PF, 90 : 10, 80 : 20, and 70 : 30 (w/w) compositions of PF/PEHA full IPNs.

enthalpy change occurs, appears to develop with an increase in the PEHA content.

The phase mixing, in case of full IPNs, appears more homogeneous, i.e., the discrete particles, as shown in micrographs (Fig. 13), are much more uniform in their composition, such that the width of transition is very narrow.

Thermogravimetric analysis

Thermograms of both semi- and full IPNs of PF/PEHA system are shown in Figures 10 and 11, respectively. A typical two-step degradation phenomenon for phenolic resin is evident here.^{18–20} At 500°C, carbonyl groups were detected in the resin although the degradation was taking place in an inert atmosphere, and thus it was concluded that a process of auto-oxidation of the methylene bridges occurred.^{21–24} The polymer itself was thought to contribute to oxidation through producing either OH radicals or water, which might act as an oxidizing agent, leading to the formation of oxidized terminal groups such as aldehydes and carboxylic acids followed by evolution of carbon dioxide.

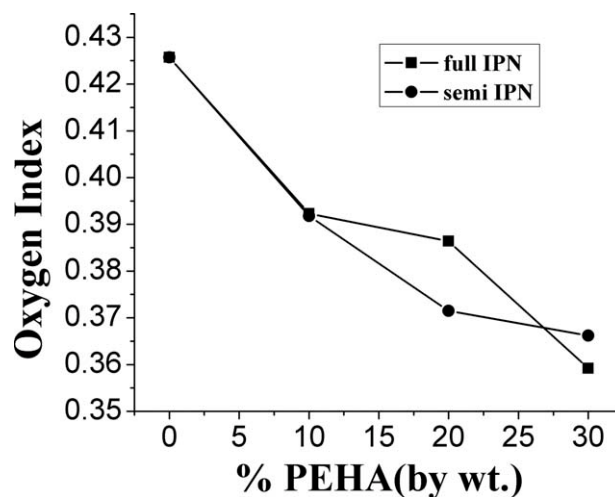


Figure 12 Variation of oxygen index of novolac-PEHA semi- and full IPNs with variation of novolac-PEHA blend ratios (w/w).

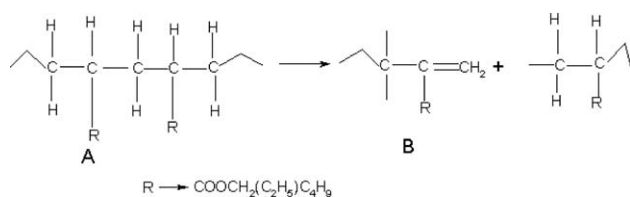
The onset temperature of degradation of different IPNs appears to vary with their composition. However, semi-IPNs show a lowering of the onset temperature compared with that of the pure PF. On the other hand, full IPNs display a higher onset temperature, and this clearly indicates an initial resistance to thermal degradation, particularly in its first phase (i.e., up to a temperature of 250°C).

Although the initiation of degradation for full IPNs is delayed, the subsequent degradation occurs at a much faster rate than that of pure phenolic resin, and the ultimate percentage of residue left behind is far less. 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 PEHA is thermally more stable than the linear PEHA chains, as present in semi-IPNs.

A comparative picture of the thermal data characteristics, including the oxygen index value (O.I.), is furnished in Table I. Van Krevlin²⁵ showed that the oxygen index of a material could be taken as measure of its nonflammability. The oxygen index values were calculated based on carbonaceous residue (C.R.) as related by empirical equation

TABLE I
Thermal Data Characteristics

Sample	Percentage of weight loss at various temperature (°C)								O.I.
	30	100	200	300	400	500	600	700	
PF	0	0.493	3.109	3.881	3.345	11.621	12.629	37.307	0.4257
S-9	0	0.283	3.322	5.239	6.884	17.547	10.478	45.802	0.3918
S-8	0	0.185	3.286	5.249	7.013	17.838	11.55	50.882	0.3715
S-7	0	0.803	4.157	5.791	5.734	15.367	12.156	52.208	0.3662
F-9	0	0.204	2.84	4.881	4.626	18.707	11.429	45.663	0.3923
F-8	0	0.449	3.429	6.37	8.129	16.746	10.222	47.156	0.3864
F-7	0	0.385	4.064	5.939	6.114	16.153	10.214	46.041	0.3592

