

Latex Interpenetrating Polymer Networks Based on Polyacrylates and Polystyrene. II. Effect of Methacrylic Acid Concentration in the Seed

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SYNOPSIS

Latex interpenetrating polymer networks (LIPNs) were prepared by swelling the polyacrylate seed (comprised of methyl methacrylate and *n*-butyl acrylate in the ratio of 45 : 55 by weight), having different amounts of methacrylic acid (MAA) ranging from 0 to 6 wt %, with styrene monomer, whose polymer constituted the other network, to study the effect of MAA content in the seed on the final latex properties. The swelling and polymerization of styrene monomer and the crosslinker were done at two different pH values (viz., 3.3 and 8.5) for all the LIPNs. The LIPNs with the minimum MAA amount of 1.2 in the seed yielded translucent film at low pH and transparent film at high pH, upon drying at ambient temperatures. The LIPNs showed multiphase morphology with seeds having minima of 0.2 and 0.5% MAA when processed at high and low pH, respectively. Tensile strength and hardness (Shore-D) also increased from 4 to 13.2 MPa and 35 to 52, respectively, with an increase in the acid concentration from 0 to 6% as a result of increased mixing of the two polymers. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Polymeric latexes are colloidal sols, and their stability is improved by the addition of surfactants or by the inclusion of some of the functional monomers (e.g., carboxylic acids, 2-sulfoethyl methacrylate, 2-hydroxy ethyl acrylate) during polymerization in small amounts (ca. 1–5%).¹ Almost all common acrylic latexes contain some carboxylic groups in the polymer chains, some of which also appear on the particle surface. These latexes give excellent stability against mechanical shear, added electrolytes, and freeze–thaw. Inclusion of the functional groups (—OH, —SO₃H, —COOH, etc.) often improves the adhesion of the latex films to the substrates.

Okubo et al.^{2,3} reported that the surface acid concentrations of methacrylic acid (MAA) incorporated in the acrylic latex polymers increase with the addition of alkali and/or with the addition of organic

solvents. Addition of alkali makes the polymeric chains more hydrophilic, and addition of solvent enhances the movement of the polymer chain. Thus, the carboxylic groups are dragged out more toward the surface. Preparation of the linear combination of the two different polymers, by two-stage latex (TSL) emulsion polymerization using more hydrophilic seed, results either in the formation of polymer II dispersed in polymer I (if polymer I is of high molecular weight) or inverse core–shell formation (if polymer I is of low molecular weight and polymer II is more hydrophobic and incompatible⁴).

LIPNs are produced by TSL emulsion polymerization (i.e., the polymerization of monomer II and a crosslinker on a crosslinked polymer I seed latex^{5–7}). In the previous article, it was reported that by selecting a highly hydrophilic seed (i.e., with the incorporation of methacrylic acid and at a pH of 8.5) and by following the absorption method (i.e., swelling of the seed latex), the mixing of the two incompatible polymers (viz., polyacrylates and polystyrene) can be improved, yielding broad glass transition temperatures with high strength and hardness.⁸ It was thought appropriate to study the

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effect on the final properties of the latex IPNs of concentrating methacrylic acid in the seed and swelling the seed with a mixture of styrene monomer and crosslinker, and subsequently polymerizing the styrene at two different pH values (3.3 and 8.5), with an objective of obtaining LIPNs with good strength and hardness. A set of LIPNs was prepared as the seed; the LIPNs had different amounts of MAA, ranging from 0 to 6%. Their effects on the final properties (such as the film formation, surface acid distribution, glass transition temperature, tensile strength, and hardness) have been investigated in this study.

