

# Latex Interpenetrating Polymer Networks Based on Polyacrylates and Poly(methyl methacrylate)

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## SYNOPSIS

The effect of methacrylic acid (MAA) concentration in the polyacrylate seed on the formation of latex interpenetrating polymer networks (LIPNs) with poly(methyl methacrylate) (PMMA) as polymer II in the ratio of 65 : 35 (w/w) has been studied. LIPNs were prepared using three different seeds having the compositions of *n*-butyl acrylate (BA), methyl methacrylate (MMA), and tetra(ethylene glycol)dimethacrylate (TEGDM) in the ratio of 55 : 45 : 0.7 by weight and varying amounts of MAA (0, 2.5, and 6% by wt) at two different pH values ( $\sim$  3.3 and 8.5). LIPNs prepared from seeds having MAA > 2.5% resulted in the formation of continuous films, whereas LIPNs without MAA in the seed yielded discontinuous films (i.e., films with many cracks). Characterization using differential scanning calorimetry (DSC) showed the presence of multiphase morphology in all the LIPNs, indicating better mixing of the two polymers. Another set of LIPNs using the seed of the composition BA : MMA : MAA : TEGDM in the ratio of 63 : 37 : 6 : 0.7 by wt, possessing a glass transition temperature of 0°C and PMMA as polymer II, was prepared at two different pH values, as mentioned earlier, and with two different initiators—namely, 2,2'-azobisisobutyronitrile (AIBN) and potassium persulfate (PPS)—for the polymerization of monomer II. The tensile strength and hardness of both the LIPNs processed at high pH (8.5) did not show significant differences, whereas the LIPNs prepared at low pH using the AIBN initiator showed an inverted core-shell morphology possessing very low hardness and tensile strength with high elongation. The PPS-initiated polymer showed core-shell morphology yielding film of poor strength. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Latex interpenetrating polymer networks (LIPNs) are produced using the two-stage latex (TSL) emulsion polymerization method: A crosslinked seed latex (polymer I) was prepared first, followed by the polymerization of the monomer II with crosslinker to form polymer II.<sup>1-3</sup> The morphology of the final latex particles prepared sequentially by the TSL method ranges from homogeneous through simple domain to the core-shell structures. Some of the factors which influence the final morphology of the LIPNs are sequence of polymerization, composition, mutual compatibility of polymers I and II, and degree of crosslinking.<sup>4-13</sup>

Apart from the aforementioned criteria, the relative hydrophilicity of the two polymers has a significant influence on the morphology of the latex particles prepared by the TSL emulsion polymerization method. For a linear TSL system, the core-shell arrangement is thermodynamically favored when polymer II is more hydrophilic than polymer I, whereas an inverted core-shell formation is favored when polymer I is much more hydrophilic than polymer II.<sup>14</sup>

Almost all common acrylic latexes contain some amount of carboxylic groups in the polymer chains. Some of these also appear on the particle surface, thereby improving the stability of the latexes. The hydrophilicity of the copolymeric latex particles can be increased to a greater extent with an increase of methacrylic acid as one of the components. These latexes give excellent stability against mechanical shear, added electrolytes, and freeze-thaw.<sup>15</sup>

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**Table I The General Recipe Used to Produce LIPNs**

Water	70%
Sodium dodecyl sulphate	0.36% (by wt)
Initiator used for the seed preparation	Potassium persulfate (PPS) (0.4 phm)
Seed : polymer II	65 : 35 (by wt)
Total solids	30%

LIPNs with a broad transition range, useful for coating for vibration damping, were prepared from the semicompatible polymers like poly(methyl methacrylate)/poly(ethyl acrylate) (PMMA/PEA).<sup>16</sup> However, the polymerization of MMA by the emulsion polymerization technique with the PEA seed favors the formation of core-shell morphology.

