

Latex Interpenetrating Polymer Networks Based on Polyacrylates and Polystyrene. I. Synthetic Variations

P. NAGARAJAN, C. K. MITAL, and M. K. TRIVEDI*

Department of Chemical Engineering, Indian Institute of Technology, Bombay-400 076, India

SYNOPSIS

Two different acrylic copolymeric seeds (with 0 and 6% methacrylic acid), having very high variation in the hydrophilicity, were used to develop latex interpenetrating polymer networks (LIPNs) with polystyrene as polymer II, to study the effect of the mode of monomer II addition, such as continuous monomer addition and absorption method/swelling the seed with monomer II, followed by polymerization. Linear combination of the two polymers were also prepared to understand the above effects on the final properties such as the glass transition temperature, hardness, and tensile strength of the different samples prepared. The results showed that the addition of styrene monomer by the absorption method and the increase in hydrophilicity of the seed improved the mixing of the two polymers, thus resulting in producing LIPNs possessing broad glass transition with high strength and hardness. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Interpenetrating polymer networks are combinations of two or more crosslinked polymers. Often they exhibit multiphase morphology, resulting in superior properties as compared to homopolymers or linear blend or the homogeneous copolymer prepared from the same basic components.¹⁻³

Latex interpenetrating polymer networks (LIPNs) are produced using the two-stage latex (TSL) emulsion polymerization method, namely (a) the polymerization or crosslinking of monomer I and (b) the above latex is subsequently used as a seed for the polymerization or crosslinking of monomer II. LIPNs have been claimed by many workers to exhibit complex morphologies including the core-shell and cellular structures. The sequential emulsion polymerization procedure can yield a wide range of morphologies depending on the mode of addition of monomer II, sequence of polymerization, composition, relative hydrophilicity of the polymers, mobility of the polymer, solubility of polymer I in monomer II, degree of crosslinking, and degree of grafting.⁴⁻¹⁴

Narkis et al.¹⁵ reported that addition of styrene monomer to a polyacrylate seed latex yielded elastomers having significant strength properties than the elastomers produced by the reversal of the sequence of monomer addition, i.e., addition of acrylic monomer to polystyrene seed. These have been attributed to the different morphologies arising from the two different preparation methods.¹⁶ Dynamic mechanical analysis showed two distinct glass transition (T_g) temperatures corresponding to the individual T_g 's indicating the high incompatibility of polyacrylate and polystyrene.

The selection of more hydrophilic seed for preparing a linear combination of the two polymers by TSL emulsion polymerization results in the formation of polymer II dispersed in polymer I, if polymer I has a very high molecular weight; if the polymer I is of low molecular weight or a soft polymer and polymer II is more hydrophobic and incompatible, then an inverse core-shell formation takes place.¹²

Most of the LIPNs reported in the literature were prepared by polymerizing the second monomer by continuous addition of the mixture of monomer and crosslinker. Hourston et al.¹⁷ reported that the increase in swelling time of seed by the mixture of monomer II and crosslinker II enhanced the mixing of the two polymers in the LIPN system of

*To whom correspondence should be addressed.

poly(ethyl acrylate)/poly(ethyl methacrylate). The mixing resulted in the inward shifting of the respective T_g 's.

LIPNs based on acrylic copolymer seed without methacrylic acid (MAA) and with this monomer (6% on weight basis) and the polystyrene as polymer II were developed by adding styrene monomer either by continuous monomer addition or absorption (swelling of the seed with the monomer II for a specified time followed by polymerization). The effect of the different mode of addition was followed by the change in the properties such as glass transition temperature (T_g), tensile strength, and hardness of the LIPNs.

EXPERIMENTAL

The general recipe and the process variables of LIPNs prepared through different modes of addition of second monomer are given in Tables I and II, respectively. Linear combination of the two polymers with the two different seeds have also been prepared by two-stage latex emulsion polymerization method to demonstrate the role of network in the polymers in hindering the phase separation in interpenetrating networks (IPNs).

Preparation of LIPNs

To the distilled, deaired, and stirred water in the kettle, kept in a thermostated water bath, the surfactant (sodium dodecyl sulfate) was added, followed by the addition of a first dose of persulfate solution. The temperature was raised to $75 \pm 2^\circ\text{C}$ and the mixture of monomer I and crosslinker I of the component I was added dropwise over a period of 3 h. The temperature was maintained for an additional 3 h to allow the polymerization to go to completion.