EXPERIMENTAL

Different crosslinked polyacrylate seeds with the composition of *n*-butyl acrylate (BA), methyl methacrylate (MMA), and tetra(ethylene glycol)dimethacrylate (TEGDM) in the ratio of 55 : 45 : 0.7 by weight (wt) and varying amounts of MAA (0 to 6% by wt) have been prepared by dropwise addition of the monomeric mixture for 3 h to the reaction kettle, which contained water, surfactant (sodium dodecyl sulphate), and 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 styrene monomer and divinylbenzene (DVB) at room temperature (30°C) for 4 h, followed by polymerization at 80°C for 4 h. The process of the LIPN synthesis has been followed as per our work reported earlier.⁸ The general recipe and the set of variables employed to prepare different LIPNs using

Table I General Recipe for the Formation of LIPN

Batch size	250 g
Distilled water	70%
Sodium dodecyl sulphate	1.2 parts per hundred of monomer (phm)
Potassium persulphate	0.4 phm on both the stages
Total solids	30%
Polymer I	MMA : BA (45 : 55) + MAA (0 to 6% by wt)
Crosslinker I	TEGDM (0.7% by wt)
Polymer II	Styrene
Crosslinker II	DVB (2.0% by wt)
Network I : II	65 : 35

Table II Process Variables to Produce LIPNs with Variation in Amount of MAA in the Seed

Code	Network I : II	MAA in Seed (wt %)	pH
A0S	65 : 35	0.0	At two levels of pH (3.3 and 8.5)
A0.2S		0.2	
A0.5S		0.5	
A1.2S		1.2	
A2.5S		2.5	
A6.0S		6.0	

seeds with variation in the hydrophilicity are given in Tables I and II, respectively.

The polymers were analyzed for glass transition temperature (T_g) using dried coagulated samples, by differential scanning calorimetry (DSC) (DuPont Instruments 910), from -50°C to 150°C at a heating rate of 10°C/min. The polymeric films were subjected to the tensile test at 30°C using a J. J. Lloyds tensometer, model T2001. The crosshead speed was maintained at 100 mm/min. Hardness of the hot-pressed samples was measured using a Shore-D durometer. Details of the preparation of different samples for various analyses were the same as reported earlier.⁸

The translucent/transparent nature of films has been estimated as the absorbance coefficient. Monochromatic light of wavelength 550 nm was passed using a UV-visible spectrophotometer, through films of thicknesses ranging from 80 to 100 μ m. Absorbance was measured to calculate the absorbance coefficient K using the following relation:

$$K = A/T$$

where A is the absorbance at the particular wavelength, and T is the thickness of the film in centimeters.

The surface acid concentration of LIPNs prepared from seeds having MAA concentrations of 1.2% and above has been determined by conductometric titration, as per the procedure of John Hen.⁹ After treatment with mixed ion-exchange resins, the latexes were initially adjusted to a pH of 11.5 with dilute alkali, and the samples were titrated against standard sulphuric acid of 0.12 N. Both the conductance and pH were studied as a function of the volume of acid consumed until a pH of 2.4 was reached.

RESULTS AND DISCUSSION

Surface Acid Distribution

In a carboxylated latex, the carboxylic acid monomer may be available in the following forms: surface bound, buried in matrix, and free acid. The amount of free acid is highly negligible if MAA is used since the partition of MAA toward the oil phase is more than that of acrylic acid (AA).^{10,11} After subjection to ion exchange, the latex contains only the first two type of acids (viz., surface bound and buried acids). Conductometric titration yields only the surface bound acids. The distribution of MAA at the surface of the different IPN latex particles is presented in the Table III.

Although the LIPNs were processed at two different pH values, it has been observed that the difference in the distribution of the acids is not appreciable in the latexes of the same acid content processed under different pH conditions. This indicates that irrespective of the pH at which the LIPNs were processed, 35 wt % of styrene monomer may not be sufficient to form a thick shell of polystyrene and to bury a fraction of the surface acid groups of the network I.

Film Characteristics

All the polymer samples have been found to form continuous film upon drying at ambient temperature. This clearly indicates that the polyacrylate forms the continuous matrix in which polystyrene phases are dispersed.

Spectrophotometric studies of the different latex films showed a vast difference in the absorption coefficient (K) among the latexes processed at different values of pH and acid levels. The LIPNs prepared at low (3.3) and high (8.5) pH values are coded as S3 and S9, respectively, for the convenience of the following discussion. The films of S3 all yielded translucent films, and the translucency decreases as the MAA concentration is increased. The degree of translucency/transparency of the different films, estimated as the absorption coefficient (K), is given in Table III.