PMMA is more hydrophilic than polystyrene (PS). In the case of PS/PMMA two-stage latexes using persulphate as the initiator, irrespective of the monomer-II addition method (continuous addition/absorption), PMMA was found to be localized mostly at the shell, as determined by the soap titration technique.<sup>17</sup>

By selecting a highly hydrophilic seed (i.e., with the incorporation of 6% MAA in the seed and at a pH of 8.5) and by following the absorption method (swelling of the seed latex by the mixture of monomer II and crosslinker II), mixing of the two incompatible polymers (viz., polyacrylate and polystyrene) can be improved, thus yielding LIPNs with a broad glass transition temperature and films of high strength.<sup>18</sup> In the present study, the formation of

LIPNs with PMMA as polymer II and seeds with a high degree of variation in their hydrophilic nature, composed of polyacrylate (PA) copolymer, has been investigated by preparing LIPNs using three different seeds (with a variation in the MAA concentration of, say 0, 2.5, and 6% by wt and at two different pH values of 3.3 and 8.5). The effect of the different types of initiators on properties such as strength of the films and hardness of the hot-pressed samples of the LIPNs has also been studied by employing 2,2'-azo(bis)isobutyronitrile (AIBN) and potassium persulfate (PPS) for the polymerization of MMA (monomer II) at two different pH levels, as mentioned earlier, using the seed having 6% MAA and possessing a glass transition temperature of 0°C.

## EXPERIMENTAL

Different crosslinked polyacrylate seeds were prepared by dropwise addition of the monomeric mixture for 3 h to the reaction kettle, which contained water, surfactant (sodium dodecyl sulfate), and the initiator (potassium persulfate), at 75°C. The temperature was maintained for another 3 h for completion of the polymerization. LIPNs were prepared at two different pH values (viz., 3.3 and 8.5) by swelling the seed with MMA monomer and crosslinker at room temperature (30°C) for 4 h, followed by polymerization at 80°C for 4 h. The process of LIPN synthesis was followed as per our work reported earlier.<sup>18</sup> The general recipe and the set of variables employed to prepare different LIPNs using seeds of high variation in the hydrophilicity are given in Tables I and II, respectively.

**Table II Process Variables to Produce the Various LIPNs**

Seed	Code	MAA (%)	pH	Initiator <sup>a</sup>
A	A0.0M3	0.0	3.3	PPS <sup>b</sup>
	A2.5M3	2.5	3.3	PPS <sup>b</sup>
	A2.5M9	2.5	8.5	PPS <sup>b</sup>
	A6.0M3	6.0	3.3	PPS <sup>b</sup>
	A6.0M9	6.0	8.5	PPS <sup>b</sup>
Low $T_g$	Low $T_g$ MP3	6.0	3.3	PPS <sup>c</sup>
	Low $T_g$ MP9	6.0	8.5	PPS <sup>c</sup>
	Low $T_g$ MA3	6.0	3.3	AIBN <sup>c</sup>
	Low $T_g$ MA9	6.0	8.5	AIBN <sup>c</sup>

A—BA : MMA : TEGDM : MAA, 55 : 45 : 0.7 : Variable (by wt).

Low  $T_g$ —BA : MMA : TEGDM : MAA, 63 : 37 : 0.7 : 6 (by wt).

Polymer II—MMA : TEGDM, 100 : 0.7 (by wt).

<sup>a</sup> Used for the polymerization of the monomer II (MMA).

<sup>b</sup> PPS, 0.4 phm.

<sup>c</sup> PPS, 0.6 phm, and AIBN, 0.6 phm.

The polymers were analyzed for glass transition temperature ( $T_g$ ) using dried coagulated samples, by differential scanning calorimetry (DSC) (DuPont Instruments 910), from  $-50^\circ\text{C}$  to  $150^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$ . The polymeric films were subjected to the tensile test at  $30^\circ\text{C}$  using a J.J. Lloyds tensometer, model T2001. The crosshead speed was maintained at  $100\text{ mm}/\text{min}$ . Hardness of the hot-pressed samples was measured using a Shore-D durometer. Details of the preparation of the different samples for various analyses were the same as reported earlier.<sup>18</sup>

