

Latex Interpenetrating Polymer Networks Based on Polyacrylates and Network II Comprised of Poly(styrene-co-methyl methacrylate)

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SYNOPSIS

Latex interpenetrating polymer networks (LIPNs) were prepared using the polyacrylate seed, comprising of *n*-butyl acrylate, methyl methacrylate, tetraethylene glycol dimethacrylate in the ratio of 55 : 45 : 0.7 by weight (wt), and with different amounts of methacrylic acid (MAA) ranging from 0 to 6% on monomer wt. basis and the copolymer of styrene and methyl methacrylate (53 : 47 by wt) as the second network, to study the effect of the increase in the hydrophilicity of the seed on the final latex properties. The swelling and polymerization of mixture of the monomers II and the crosslinker II were done at two different pHs (viz. 3.3 and 8.5). All the latexes yielded continuous films upon drying at ambient temperature. All the LIPNs possess multiphase morphology. Tensile strength and shore-D hardness have been found to increase with an increase in MAA concentration in the seed. Different properties like film formation, glass transition temperature, and tensile strength of the LIPNs thus prepared have been compared with the set of LIPNs produced using the same seed, but with polymer II comprising of the either polystyrene (PS) or poly-MMA (PMMA) homopolymer. The LIPNs having the copolymeric combination showed the combined effect of both the constituents. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The industrial production of latexes involves several different polymer families, each with its own field of applications. The composite latex particles are an extremely important class of materials known to exhibit a variety of unique properties, arising out of their particle morphologies. Interpenetrating polymerization is a mode of blending two or more polymers to produce a mixture in which phase separation is not as extensive as it would be in normal blending or mixing. This results in multiphase morphology. Latex interpenetrating network of polymers (LIPNs) forms a special category of the composite latex particles and is being given wide importance in recent times. LIPNs are produced by two-stage emulsion polymerization, i.e., the crosslinking of the second network in the presence of the

crosslinked seed.¹⁻³ The final latex particles possess a wide range of morphologies depending on the sequence of polymerization, composition, relative hydrophilicity of the polymers, solubility of polymer I in monomer II, and amount of crosslinking.³⁻¹³

The monomers, such as styrene (St) and methyl methacrylate (MMA) having different solubility in water, thus have different modes of initiation in emulsion polymerization. Styrene polymerizes by micellar nucleation whereas MMA undergoes polymerization by micellar aqueous phase nucleation.¹⁴

The mode of addition of monomer II also influences the morphological characteristics of the final latex particles. The addition of St monomers by the absorption method reduces the amount of polystyrene (PS) at the surface as compared to the dropwise monomer addition in a two-stage latex (TSL) system of poly-MMA and PS (PMMA-PS). But, irrespective of the mode of addition of MMA monomers, PMMA has been found to be localized mainly at the surface of the particles due to the high hydrophilic nature, in the system of PS-PMMA.¹⁵

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Table I General Recipe Used to Produce LIPNs

Ingredient	Amount
Water	70%
Sodium dodecyl sulphate	1.2 parts per hundred of monomer (phm)
Potassium persulfate (PPS)	0.4 phm at both stages
Total solids	30%
Seed (BA : MMA : TEGDM : MAA)	55 : 45 : 0.7 : variable (by wt)
Polymer II (St. : MMA : DVB)	53 : 47 : 2

In the present work, the copolymer having the azeotropic composition¹⁶ of the above two polymers (MMA-St, 47 : 53 by wt) has been selected as the polymer II to study the effect of this copolymer on the LIPN formation using seeds with varying hydrophilic nature. LIPNs have been characterized for the formation of continuous films, their strength, and the change in the glass transition temperature (T_g). The above-mentioned properties of the two LIPNs prepared with seeds possessing two extremes in the hydrophilicity have been compared to that of the similar LIPNs produced only with the constituent homopolymers, such as PS and PMMA as polymer II.

EXPERIMENTAL

Different polyacrylate (PA) seeds were prepared with *n*-butyl acrylate (BA), MMA, and tetraethylene glycol dimethacrylate (TEGDM) in the ratio of 55 : 45 : 0.7 on wt basis and different amounts of MAA (0, 2.5, and 6% on wt basis). LIPNs were prepared using the different seeds and poly(MMA-co-St) as polymer II as described previously.¹⁷ The swelling of the seed and polymerization of the mixture of monomer II and crosslinker II has been done at two different pHs (viz. 3.3 and 8.5). The general recipe and the set of variables employed to prepare different LIPNs using seeds with vary-

Table II Process Variables to Produce the Various LIPNs

Code	MAA in seed (%)	pH
A0.0MS3	0.0	3.3
A2.5MS3	2.5	3.3
A2.5MS9	2.5	8.5
A6.0MS3	6.0	3.3
A6.0MS9	6.0	8.5

ing hydrophilicity are given in Tables I and II, respectively.

