# Engineering Properties of Novolac Resin-PMMA{Poly(methyl methacrylate)} IPN System

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Received 28 August 2003; accepted 27 February 2004 DOI 10.1002/app.20673 Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Full and semi interpenetrating polymer networks (IPNs) based on phenol-formaldehyde resin (Novolac) and poly(methyl methacrylate) have been made by *in* situ sequential technique of IPN formation. These systems of different compositions were characterized with respect to their mechanical properties, such as, ultimate tensile strength (UTS), percentage elongation at break, modulus, and toughness. Thermal properties were studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Extent of phase mixing of the two polymers was envisaged from the micrographs obtained by polarizing light microscopy (PLM). The effects of variation of the blend ratios on the above-mentioned properties were examined. There was a decreasing trend of modulus and UTS with consequent increases in elongation at break and toughness for both types of IPNs with increase in proportions of PMMA. Lowering of glass transition temperatures (with

## INTRODUCTION

In recent years, much research has been carried out on polymer blends, mainly because of the enhanced mechanical properties that these materials may possess.<sup>1</sup> Interpenetrating polymer networks (IPNs) are more or less incompatible polymer blends in which macroscopic phase separation is prevented by suitably engineering the morphologies of the participating components.<sup>2-4</sup> Here, one polymer is synthesized or crosslinked in the immediate presence of the other.<sup>5</sup> Owing to their permanent interlocking configuration, the tendency towards phase separation at the end of their synthesis is almost frozen in, so that the ultimate properties are not influenced due to ageing and the constituent polymers cannot be separated unless chemical bonds are broken.<sup>6</sup> The morphology is dependent on crosslink density and the sequence of formation of the two networks. The permanent physical interlocking (cocatenation) of the component polyrespect to pure crosslinked Novolac resin) of the IPNs with increasing proportions of PMMA was observed, indicating a plasticizing influence of PMMA on the rigid and brittle matrix of phenolic resin. The TGA thermograms exhibit lowering in thermal stability of the IPNs with respect to pure phenolic resin in the regions of higher temperatures. With increase in proportion of PMMA the onset of degradation of the IPNs is shifted towards lower temperature zone. The surface morphology as revealed by PLM indicates distribution of discrete domains of PMMA in the phenolic resin matrix. The two phase interfaces are quite sharp at higher concentrations of PMMA. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 2764–2774, 2004

**Key words:** compatibility; degradation; interpenetrating networks; toughness.

mers causes a wide spectrum of properties ranging from toughened elastomers to high impact plastics.<sup>7–11</sup>

Phenol-formaldehyde is a widely known thermosetting resin. It shows excellent insulation property, but its mechanical properties are rather poor, even after crosslinking. Hence, reinforcement becomes necessary for many applications. Various toughening agents are incorporated into phenolics to reduce the brittleness.<sup>12–17</sup>

In this present study, an attempt has been made to compensate the usual loss in mechanical strength of crosslinked phenolic resin due to irregularity in chain structure brought about by intrusion of a toughening agent by selecting a rigid and hard glassy polymer, PMMA, as the impact modifier.

The possibility of achieving toughened IPNs has been investigated as a function of the dosage of PMMA in the IPN systems.

## EXPERIMENTAL

#### Materials

An overview of the various materials used in our work is given in Table I.

Novolac, the precursor of the crosslinked phenolic resin, was used as received without further purifica-

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Journal of Applied Polymer Science, Vol. 93, 2764–2774 (2004) © 2004 Wiley Periodicals, Inc.

An Overview of Various Materials Used in our Work				
Sl no.	Materials	Description	Source	Code
1.	Phenol-formaldehyde resin	Novolac Pale yellow free flowing fine powder mixed with 10% of HEXA (Hexa methylene tetramine)	Hindustan Adhesives and Chemicals, Kolkata, India	PF
2.	Methacrylic monomer	Methyl methacrylate	FLUKA, Germany	MMA
3.	Free radical initiator	Benzoyl peroxide	B.D.H, India	$Bz_2O_2$
4.	Methacrylic cross-linking agent	2-Ethyl-2-(hydroxymethyl)-1,3-propanol trimethacrylate	Aldrich Chemical Company, U.S.A.	EHMPTMA

TABLE I n Overview of Various Materials Used in our Work

tion. MMA was freed from inhibitor by washing first with 2% aqueous sodium hydroxide (NaOH) solution and then by thorough and repeated washing with distilled water and then by drying over fused Calcium chloride (CaCl<sub>2</sub>). It was finally vacuum distilled.