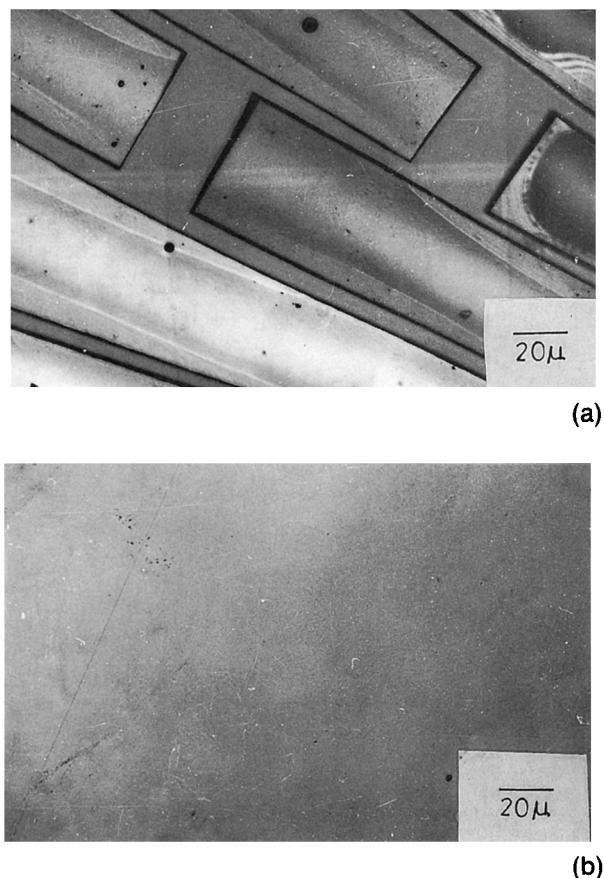
The nature of the films, obtained after drying the different LIPNs at  $35^\circ\text{C}$  on a glass plate, has been characterized by the Nikon optiphot (optical) microscope.

## RESULTS AND DISCUSSION

### LIPNs Prepared Using Seeds of Varying Hydrophilicity

Latexes form continuous film, upon drying at room temperature, provided that the  $T_g$  of the latex is less than room temperature. LIPNs prepared at low pH using seeds having MAA  $> 2.5\%$  produced continuous film [Fig. 1(b)], whereas LIPNs without MAA in the seed yielded discontinuous films [i.e., films with several cracks, as is evident from the optical micrograph; Fig. 1(a)]. Because the  $T_g$  of the seed is well below the ambient temperature at which the films were cast, the discontinuity in the film formation of AOM3 may be mainly due to the localization of PMMA at the surfaces of the latex particles, thus preventing complete coalescence. Formation of the continuous films from LIPNs prepared with the inclusion of the MAA in the seed clearly indicates that with increasing acid concentration, localization of the PMMA at the surface might have been reduced, in contrast to the LIPN prepared without acid in the seed. Thus, these experiments clearly indicate that the morphology of the latex particles changes with the hydrophilicity of the seed polymer.

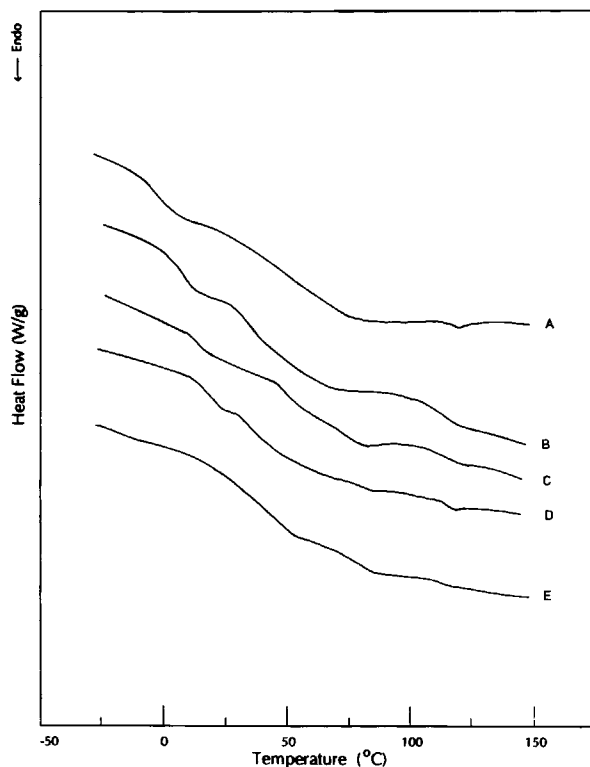
The  $T_g$  values of three seeds having 0, 2.5, and 6% MAA were determined by DSC and were found to be  $-2$ ,  $4$ , and  $14^\circ\text{C}$ , respectively. The difference in the  $T_g$  values is mainly due to the inclusion of MAA in different proportions to the same composition of MMA-BA in the seed. It is well known that the first derivative of the heat flow with respect to the temperature of the normal DSC curve gives the sharp peak reflecting the transition. The normal and derivative curves of the various LIPNs are shown



**Figure 1** Optical micrographs showing the (a) discontinuous films with several cracks of AOM and (b) the continuous film formation of A2.5M. (The dark spots are the dust particles attached during drying.)

in Figures 2 and 3, respectively. The multiple transition peaks in all the LIPNs showed a better mixing of the two polymers, resulting in the formation of multiphase morphology. This may be mainly due to the minor difference in the solubility parameters of the two polymers<sup>19,20</sup>: ( $\delta_{\text{seed}} = 8.96$  and  $\delta_{\text{PMMA}} = 9.00$  ( $\text{cal}/\text{cm}^3$ )<sup>1/2</sup>).