Table I General Recipe for the Formation of LIPN

Batch size, 250 g
Distilled water, 70%
Sodium dodecyl sulfate, 1.2 parts per hundred of monomer (phm)
Potassium persulfate, 0.4 phm on both stages
Total solids, 30%
Network I, MMA : BA (45 : 55) + MAA (0 and 6% on wt. basis)
Crosslinker I, TEGDM (0.7% on wt. basis)
Network II, styrene
Crosslinker II, DVB (2.0% on wt. basis)
Network I-II, 65 : 35

Table II Process Variables for the Preparation of LIPNs with Different Modes of Addition of Second Monomer

Code	Type of Latex	MAA in Seed (wt %)	Monomer Addition	pH
LO	Linear	0	Absorption	3.3
L6	Linear	6	Absorption	8.5
B0	IPN	0	Absorption	3.3
B6	IPN	6	Absorption	8.5
C0	IPN	0	Continuous	3.3
C6	IPN	6	Continuous	8.5

Then the contents were cooled to room temperature to get the seed polymer.

Latex IPNs were prepared by adding the mixture of monomer II and crosslinker II to the seed either by the continuous monomer addition technique or the absorption technique. In the continuous addition technique, the second dose of persulfate solution was added at room temperature, followed by the dropwise addition of monomer II along with crosslinker II at $75 \pm 2^\circ\text{C}$ for 3 h, and the temperature was maintained for another 3 h for the completion of the polymerization.

In the absorption technique, the following sequence was followed: The seed was swelled with the mixture of monomer II and crosslinker II for a definite period of time (4 h at 30°C) and adding the persulfate solution just before heating the contents to the polymerization temperature. The temperature was maintained at 80°C for 4 h for the completion of the polymerization.

The pH of the seed latex was found to be approximately 3.3. The LIPNs without MAA in the seed were prepared at low pH (approx. 3.3) and pH of the seed having 6% MAA was adjusted to 8.3–8.6 with the addition of NaOH before swelling the seed with the styrene monomer.

Characterization of the Latexes

Glass Transition Temperature (T_g)

The pure dry polymers were obtained from the latexes by coagulating the emulsion by adding acetic acid; the coagulum was continuously washed with water to remove the surfactants till the turbidity vanishes; followed by drying the polymers at 60 – 65°C in the vacuum oven under 10 mm Hg for 2 h. The polymers were analyzed for T_g with the help of DuPont Instruments 910 (DSC) equipped with a thermal analyzer 2000. The temperature was scanned from -50 to 150°C at a heating rate of

10°C/min. The normal and derivative differential scanning calorimetry (DSC) curves have been reported after giving a smoothing criteria of 0.3 min and 12°C, respectively.

Tensile Strength and Hardness

Latex films of 0.2–0.23 mm thickness were obtained by casting the latex (at a pH of 9.0) carefully onto clean, grease-free glass plates, and were dried at room temperature ($\sim 35^\circ\text{C}$). After conditioning for 30–35 days, time sufficient for the completion of further gradual coalescence, the polymeric films were subjected for the tensile test at 30°C using J.J. Lloyds tensometer, model T2001. The crosshead speed was maintained at 100 mm/min. The tensile strength of each sample has been reported as an average of several readings. Hardness of the hot pressed samples was measured using Shore type-D durometer.

RESULTS AND DISCUSSION

Latexes form continuous film, upon drying at room temperature, provided that the T_g of the latex is less than the room temperature. The formation of the continuous film from all the LIPNs at ambient temperature indicates that xPS domains are dispersed in the continuous xPA matrix.

The T_g of two seeds having 0 and 6% MAA were found to be -2 and 14°C as determined by DSC. It is well known that the first derivative of heat flow with respect to temperature of the normal DSC curve gives the sharp peak reflecting the transition. The DSC curves have been presented in the Figures 1 and 2. Both the linear polymer combinations (L0 and L6) show only the respective individual T_g 's indicating the complete phase separation of the two polymers (PA and PS). The other latexes prepared with the seed without MAA also showed two distinct T_g 's, emphasizing the complete phase separation in all the cases. Though the two polymers are in the phase separated form in B0 and C0, they are still considered as IPNs. In these LIPNs, the PS domains interconnected by DVB are dispersed in crosslinked polyacrylate (xPA) matrix. The higher T_g of the xPS observed in B0 and C0 as compared to the linear PS may be due to the crosslinking of polystyrene.