Bz<sub>2</sub>O<sub>2</sub>, was purified by repeated crystallization from chloroform. Methacrylic crosslinking agent was used as received.

#### **IPN** synthesis

A weighed amount of purified MMA was taken in a test tube and thoroughly mixed with 2% by weight (based on MMA) of recrystallized Bz<sub>2</sub>O<sub>2</sub>. The Novolac resin (premixed with its crosslinker HEXA in proportion required for its complete curing) was weighed in a glass jar to maintain a suitable ratio with MMA as weighed earlier. The contents of the test tube were then transferred into the jar where they were mixed thoroughly and uniformly with the Novolac powder until the whole mass turned almost to a paste. With increase in proportions of MMA the consistency of the paste, however, got diluted. The resulting mass was then allowed to mature overnight. The paste was then transferred into a positive type compression sheet mold, which was preheated to 80°C. The mold was then closed with a mild pressure to keep the mold airtight so as to ensure no air entrapment into the molded sheet. This condition was maintained for half an hour to allow the acrylic polymerization to be initiated and propagated to some extent. Once the stipulated time period for the acrylic polymer formation was over, the temperature of the mold was raised to 150°C with simultaneous increase in pressure to about 5 tons/cm<sup>2</sup>. The mold was kept under such conditions for another half hour. 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 seven days.

In the case of full IPNs, the said comonomer crosslinker was mixed (2% w/w with respect to the MMA monomer taken) with MMA containing the initiator prior to the addition to Novolac resin. All other steps remained unaltered.

## Measurements

#### Mechanical properties

Stress-strain behavior. An Instron Universal Testing Machine (Model 4204; High Wycombe, UK) 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 5mm/min was maintained. All testings were 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, and typical scattering range of the results was  $\pm$  5%. Hardness. Shore D hardness of various IPNs were evaluated according to the ASTM specification in a humidity controlled room at 30°C.

## Physical properties

*Percent equilibrium swelling.* This was determined for various IPN samples by immersing preweighed samples in distilled acetone and taking their weight after every 24 h unless a constant weight of the swelled samples was reached.<sup>5</sup>

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

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

About 8–10 gms of sample were taken in a small aluminum pan. The empty pan was kept in a thermostatic bath maintained at a constant temperature of 150  $\pm$  5°C. Once the samples attain the temperature of the bath, the stop watch is started and a wooden probe is 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.



Figure 1 Variation of modulus with IPN composition (as % MMA) for semi and full IPN system

# Thermal properties

*Thermogravimetric analysis.* (TGA) thermograms were obtained by a Perkin–Elmer Delta Series TGA (Thermogravimetric Analyzer; Wellesly, MA) under nitrogen atmosphere at a heating rate of 20°C/min. The samples ranging between 6 to 10gms in weight were used for the TGA. *Differential scanning calorimetry.* A Du-Pont 2100 instrument (Boston, MA) 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.

#### Morphology

Phase morphology was examined in an Optical Microscope from Krüss (Optronic), Germany.

#### **RESULTS AND DISCUSSION**

In the present study, two series of IPN samples were synthesized: a series in which both constituents in



**Figure 2** Variation of ultimate tensile strength with IPN composition (as % MMA) for semi and full IPN system



**Figure 3** Variation of percent elongation at break with IPN composition (as % MMA) for semi and full IPN system

network forms are physically entangled, full IPN; and a series in which only phenolic resin is crosslinked in presence of *in situ* formed linear poly(methyl methacrylate) in the semi IPN.