It can be visualized that at a higher pH of 8.5, the latex particles with the greater extent of ionization of carboxylic groups at the surface become highly hydrophilic as compared to the low pH counterpart because of a low degree of ionization of carboxylic groups at the surface. The increase in hydrophilicity at a high pH of the seed significantly suppresses the localization of PMMA at the surface of the latex particles, thus leading to better mixing of the two polymers. This can be seen by comparing the DSC curves of the LIPNs processed at low and high pH values using the same seed [Figs. 3(b) through 3(e)]. The curves show that the lower  $T_g$ ,



**Figure 2** Normal DSC curves of the LIPNs prepared with different amount of MAA in the seed and PMMA as polymer II at different pH values. MAA concentrations in the seed at low pH—0 (A); 2.5 (B); 6 (D); at high pH—2.5 (C), 6 (E).

pertaining to the seed, has been shifted to a higher value, indicating better mixing of the two polymers when the LIPNs were processed at a higher pH than at a lower one.

The polymeric films of A2.5M and A6M, when subjected to the tensile test, showed brittle fracture with a very low elongation. This may be attributed to the localization of PMMA at the shell, leading to poor film formation in A2.5M, or the lower  $T_g$  of A6M [25°C; Fig. 3(e)], which is close to the temperature at which the tensile tests were carried out.

The improvement in the formation from discontinuous film (A0M) to the continuous film from the LIPNs prepared using the more hydrophilic seed (A6M), despite the high  $T_g$  of the seed in the latter one, indicates that the variation in the hydrophilicity of the seed has a marked influence on the morphological characteristics of the final latex particles.

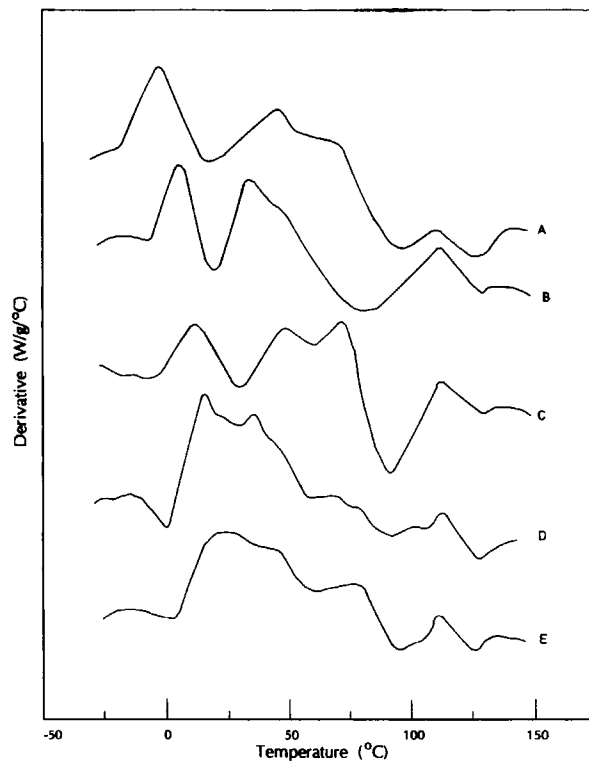
#### Effect of the Initiator II and pH

Although the aforementioned set of experiments indicates that an increase in hydrophilicity of the seed

reduces localization of the PMMA at the surface, leading to continuous film formation, the effect of an increase in the hydrophilic nature of the seed on the tensile strength properties of the final latexes could not be studied because of the brittleness of the films. Hence, a set of experiments has been designed to prepare LIPNs from the seeds with a very large difference in hydrophilicity/interfacial tension at low and high pH values. The polymerization of monomer II with two different initiators, whose functional groups attached at the end of the polymer II chain, should also have some influence on the interfacial tension of the polymer. The seed has been prepared with the inclusion of 6% MAA, which can provide a large difference in interfacial tension corresponding to a change of pH from 3.3 to 8.5. The initiators employed were AIBN and PPS.