The following observations have been made based on the values of K and the film types:

1. The transparency of the S3 latex films increases with the increase in acid level, thus showing a reduction in the K values.
2. The films of S3 latex IPNs (except A6S3) are translucent, and those of S9 (having acid level > 1.2%) are transparent.
3. The S3 and S9 films, having 0.2% and 0.5% MAA in the seeds, are translucent. But the K value of both S9 films are less than that of the S3 counterparts.
4. The S3 polymers prepared from the seeds having MAA greater than 1.2% yielded transparent films, and the K values were almost the same as that of the S9 counterparts, when the films were obtained with the addition of alkali to pH 9. This indicates that the decrease in the interfacial tension of the particles improves the coalescence of the latex

Table III Distribution of Methacrylic Acid in the Final Latex and Absorption Coefficient (K) of the Films of the LIPNs

LIPN	MAA in Seed (wt %)	pH	Surface Acid (%)	K (cm ⁻¹)	Type of Film
A0.0S3		3.3	—	70.3	Translucent
A0.2S3	0.2	3.3	—	63.7	Translucent
A0.2S9		8.5	—	42.1	Translucent
A0.5S3	0.5	3.3	—	58.3	Translucent
A0.5S9		8.5	—	35.2	Translucent
A1.2S3	1.2	3.3	0.774	35.3	Translucent
A1.2S9		8.5	0.858	9.2	Transparent
A2.5S3	2.5	3.3	1.444	27.3	Translucent
A2.5S9		8.5	1.678	8.4	Transparent
A6.0S3	6.0	3.3	3.933	18.5	S1 Translucent
A6.0S9		8.5	4.020	7.9	Transparent

The surface acid concentration of the seeds having 1.2, 2.5, and 6.0% MAA has been estimated to be 0.835, 1.672, and 4.042, respectively.

particles, leading to formation of transparent films.

The fourth observation can be related to the adsorption of surfactant due to hydrophobic attraction of the polymer and the surfactant. This prevents complete coalescence and leads to formation of translucent film at low pH and enhancement of latex particles coalescence, with accompanying reduction of interfacial tension and formation of transparent films at high pH. This phenomenon will be discussed in detail in a future article.

Change in Glass Transition Temperature of Different Systems

The T_g values of three seeds having 0, 2.5, and 6% MAA were determined by DSC and were found to be as -2 , 4 , and 14°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 *n*-butyl acrylate/methyl methacrylate in the seed.

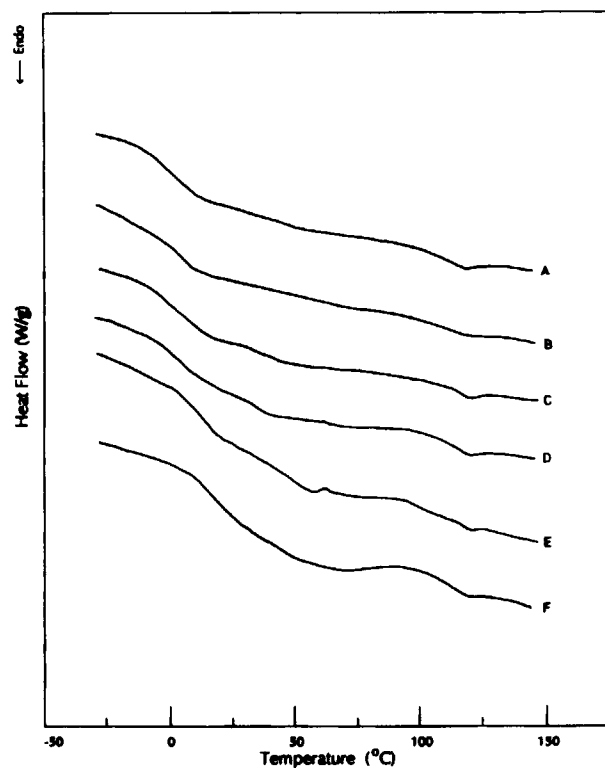


Figure 1 DSC curves of the LIPNs prepared with different MAA concentrations in the seed at lower pH (~ 3.3) (percent on monomer wt basis). A—0; B—0.2; C—0.5; D—1.2; E—2.5; F—6.0.