The copolymer having the azeotropic composition of the second component of the LIPN, namely poly(MMA-co-St) has also been synthesized by batch emulsion polymerization technique.

The characterization of T_g , tensile strength, and hardness of the final latexes were carried out as mentioned earlier.¹⁷

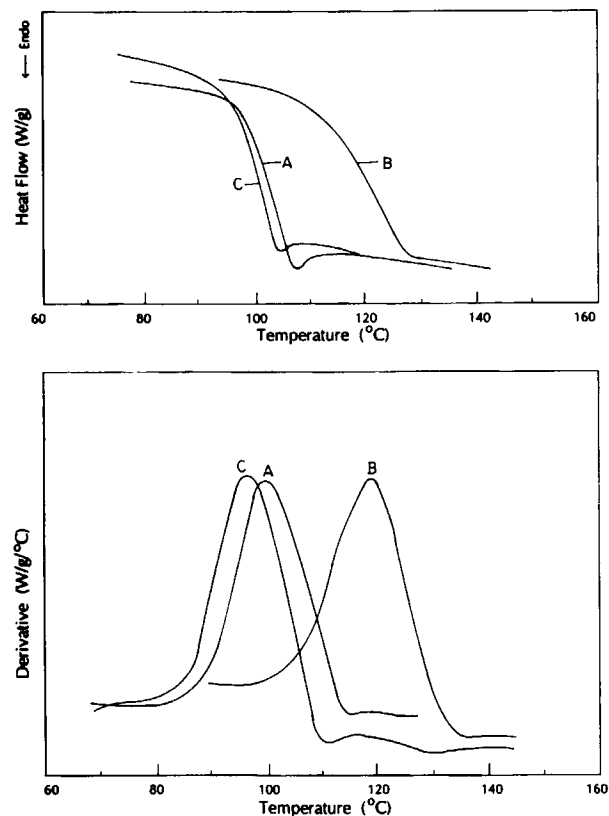


Figure 1 DSC curves showing the lower T_g of the homogeneous copolymer prepared from MMA and St, than the corresponding homopolymers: (a) T_g of PS, (b) PMMA, and (c) poly(MMA-co-St).

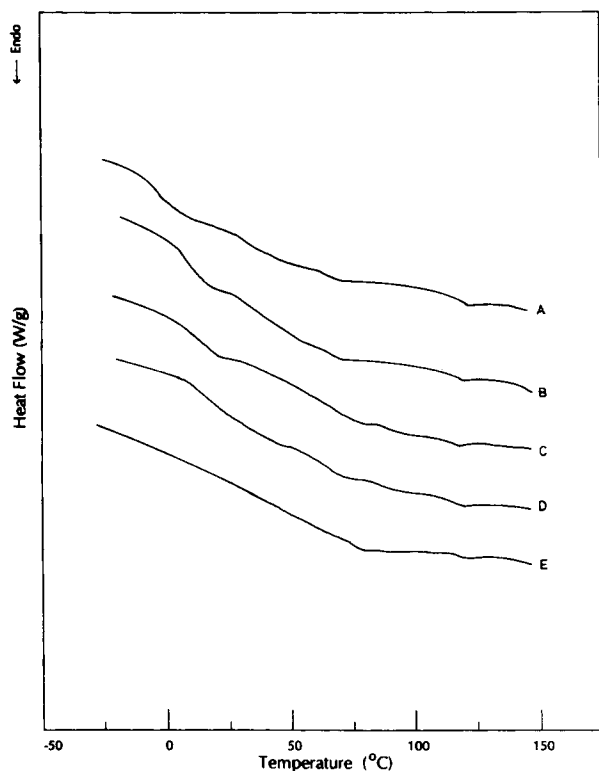


Figure 2 DSC curves of the LIPNs prepared with different amount of MAA in the seed and polymer II, comprised of the poly(MMA-co-St) at two different pHs. MAA concentration in the seed: at lower pH—(a) 0, (b) 2.5, and (d) 6; at higher pH—(c) 2.5 and (e) 6.