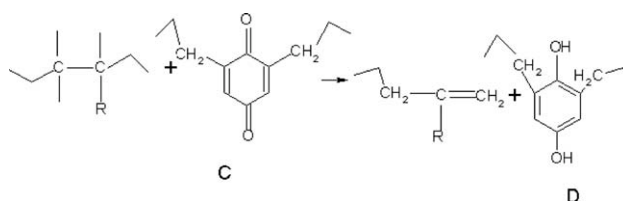


Scheme 1 Degradation mechanism of poly(2-ethylhexyl) acrylate.

$$\text{O.I} \times 100 = 17.5 + 0.4 \times \text{C.R.}, \quad (7)$$

Figure 12 shows that oxygen indices of the full IPNs are higher than the corresponding semi-IPNs. Moreover pure PF is more nonflammable than the 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 link-



Scheme 2 Plausible mechanism of combination of poly(2-ethylhexyl) acrylate and quinonoid formed during phenolic degradation.

ages. Upon further oxidation, it has been reported that sterically hindered phenols are oxidized to quinonoid-type structure.²⁰ This happens slowly and stepwise. It is quite well known that acrylates undergo depolymerization through the mechanism shown in Scheme 1.^{16,26,27}

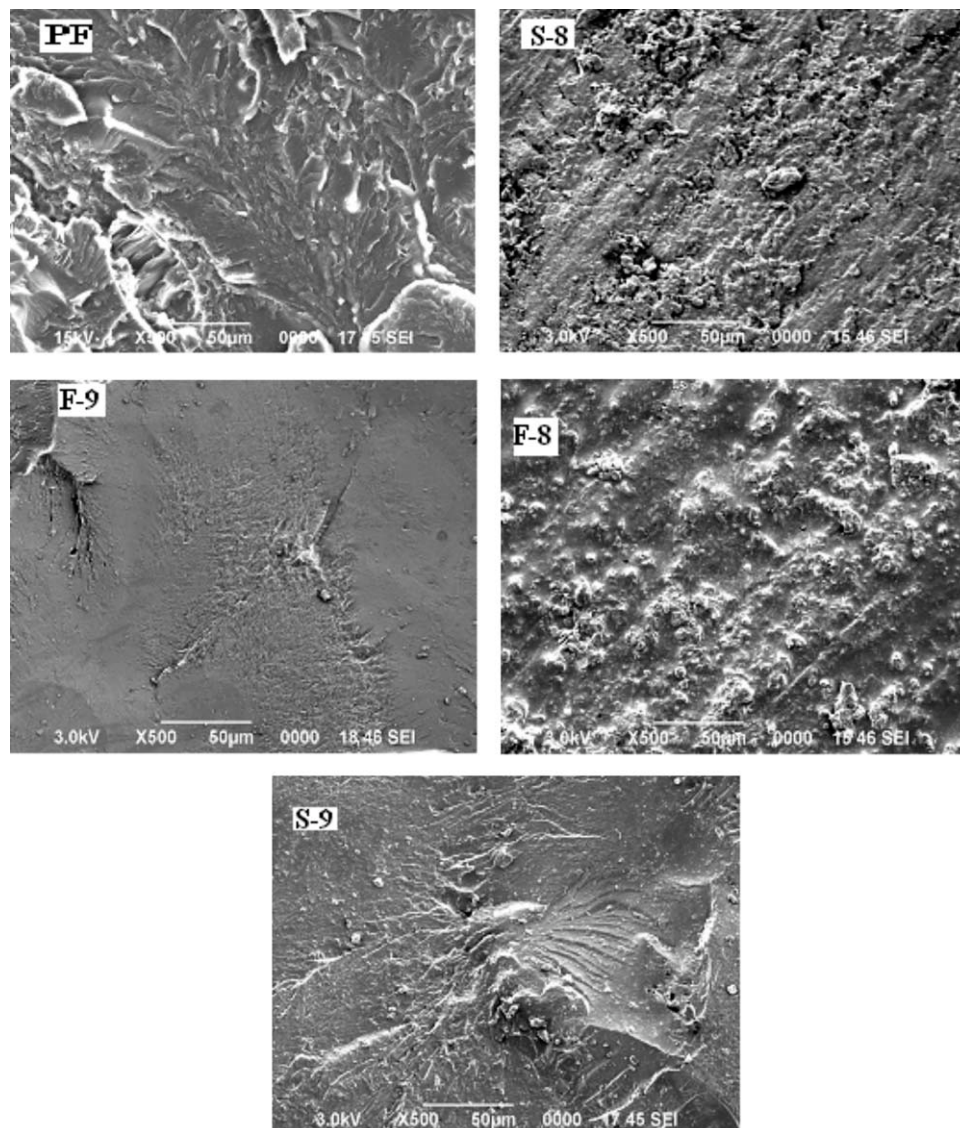


Figure 13 Scanning electron micrographs of PF/PEHA IPNs: sets of micrographs S-9 and S-8 refer to semi-IPNs having 90 : 10 and 80 : 20 (w/w) composition respectively. Sets of micrographs F-9 and F-8 refer to full IPNs having 90 : 10 and 80 : 20 (w/w) composition, respectively.

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

However, the statistically small amount of the quinonoid structure (C), formed during the thermal degradation of the phenolic resin within the temperature region of 200–250°C, may abstract the α -H atom more preferentially from PEHA (as shown in Scheme 2).

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

However, the reactions involving two macromolecules are somewhat retarded at higher concentrations of PEHA beyond 500°C. Also the stability of full and semi-IPNs merges at higher concentrations of PEHA because it is highly reactive and is a very good oxidizing agent that gets murkier because of the presence of the substituents; the splitting of the labile H-atom from the depolymerized PEHA molecule attains stability. In this process, the substituted quinone is itself reduced to a substituted hydroquinone structure, and the depolymerized PEHA molecule attains some stability with the formation of a terminal unsaturation.

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

Scanning electron microscopy