The hardness, tensile strength, and elongation of the various polymeric compositions (Table III) showed a lot of difference in all these latexes. The significant higher tensile strength, shown more in C0 and B0 (3.6 and 3.9 MPa, respectively) than in L0 (3.0 MPa), may be mainly due to the reinforce-

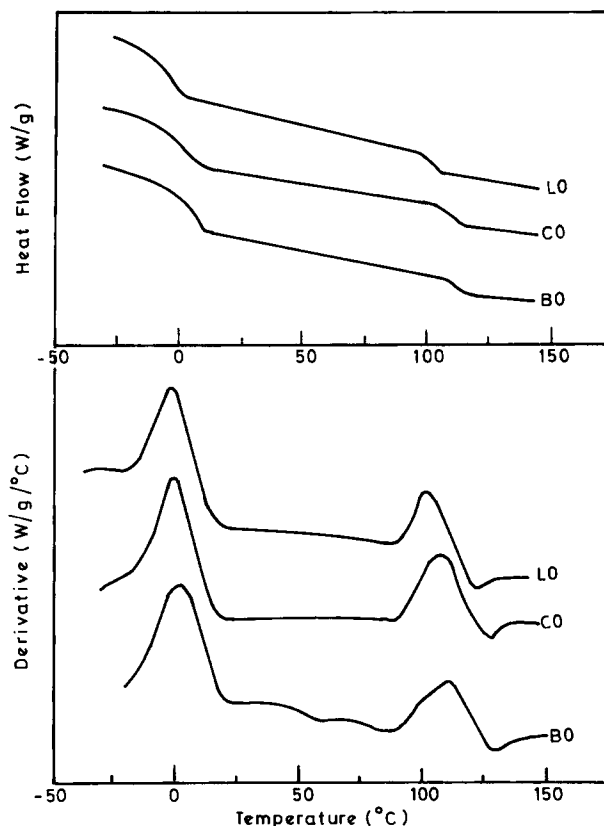


Figure 1 DSC curves of the latex IPNs, showing the variation in the mode of addition of styrene monomer to polyacrylate seed without MAA: (a) normal curve and (b) derivative curve.

ment of PS interparticle ties by DVB. Hardness of polymeric materials is generally defined as the resistance to local deformation and this can be related to the modulus, strength and elasticity. As the hardness of the C0 (Shore-D 31) is almost in the same range as of the other two LIPNs (Shore-D 30 and 35 for L0 and B0 respectively), it can be inferred that latexes of C0 do not have too thick xPS shells, which would have otherwise given higher hardness values.

Different properties of the three latexes prepared from the seed having 6% acids (Table II, L6, C6, and B6) show a marked difference in both the mode of preparation as well as the importance of network structure in preventing the phase separation. Two distinct T_g 's corresponding to the individual components have been observed in L6. However, C6 also showed two distinct peaks, slight broadening of the peaks at both the glass transitions and few more peaks in between the individual transitions indicate certain extent of mixing between the two polymers [Fig. 2(b), C6]. But one very broad transition from 0 to 60°C and another slightly broader peak than the L6 peak at higher temperature (corresponding

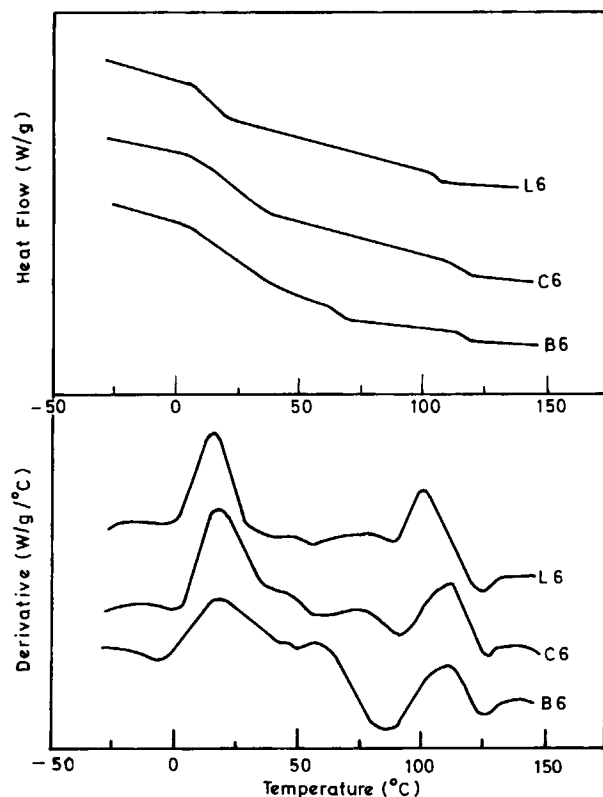


Figure 2 DSC curves of the latex IPNs, showing the variation in the mode of addition of styrene monomer to polyacrylate seed having 6% MAA: (a) normal curve and (b) derivative curve.

to the xPS) are observed in B6 [Fig. 2(b)]. The first broad transition clearly indicates that the phase separation is highly reduced due to network formation, resulting in microheterogeneous morphology in the B6 LIPN. The presence of the transition peak at the high temperature indicates that still some amount of discrete xPS domains are present apart from the microheterogeneous phase.