RESULTS AND DISCUSSION

The differential scanning calorimetric (DSC) curve of the poly(MMA-co-St) has been shown along with the homopolymers of the individual components in Figure 1. The single T_g at 97°C ascertains the retention of the azeotropic composition in the polymer as well. The T_g of the copolymer has been found to be less than the two individual polymeric components. This may be mainly due to the sequence distribution of the two monomeric units in the chain.^{18,19} The presence of styrene at the adjacent sites gives greater freedom of rotation of MMA in the copolymer, thus resulting in the reduction of T_g .

The DSC curves of the different LIPNs thus prepared have been shown in Figures 2 and 3. The multiple transitions observed in all the LIPNs indicate the presence of multiphase morphology. It has been observed that the mixing of the two polymers increases with the increase in MAA concentration in the seed and also at high pH. The increase in the hydrophilicity at a high pH of the seed highly influ-

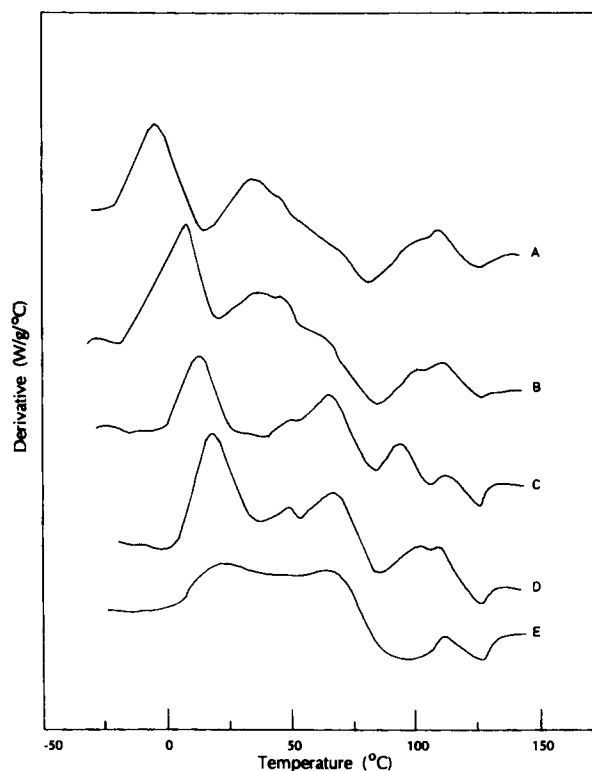


Figure 3 Derivative of heat flow w.r.t. temperature of Figure 2.

ences the morphology/mixing of the two polymers as has been observed with the LIPNs prepared with the similar kind of seeds and with PMMA as the second polymer. This effect can be seen by comparing the DSC curves of the LIPNs processed at low and high pH using the same seed [Fig. 3, (b)–(e)]. The curves show that the lower T_g pertaining to the seed has been shifted to the higher value, indicating the better mixing of the two polymers while the LIPNs were processed at a higher pH than at a lower one. The latex prepared at a pH of 8.5 using the seed having 6% acid showed a very broad transition,

Table III Strength Properties of the Films and the Hardness Values of the Hot-Pressed Samples of PA/poly(MMA-co-St.)

LIPN	Tensile Strength (MPa)	Elongation (%)	Hardness (Shore-D)
A0.0MS3	4.0	522	39
A2.5MS3	8.9	468	45
A2.5MS9	10.9	492	47
A6.0MS3	11.5	260	51
A6.0MS9	12.9	280	54

Table IV Comparison of the Different Properties of the LIPNs Based on PS, PMMA, and Poly(MMA-co-St.) as Polymer II

LIPN	Tensile Strength (MPa)	Elongation (%)	Hardness (Shore-D)	Film Characteristics
A0M3	—	—	32	Discontinuous
A0S3	3.9	550	35	Continuous, tough
A0MS3	4.0	522	39	Continuous, tough
A6M9	—	—	52	Continuous, brittle
A6S9	13.2	240	52	Continuous, tough
A6MS9	12.9	280	54	Continuous, tough

indicating the presence of morphology with microheterogeneity.

The strength properties and the hardness of the different latexes are given in Table III. Tensile strength and shore-D hardness have been found to be increased from 4 to 12.9 MPa and 39 to 54, respectively, with an increase in the acid concentration from 0 to 6%. This fully supports the above observation of better mixing of the two polymers to yield high strength materials.