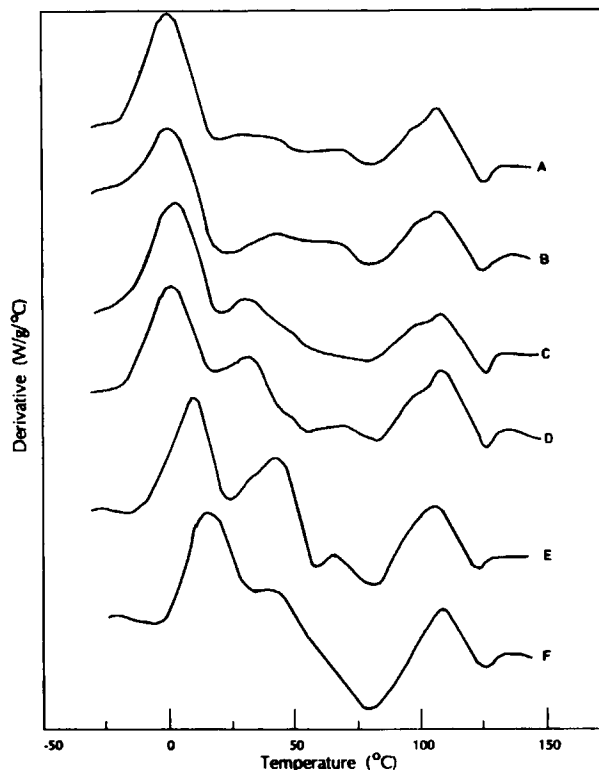


Figure 2 Derivative of heat flow with respect to temperature of Figure 1.

The change in the T_g values of the different LIPNs, prepared at two different pH values, and their derivative curves are shown in Figures 1 to 4. Apart from the individual component T_g values, all the LIPNs prepared at low pH (except A0S3 and A0.2S3) showed more transitions in between the two T_g values, indicating multiphase morphology formation in these latexes.

The appearance of multiphase morphology in all the latex IPNs prepared at lower pH from the seeds having a minimum of 0.5% MAA [Fig. 2(c)], shows that the interfacial tension may be playing a role in the formation of multiphase morphology. Multiple phases started forming in LIPNs using seeds having 0.2% MAA prepared at higher pH [Fig. 4(g)]. This also confirms that the interfacial tension plays a major part in forming the multiphase morphology. The addition of alkali to the carboxylated latex ionizes the carboxylic group, thus reducing the interfacial tension. Because of the negatively charged groups at the surface of the particles, there will be a loose shell structure and a reduction in the hydrophobic core volume,¹² where the polymerization of the styrene would take place.

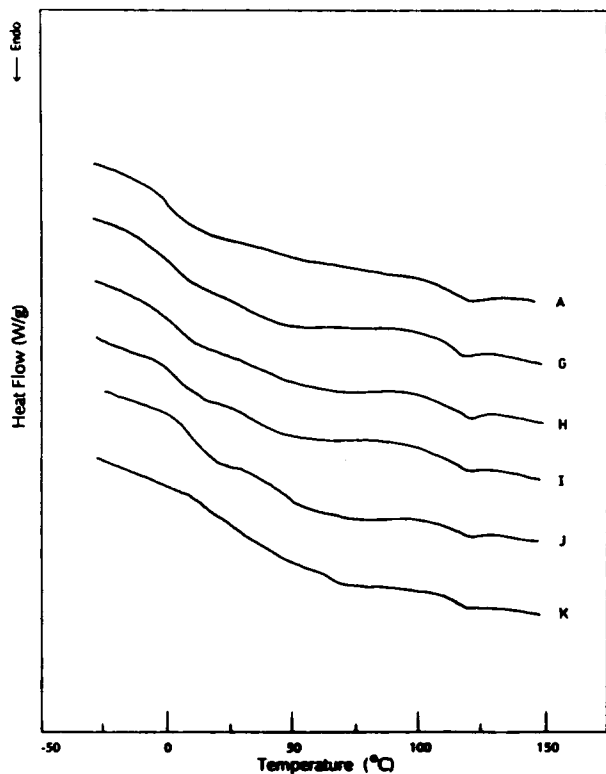


Figure 3 DSC curves of the LIPNs prepared with different MAA concentrations in the seed at higher pH (~ 8.5) (percent on monomer wt basis). A—0; G—0.2; H—0.5; I—1.2; J—2.5; K—6.0.