## Mechanical properties

## Stress-strain behavior

Figures 1 and 2 show the modulii and UTS of various IPN samples as a function of PMMA content. The trends of the curves for both full and semi IPNs exhibit that incorporation of poly(methyl methacrylate) in the phenolic resin matrix causes an abrupt decrease in modulus and UTS values. On the other hand elongation at break and toughness values as shown in Figures 3 and 4 have increased with increases in PMMA content. Thus, rigid and brittle phenolic resin appears to be relatively toughened due to the formation of IPN with the glassy PMMA, irrespective of whether it is semi or full IPN.



**Figure 4** Variation of toughness with IPN composition (as % MMA) for semi and full IPN system

It is also evident that the full IPNs always have much higher moduli and UTS values compared to the semi IPNs over the entire range of concentrations of PMMA studied.

A marked drop in the values of UTS and moduli is exhibited by both full and semi IPNs of identical compositions at the lower ranges of PMMA, and there are very little differences in their behavior. At higher methacrylate content, however, a slow, gradual, and steady decrease is demonstrated by both the full and semi IPNs. The decreasing trend of the UTS and moduli may be attributed to the following reasons: 1) Increasing number of relatively weaker stress concentrators offered by the PMMA moieties and thus, gradually decreasing the effective cross-sectional area that bears the load.<sup>18</sup> 2) Reducing the statistical possibility of complete curing of the phenolic matrix either by shielding the reactive sites of the phenolic resin by the dispersed PMMA domains and thus by not permitting the reactive sites to come closer and in this way leading to a decrease in crosslink density, a phenomenon which might have exerted a plasticizing action on the ultimate network system. The influence of crosslinking of the dispersed PMMA 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.

At higher concentrations of PMMA it may be expected that the relatively higher free volume of the randomly coiled long chains of PMMA 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 tighter crosslinked domains of PMMA restrict the mobility of the chains and reduce the degree of interpenetration. Thus it may be presumed that the effect of crosslinking in the dispersed phase in a full IPN is somewhat counterbalanced by the possibility of extensive interpenetration in a semi IPN. This has probably narrowed down the differences in the mechanical properties of the full and semi IPNs at higher levels of PMMA incorporation.<sup>19</sup>

The plasticizing effect imparted by the PMMA domains, along with a simultaneous increase in path length for the crack propagation during its tensile deformation due to the presence of a multitude of stress concentrators (PMMA moieties), can be accounted for by the observed increases in the % E.B. Consequently the energy expended in traversing a greater path will be much higher compared to pure phenolic resin. Thus the toughness may be expected to increase with increasing proportions of PMMA.<sup>20,21</sup> The influence of crosslinking of the dispersed domains in case of a full IPN is once more reflected in the mode of changes in % E.B. and toughness, respectively. Semi IPNs by virtue of having linear PMMA domains are superior to full IPNs in this aspect as it elongates relatively easily and supposedly by increases in path length through the interfaces between the linear PMMA and crosslinked phenolic resin than that expected in case of full IPN where the crosslinked PMMA is intrinsically more resistant to undergo elongation than linear PMMA. Therefore, full IPNs require less energy than semi IPNs. More energy is required to cause rupture in a semi IPN compared to that required for full IPNs. Furthermore, it is evident from the diagram that both the % E.B. and toughness of the different semi IPNs, particularly at higher levels of PMMA incorporation, increase somewhat disproportionately in relation to those shown at lower methacrylic concentrations. This is possibly due to the involvement of more and more randomly coiled long chains, as might be expected to be formed following the dependence of kinetic chain length on the monomer concentration in a free radical addition polymerization, into interpenetration, as the content of in situ polymerizing MMA increases. Thus, more and more energy is required for the crack propagation through these physical crosslinks generated due to interpenetration and entanglements particularly with the semi IPNs. Thus, the semi IPNs have higher toughness than full IPNs.