Comparison of LIPNs with LIPNs Having the Constituent Homopolymers as Polymer II

As the LIPNs have been prepared having the copolymeric combination of MMA-St as polymer II, it is worthwhile to compare the different properties like the T_g , tensile strength, and nature of the film formation to those of LIPNs prepared from the same seed with the homopolymers of PS and PMMA as polymer II. The various LIPNs prepared with the seeds possessing the two extreme ends of hydro-

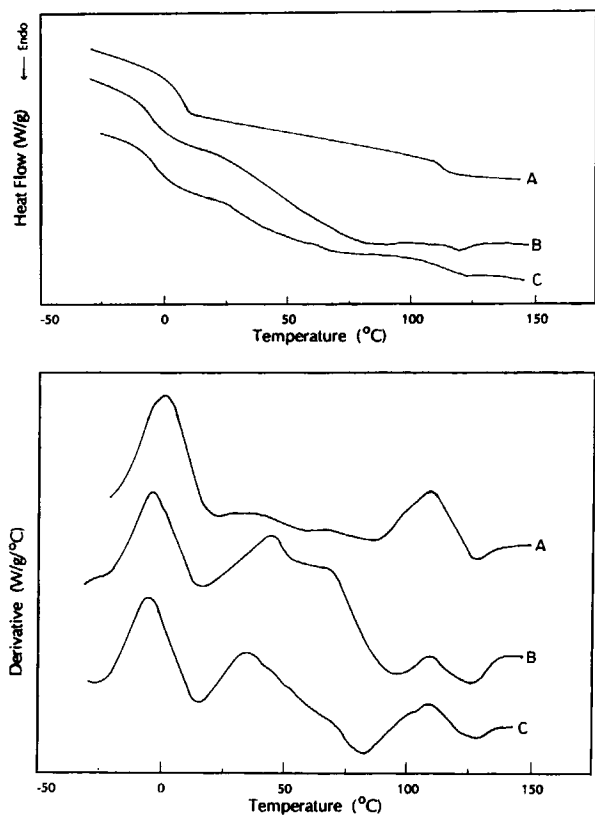


Figure 4 DSC curves of the LIPNs prepared at a pH of 3.3, using seed without MAA and polymer II, comprised of (a) PS, (b) PMMA, and (c) poly(MMA-co-St).

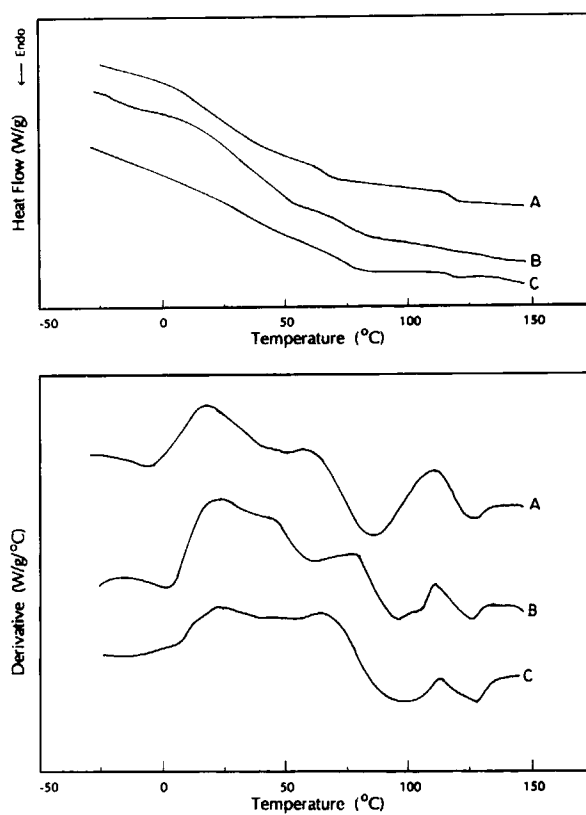


Figure 5 DSC curves of the LIPNs prepared at a pH of 8.5, using seed with 6% MAA and polymer II, comprised of (a) PS, (b) PMMA, and (c) poly(MMA-co-St).

philicity in the above study, such as the seed without MAA and the seed with 6% MAA and at a pH of 8.5, have been chosen for the comparison.

It has been observed that LIPNs produced using the seed without MAA and polymer II as PMMA produced discontinuous films and the continuous films were obtained with the MAA content greater than 2.5% in the seed. However, the all the PS and poly(MMA-co-St)-based LIPNs yielded continuous films. The PMMA-based films showed brittle fracture while performing the tensile tests, whereas, the other two sets of LIPNs showed formation of tough films, and the values of tensile strength and elongation are given in Table IV.