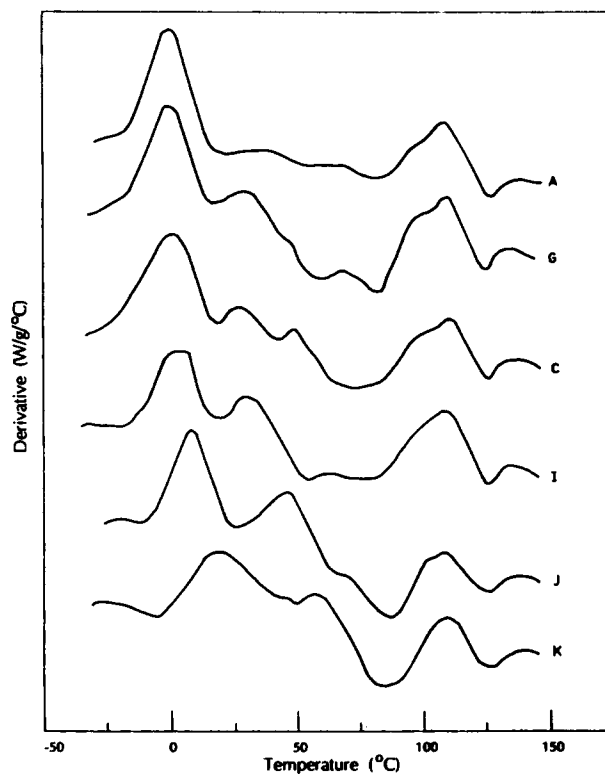


Figure 4 Derivative of heat flow wrt temperature of Figure 3.

Thus, it can be visualized that at a higher pH of 8.5, the latexes with more carboxylic groups at the surface will act as a high molecular weight anionic surfactant, with the carboxylate groups having greater affinity for the aqueous phase and leading to an increase in the hydrodynamic volume. It has also been observed that a decrease in the interfacial tension of the seed improves the mixing of the two polymers, thus nearing the formation of IPNs prepared from miscible pairs of polymers. Thus, with the inclusion of 6% MAA in the seed and processing of the LIPN at a higher pH, the composite IPN particles (with one broad transition ranging from 0 to 65°C and another broad one corresponding to the crosslinked polystyrene) were obtained.

Tensile Strength and Hardness

The hardness values of the hot-pressed samples of the different latexes are presented in Figure 5. The Shore-D hardness values also increase from 35 to 52, with an increase in MAA concentration from 0 to 6%, showing improved mixing of the two polymers.

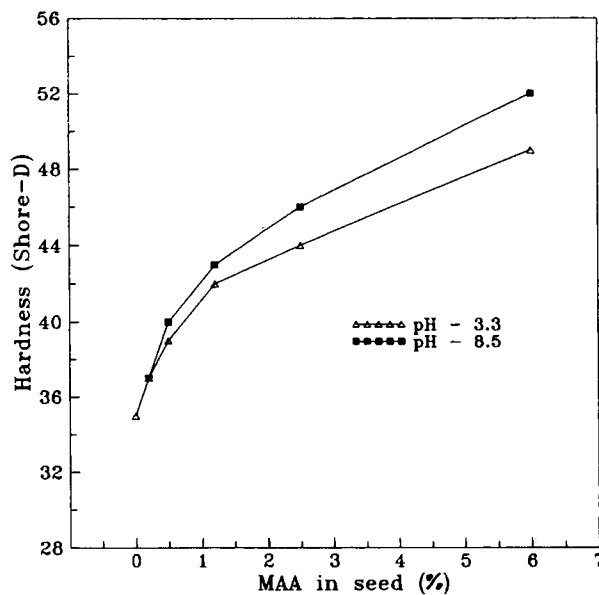


Figure 5 Hardness values of the hot-pressed samples of LIPNs prepared with different amounts of MAA in the seed and at two different pH values.