AIBN is an organic phase initiator, whereas PPS is an aqueous phase initiator. Thus, the initiation process of the two initiators is different. The polymer end groups, such as sulphate or cyanide, emanating from the fragments of the initiators also influence the morphology of the TSL PS/PMMA latex particles.<sup>21</sup>

It was shown earlier that the LIPNs prepared using the seed with 6% MAA and a  $T_g$  of +14°C



**Figure 3** Derivative of heat flow with respect to temperature of Figure 2.

yielded films which were too brittle to perform the tensile tests. Thus, a seed with a lower  $T_g$  of 0°C (composition mentioned in Table II) was prepared. The low  $T_g$  seed was used to prepare the LIPNs to study the effect of the different initiators at two different pH values on tensile strength properties.

The strength properties of the films and hardness of the hot-pressed samples of various LIPNs produced with the low  $T_g$  seed are presented in the Table III. Hardness of polymeric materials is generally defined as the resistance to local deformation. Although it is a surface property, hardness is related to mechanical properties, such as modulus, strength, and elasticity.<sup>22</sup> The LIPNs prepared using PPS and AIBN initiators have been coded as low  $T_g$  MP $y$  and low  $T_g$  MA $y$ , respectively, for the convenience of the discussion ( $y$  may be either 3 or 9, depending on the pH at which LIPNs were processed). The strength and hardness of low  $T_g$  MP9 and MA9 did not show much variation. These experiments showed that the nature of the initiator does not play any role in the formation of LIPN with PMMA while processed at high pH. This may be mainly due to the high hydrophilic nature of the seed. The distribution of PMMA in the seed latex might be of the similar type in both cases. However, there is a lot of difference in tensile strength and elongation of the samples prepared at the low pH with two different initiators. The low  $T_g$  MA3 showed the highest elongation (502%), indicating that the initiator plays a major role in determining the morphology of the latex particles. The low hardness value of the low  $T_g$  MA3 (Shore-D 30) indicates that the continuous matrix is mainly composed of polyacrylate. The highest elongation and the lowest hardness of low  $T_g$  MA3 show that with the addition of an organic phase initiator, a latex of almost inverted core-shell morphology can be obtained. However, in case of initiation using persulphate, the elongation of the film of low  $T_g$  MP3 was found to be poor. This may be due to the presence of sulfate chain end groups,

**Table III Strength Properties of the Films and the Hardness Values of the Hot-Pressed Samples of LIPNs**

LIPN		Tensile Strength (MPa)	Elongation (%)	Hardness (Shore-D)
Low $T_g$	MA9	10.7	236	45
	MP9	10.2	250	45
	MA3	9.2	502	30
	MP3	8.4	54	45

which influences the localization of PMMA at the shell and thus prevents complete coalescence of the latex particles during the film formation. The incomplete coalescence leads to the formation of film with very low strength and elongation in low  $T_g$  MP3.

Comparison of strength properties of low  $T_g$  MP3 and MP9 indicates that a reduction in the interfacial tension with an increase in the hydrophilicity of the seed in MP9 greatly reduces the localization of PMMA at the surface, compared to MP3. This results in LIPN films of high toughness with MP9 and brittle films with MP3.

## CONCLUSIONS

The effects of the different variables employed to prepare various LIPNs on the glass transition, strength properties, film-forming nature, etc., have led to the following significant conclusions:

- All the latexes show multiphase morphology irrespective of the MAA content in the seed, mainly due to close proximity of the solubility parameters of the two polymers.
- An increase in pH and MAA content in the seed result in a change in morphological characteristics of the latex particles (i.e., a reduction of the localization of PMMA at the surface of the latex particles), thus inducing formation of continuous films.
- The use of an organic initiator for polymer II formation results in formation of the inverted core-shell structure, whereas the aqueous phase initiator favors the core-shell formation when the LIPNs have been processed at a low pH.
- The pH of the latex during the swelling of the seed, followed by polymerization of MMA, has a marked influence on the final latex morphology. This leads to the formation of films of high brittleness and high strength with an increase from low pH to high pH, respectively, as seen in the case of LIPNs prepared with the low  $T_g$  seed and initiation of polymerization of MMA with PPS.

Hence, it is evident that the morphology, tensile strength, and film-forming nature of the LIPNs based on polyacrylate seeds and PMMA as polymer II depend basically on the hydrophilicity, composition, and pH of the seed and the type of initiator used for the polymerization of MMA.

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Received January 18, 1995

Accepted June 30, 1995