The DSC curves of the LIPNs prepared using the same seed and with different components constituting polymer II are given in Figures 4 and 5. The LIPNs shown in Figure 4 have been prepared with the PA seed without MAA and processed at the pH of 3.3. The latexes having PS, PMMA, and poly(MMA-co-St) as polymer II can be coded as A0S, A0M and A0MS, respectively, for the convenience of the discussion. It has been observed that A0S showed two distinct transitions corresponding to the individual components, indicating the phase separation between these two polymers, whereas the other two LIPNs (A0M and A0MS), showed multiple transitions, indicating better mixing leading to the formation of multiphase morphology.

Figure 5 represents the DSC curves of LIPNs prepared with seed having 6% MAA and at the pH of 8.5. Here also the latexes can be coded as A6S, A6M, and A6MS depending the polymer II for the discussion. One broad transition and another transition corresponding to the PS have been observed in A6S, indicating that even in the presence of the high hydrophilic seed, discrete PS domains are present, indicating phase separation. But it has been observed that both A6M and A6MS produced LIPNs having very broad transitions.

CONCLUSIONS

The increase in the hydrophilicity of the seed increases the mixing of the two polymers and the increase in the tensile strength. Thus, it has been seen that LIPNs produced with the copolymeric combination produced tough films like that of the styrene-based latexes, whereas the glass transition behavior/mixing characteristics of the two polymers has been influenced much by the MMA in the copolymer. Thus, LIPNs of the copolymeric combination have the synergistic

effect of the constituent homopolymers in the network. The latex prepared at a pH of 8.5 using the seed having 6% MAA showed a very broad transition, indicating the presence of morphology with microheterogeneity. The broad transition indicates that these systems can be used as the noise and vibration damping materials over a wide temperature range.

REFERENCES

1. L. H. Sperling, *Interpenetrating Polymer Networks and the Related Materials*, Plenum Press, New York, 1981.
2. L. H. Sperling, *J. Polym. Sci., Macromol. Rev.*, **12**, 141 (1977).
3. D. Klemperer and L. Berkowski, *Encyclopedia of Polymer Science and Technology*, H. F. Mark, N. M. Bikales, C. G. Overberger, and G. Menges, Eds., Vol. 8, 1989, p. 279.
4. M. S. El-Aasser, T. Makgawinata, and J. W. Vanderhoff, *J. Polym. Sci., Polym. Chem. Ed.*, **21**, 2363 (1983).
5. D. J. Hourston, R. Satgurunathan, and H. C. Varma, *J. Appl. Polym. Sci.*, **34**, 901 (1987).
6. D. J. Hourston, R. Satgurunathan, and H. C. Varma, *J. Appl. Polym. Sci.*, **33**, 215 (1987).
7. J. W. Vanderhoff, H. R. Sheu, and M. S. El-Aasser, NATO ASI Ser., Ser. C. (*Scientific Methods for the Study of Polymer Colloids and Their Applications*), **303**, 529 (1988).
8. M. Narkis, Y. Talmon, and M. S. Silverstein, *Polymer*, **26**, 1359 (1985).
9. M. S. Silverstein, Y. Talmon, and M. Narkis, *Polymer*, **30**(3), 416 (1989).
10. M. S. Silverstein and M. Narkis, *J. Appl. Polym. Sci.*, **40**, 1583 (1990).
11. V. L. Dimonie, M. S. El-Aasser, A. Klein, and J. W. Vanderhoff, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 2197 (1984).
12. D. I. Lee, T. Kawamura, and E. F. Stevens, NATO ASI Ser., Ser. E. (*Future Dir. Polym. Colloids.*), **138**, 47 (1987).
13. S. Muroi, H. Hashimoto, and K. Hosoi, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 1365 (1984).
14. J. W. Vanderhoff, *Chem. Eng. Sci.*, **48**(2) 203 (1993).
15. M. Okubo, A. Yamada, and T. Matsumoto, *J. Polym. Sci., Polym. Chem. Ed.*, **16**, 3219 (1980).
16. R. Leicht and J. Fuhrmann, *J. Polym. Sci., Polym. Chem. Ed.*, **21**, 2222 (1983).
17. P. Nagarajan, C. K. Mital, and M. K. Trivedi, *J. Appl. Polym. Sci.*, to appear.
18. N. W. Johnston, *J. Macromol. Sci.-Rev. Macromol. Chem.*, **C14**(2), 215 (1976).
19. D. Braun, B. Bohringer, and N. Eidam, *Polym. Bull.*, **21**, 63 (1989).

Received January 18, 1995

Accepted April 17, 1995