Figure 13 shows the scanning electron micrographs of the fractured surfaces of different semi- and full IPN specimens undergoing tensile failure. In the lower ranges of concentrations, when PEHA forms dissolved rubbery domains, irrespective of semi- or full IPNs, shear yielding was found to be the predominant failure mechanism. With increase in elastomeric PEHA content, a combination of shear yielding and crazing may be assumed to be the fracture mechanism from the figure.

In some cases, e.g., 9 s and 8 s, cavitation with the formation of small holes in the tensile stress field was seen. This may be due to poor interfacial force of adhesion between the PEHA rich domains and novolac rich phase matrix especially in semi-IPNs in comparison to that of full IPNs of corresponding composition.

In the later case, the comonomer crosslinker molecules, formed *in situ*, are expected to act as the tie molecules at the interface between phenol-formalde-

hyde resin matrix and compact domains of PEHA to gear up phase mixing.

CONCLUSIONS

Specific gravity values of PEHA/PF IPNs are found to be higher than the values obtained by using rule of additivity. Also full IPNs showed higher specific gravity than that of corresponding semi-IPNs. With increase in acrylate concentration in the IPNs, overall gel time, which is a cumulative effect of chain polymerization of acrylic monomer and crosslinking of novolac resin, increases, within the range of acrylate content studied. IPNs possess lower crosslink density compared with that of pure PF and also with increase in PEHA content in the IPNs, there is a gradual decrease in the crosslink density.

Toughening of PF matrix upon IPN formation with PEHA, is revealed by the mechanical properties. Toughness and % E. B. of the IPNs increased with increase in PEHA concentration whereas modulus and UTS values decreased with respect to that of pure PF. Inward shifting of the T_g values in the DSC thermograms also support the toughening of PF upon formation of IPN with PEHA. However, thermal stability of IPNs was found to be less than that of pure PF resin. Better phase mixing was observed in case of full IPNs from the electron micrographs. Also the width of endothermic enthalpy change, in DSC thermograms, became narrower for the full IPNs compared with that of the corresponding semi-IPNs.

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