#### Hardness

Figure 5 shows the hardness of various IPN samples, as a function of PMMA content. Hardness values for full IPNs are higher compared to those for semi IPNs as the chain rigidity of the polymers involved increases because of crosslinking. However, it is note-worthy that there is a significant influence of the crosslinker of the dispersed PMMA moieties on the surface hardness of the IPNs.<sup>22–24</sup>

#### Physical properties

#### Specific gravity

Specific gravities of both the semi and full IPNs exhibit dual characteristic (Fig. 6). After an initial increase in



**Figure 5** Variation of hardness with IPN composition (as % MMA) for semi and full IPN system



Figure 6 Variation of specific gravity with IPN composition (as % MMA) for semi and full IPN system

specific gravity up to an incorporation of 10 parts of PMMA, both the network systems display a decreasing trend with progressive increases in PMMA; the full IPNs, however, show higher values than the semi ones always. When compared to the theoretically predicted figures (calculated on the basis of principle of additivity), we can find that both semi and full IPN have higher specific gravities up to a range of 20–25 parts of PMMA incorporation with respect to datum theoretical line beyond which it falls off. It may possibly be argued that at lower ranges of PMMA, the small particles of PMMA occupy the spaces between the crosslinks of the resin matrix and consequently lead to an increase in mass per unit volume. With increase in PMMA content, the resin matrix becomes less dense, which may possibly be attributed to the large free volumes of PMMA (high molecular weight) and hence lead to a decrease in density.

#### % Equilibrium swelling

Figure 7 shows an increasing trend in swelling characteristic for both full and semi IPNs with increase in PMMA content. The percent swelling values are, however, higher for semi IPNs compared to those for the full IPNs. The figure for % equilibrium swelling which may be assumed to be an indirect measure of the compactness or the extent of chemical crosslinking in a thermoset network of various IPN samples under study clearly exhibits an widening gap between full and semi IPNs, which are found to undergo somewhat disproportionate swelling at the higher ranges of PMMA content under study. This may possibly be attributed to large increases in free volume resulting from the cumulative effects of incomplete crosslinking of the Novolac, and increased intermolecular chain separation and threading of linear PMMA chains that

themselves have higher free volume creating void spaces and thus allowing more solvent to imbibe. In case of full IPNs, however, the crosslinked network of Novolac in combination with crosslinked PMMA does not permit the solvent to diffuse and swell.

#### Gelling behavior

In the present study, the growth of the two polymeric components occurs by two different noninterfering mechanisms, PMMA by a fast chain growth and Novolac resin by a slower step-growth process. The acrylic polymerization occurs fast and with an increase in acrylic monomer concentration, with both the rate of polymerization and the kinetic chain length (hence, the molecular weight) increase as suggested by equations 1 and 2.<sup>25,26</sup>

$$R_{p} = k_{p} (k_{d}/k_{t})^{1/2} [I]^{1/2} [MMA]$$
(1)

$$DP = R_p / R_t = k_p [MMA] / 2(k_d)^{1/2} (k_t)^{1/2} [I]^{1/2}$$
(2)

where  $k_{d_i} k_{p_i}$  and  $k_t$  are the rate constants of initiator decomposition, chain propagation, and termination, respectively; and [I] and [MMA] represent the molar concentrations of initiator and MMA, respectively.  $R_t$  is rate of termination of the acrylic polymerization.

However, polymerization of acrylic monomer starts at lower temperature (80°C) compared to the crosslinking temperature (160°C) of the Novolac resin. The growing chains of PMMA thus formed initially appear to get associated at the reactive sites of the short linear Novolac chains. In other words shielding of the methylol side groups of phenolic resin occurs. Also, the movement of macroradicals of PMMA is somewhat restricted due to the presence of the chains of the other resin in the system. Therefore, propagation of the PMMA chains occurs predominantly com-



**Figure 7** Variation of percent equilibrium swelling with IPN composition (as % MMA) for semi and full IPN system



**Figure 8** TGA plots for full IPN systems. Pure PF, (—); PF: PMMA (90 : 10), (– –); PF: PMMA (80 : 20), (— · · —); PF: PMMA (70 : 30), (— · —).

pared to the termination resulting "autoacceleration" effect. This may cause reduction in overall gelation time as the content of MMA increases in the medium.