The tensile strength also increases with increasing acid concentration. Variations in tensile strength of LIPNs processed at two different pH values, with the different acid concentrations, are shown in Figure 6. The elongation remains almost constant for all the latexes except latexes prepared from seeds having 6% MAA. This indicates that the crosslinked polyacrylate forms the continuous phase, wherein the crosslinked polystyrene microdomains are dispersed. The low elongation of the samples of A6S' may be due to the higher T_g values of the seed. In our present work, we have demonstrated that by preparing the LIPNs from seed having 6% MAA and at higher pH values with crosslinked polysty-

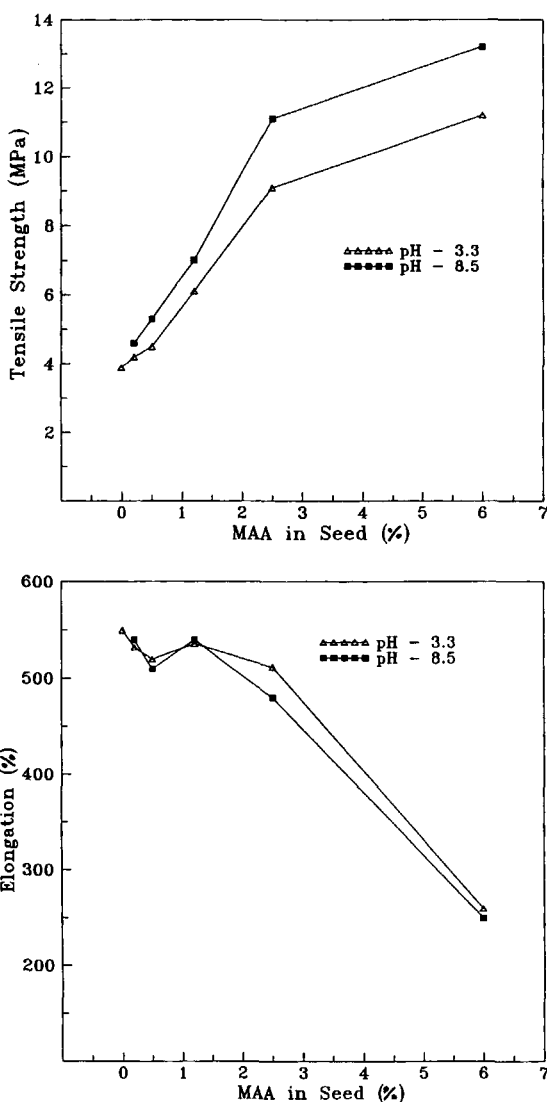


Figure 6 Strength properties of the films of LIPNs prepared with different amounts of MAA in the seed and at two different pH values.

rene, the tensile strength of the film can be improved and it was possible to achieve values up to 13 MPa.

The significant results of the present study can be summarized as follows:

- The LIPNs produce transparent films at higher pH (8.5), with the minimum amount of 1.2% MAA in the seed.
- An increase in MAA in the seed decreases the interfacial tension between the particles and the water, reduces the hydrophobic core volume, and thus enhances the mixing of the two incompatible polymers (viz., polyacrylates and polystyrene).
- LIPNs with multiphase morphology can be obtained if the LIPNs are processed at lower and higher pH values with minimum MAA concentrations of 0.5 and 0.2%, respectively, in seeds.
- Tensile strength and hardness also increase with an increase in acid concentration as a result of increased mixing of the two polymers.

The present work clearly shows that the inclusion of MAA, even in small amounts (e.g., 1.2%), in the seed can influence final properties—for example, it can lead to a reduction in interfacial tension and better coalescence of latex particles, which in turn can lead to transparent films with a change of pH from low to high values.

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