On the contrary, crosslinking of phenolic resin, which is supposed to start at the later stages inside the mold, is somewhat suppressed due to availability of insufficient number of the methylol side groups for the reaction. However, at higher PMMA concentration (30-40%), there is a possibility of phase separation before gelation and as a consequence, no substantial improvement in physical properties of the IPNs occurs, as was observed at lower MMA content.<sup>27,28</sup>

## Thermal properties

Thermogravimetric analysis

The thermogravimetric analysis (TGA) of both the full and semi IPNs (Figs. 8 and 9, respectively) appear to exhibit results typical for such systems.

The onset of degradation of the different IPN systems appears to be delayed with respect to pure phenolic resin. This holds true for both semi and full IPNs. However, the onset seems to be accelerated with increasing proportions of PMMA.



Figure 9 TGA plots for semi IPN systems. Pure PF, (---); PF: PMMA (90:10), (---); PF: PMMA (70:30), (---).





Once the temperature reaches 170°C, the IPN systems appear to exhibit marginally increased stability with respect to pure phenolic resin. In case of both the semi and full IPNs, the stability is found to undergo an increase with increasing proportions of PMMA within the range of concentrations of PMMA studied. The semi IPNs, however, appear to be more stable beyond the onset temperature, although at further elevated temperatures they exhibit somewhat different thermograms.

Beyond 200°C, both semi and full IPNs degrade at a much faster rate than the pure phenolic resin and clearly exhibit a decreased thermal stability at elevated temperatures considered in our study. Here again, the semi IPNs appear to be more thermally stable than the full ones. Both types of IPNs follow the similar pattern of decreasing thermal stability with increasing proportions of PMMA content.

From the lower temperature studies,<sup>27–30</sup> the course of degradation of a phenolic resin was found to be primarily oxidation at the bridging methylene linkages. This initial step in the oxidation route of phenolic decomposition is assumed to take place as shown in Scheme 1.

Upon further oxidation it has been reported<sup>31</sup> that sterically hindered phenols are oxidized to quinone



Scheme 2



type structures. Oxidative degradation thus proceeds further as shown in Scheme 2.<sup>32</sup>

It is well known that the poly (alkyl methacrylate) undergoes depolymerization by an unzipping reaction mechanism yielding almost 100% monomer.<sup>33</sup>

Thus it is obvious that the two polymers involved in IPN formation undergo degradation by two different noninterfering mechanisms in a manner similar to their modes of formation, which involve step growth condensation reaction for the formation of phenolics and fast chain growth addition polymerization for the formation of PMMA.

Thermal degradation of phenolic resin resulting in the formation of quinonoid structure is a slow process and occurs in a stepwise manner. However, the statistically small number of such structures formed within the temperature region of 170°C–250°C can retard the free radical initiated depropagation of PMMA macroradicals by simply scavenging them, thereby causing the reaction to go forward slowly.



DSC TRACINGS OF NOVOLAC-PMMA FULL IPNs

Figure 10 DSC plots for full IPN systems.



Figure 11 DSC plots for semi IPN systems.

The quinonoid radical produced during the oxidative degradation of phenolic resin can further retard the depropagation of PMMA macro radicals by simply coupling with it. This retardation may further be enhanced because of the presence of poly alkyl substituted phenols and may be given as shown in Scheme 3.

The rate of depropagation increases with increase in temperature as well as increases in %PMMA. At elevated temperature the rate of formation of MMA becomes high as also the comparatively slower generation of quinonoid structure (D). As the quinonoid species gets depleted from the system according to the



**Figure 12** Variation of glass transition temperatures with IPN composition for semi and full IPN system

DSC TRACINGS OF NOVOLAC-PMMA SEMIIPNS



**Figure 13** Polarizing light micrographs for semi and full IPN systems. (a) Pure PF. (b) PF: PMMA—90 : 10 (full IPN). (b<sub>1</sub>) PMMA—90 : 10 (semi IPN). (c) PF: PMMA—80 : 20 (full IPN). (c<sub>1</sub>) PF: PMMA—80 : 20 (semi IPN). (d) PF: PMMA—70 : 30 (full IPN). (d<sub>1</sub>) PF: PMMA—70 : 30 (semi IPN). (e)

above mechanism slowly but steadily, the forward degradation of phenolic is favored more and more, ultimately leading to a faster process of degradation. It may further be postulated that the species (E) formed at intermediate stages may be coupled with the products like (D) and the reaction gets faster.

The polymer fragment as joined to quinonoid moiety may further depropagate at elevated temperatures, leading to an overall destabilization of the systems.

The comparatively higher thermal stability of the semi IPNs over the full ones may be attributed to the

effect of interpenetration, which has even offset the effect of covalent crosslinks present in PMMA moieties. It may also be presumed that the crosslinker, besides generating the chemical crosslinks, may get involved in copolymer formation with the MMA monomer, the ultimate copolymer having lower thermal stability than the linear homopolymers.

## Differential scanning calorimetry studies (DSC)

DSC tracings of the representative samples of both full and semi IPN systems have been depicted in Figures 10 and 11, respectively. The midpoint of the endothermic enthalpy change in each DSC tracing has been considered as the glass transition temperature of the corresponding IPN system. Figure 12 shows the variation of the observed values of  $T_{q}$  (experimental ones) vis-à-vis those calculated from Gordon-Taylor and Fox equation (theoretical 1 and theoretical 2 curves, respectively). The progressively increasing plasticizing influence of PMMA phase domains on the rigid, hard, and brittle continuous matrix of phenolic resin is quite evident irrespective of the nature of IPN systems, that is, whether it belongs to semi or full IPNs. The full IPNs, however, exhibit higher glass transition temperature  $(T_{o})$  over those for the corresponding compositions of the semi IPNs, although they do not differ much because of the predominating influence of the phenolic matrix. Crosslinking of both the polymers in full IPNs causes the chain mobility to be very much restricted compared to that in semi IPNs. Also, the increased chain mobility of the linear PMMA in semi IPNs might be expected to hinder the crosslinking process of subsequently formed network of phenolic resin resulting in increase in free volume and, hence, the lowering in  $T_{q}$  for semi IPNs.

Extent of phase mixing also plays an important role in variation of  $T_g$ . The full IPNs show relatively higher extent of phase mixing compared to the semi IPNs, with increasing proportions of PMMA as exhibited by the extended widths of the endothermic changes near the  $T_g$ s. This may possibly be due to the presence of comonomer crosslinker of PMMA, which, besides forming intermolecular crosslinks among the PMMA chains, may form some homopolymers leading to better phase mixing. In case of semi IPNs, however, the phase mixing as indicated by the endothermic enthalpy change near  $T_g$  appears to undergo a decrease with increasing proportions of PMMA.

#### Morphology

#### Polarizing light microscopy

The micrographs of both semi and full IPNs are exhibited in Figure 13.

In both cases, a bimodal distribution of dark PMMA phase domains in crosslinked phenolic matrix is indicated. In semi IPNs the PMMA domains appear to be somewhat compressed and sometimes distorted in shape. And we get a distribution of apparently elliptical and apparently spherically shaped domains. While the PMMA domains in full IPNs are more compact, dense, and almost spherical in shape, they might be expected to offer substantial resistance to compression exerted by the subsequently formed phenolic matrix during crosslinking in a full IPN. On the other hand, the linear and uncrosslinked PMMA moieties in case of semi IPNs appear to withstand a compressive force (due to shrinkage of network on crosslinking) exerted by the crosslinked continuous network of phenolic resin and undergo deformation leading to elongated spherical and elliptical shapes. Relative proportions of bigger domains gradually increase in the IPNs as the PMMA content increases.

The extent of phase mixing seems to decrease with increasing proportions of PMMA. The dispersed domains of PMMA appear to contain varying proportions of occluded phenolic resin in both cases of semi and full IPNs.

It also appears that the growth of the domains occurs from outside to inside. From the mode of synthesis, it may be assumed that cellular domains of PMMA were first nucleated, containing growing chains of PMMA, MMA monomer, and thermoplastic Novolac structure. The amount of macro radicals and monomer entrapped within the nucleus, of course, depends on the concentration of MMA in various compositions of the IPNs. Subsequent heating led to the formation of polymer, which got deposited on the wall itself.<sup>34–36</sup>

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