The microscopic study of the latex in the cold-stage transmission electron microscope (TEM) and freeze-fractured hot-pressed sample by scanning electron microscope (SEM) showed the absence of PS homopolymer domains in the LIPN system of 75 xPA/25 xPS. Despite the absence of the PS domains on the order of 50 nm in the LIPN system of 75 xPA/25 xPS, investigated by both TEM and SEM,¹⁵ the dynamic mechanical spectroscopy (DMS) and DSC showed that two distinct transitions corresponding to the individual components was reported by Silverstein et al.¹⁶ Based on the microscopic studies and the thermal analyses, they suggested that the PS domains detected by thermal analysis must be at least of the order of 5 nm. In our work, as it has been evident from the broad

transition in B6, the mixing of the two polymers has been tremendously enhanced. This is due to the high hydrophilic seed and the addition of the mixture of styrene and DVB by following the absorption method. The PS dispersed phase might be of the order of a few nanometers in B6.

It has been already mentioned that the TSL leads to an inverted core-shell latex if the seed is more hydrophilic than polymer II and both the polymers are incompatible. Very low hardness value (Shore-D 31) of the hot-pressed sample of L6 indicates the formation of "inverted core-shell," showing the PA continuous matrix. The lowest tensile strength (8.7 MPa) among the three latexes prepared with 6% acid in the seed also reflects the structure of the film with xPA shells forming a continuous matrix containing embedded xPS cores which might be acting like a glassy filler in polyacrylate matrix in L6.

The tensile strength (13.2 MPa) and the hardness (Shore-D 52) of B6 are the highest among all the polymers. This clearly indicates the improved mixing of the two polymers, resulting in the high reinforcement of the xPA matrix by xPS, with a dual-phase continuity in B6. Since the xPS might be localized mainly at the subsurface in C6, the tensile strength observed (11.4 MPa) is in between that of the L6 and B6 (8.7 and 13.2 MPa, respectively).

CONCLUSIONS

The following points emerged noteworthy from this work.

Phase separation is imminent in mixing two highly incompatible polymers such as polyacrylate and polystyrene, and it takes place as the polymerization proceeds. The comparison of the different properties of the linear combinations and the LIPNs prepared, either by the dropwise addition or the ab-

Table III Strength Properties of the Films and the Hardness Values of the Hot Pressed Samples of LIPNs Prepared by Different Modes of Addition of Monomers

Code	Type of Latex	Tensile Strength (MPa)	Elongation (%)	Hardness (Shore-D)
L0	Linear	3.0	640	30
L6	Linear	8.7	324	31
B0	IPN	3.9	550	35
B6	IPN	13.2	240	52
C0	IPN	3.6	420	31
C6	IPN	11.4	212	42

sorption method of the mixture of styrene and divinyl benzene, showed that the incorporation of the crosslinking decreases the phase separation with the formation of multiphase morphology in IPNs. This phenomenon enhanced the tensile strength of the films and the hardness of the hot-pressed samples.

The LIPNs prepared using the seed with 6% MAA and at high pH showed multiple transitions exhibiting multiphase morphology in contrast to the LIPNs produced using the seed without MAA, which showed two distinct transitions corresponding to the individual components, exhibiting the complete phase separation of the two polymers. The improved mixing of the two polymers as observed in the former are mainly attributed to the decrease in the interfacial tension and the reduction in the hydrophobic core volume. The absorption method produces LIPNs of higher tensile strength (approx. 13.2 MPa) and broad glass transition, indicating better mixing of the two polymers as compared to LIPNs prepared by the continuous monomer addition technique.

Hence, it is clearly evident that by the proper selection of the method of preparation and with high hydrophilic polymer as seed, the mixing of the two incompatible polymers can be improved to get LIPNs with broad glass transition temperature and films of high strength.

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., Wiley, New York, Vol. 8, 1989, p. 279.
4. S. Lee and A. Rudin, *J. Polym. Sci., Polym. Chem. Ed.*, **30**, 865, (1992).
5. R. A. Dickie, M. F. Cheng, and S. Newmann, *J. Appl. Polym. Sci.*, **17**, 65 (1973).
6. M. S. El-Aasser, T. Makgawinata, and J. W. Vanderhoff, *J. Polym. Sci., Polym. Chem. Ed.*, **21**, 2363 (1983).
7. T. I. Min, A. Klein, M. S. El-Aasser, and J. W. Vanderhoff, *J. Polym. Sci., Polym. Chem. Ed.*, **21**, 2845 (1983).
8. M. Okubo, Y. Katsuta, and T. Matsumoto, *J. Polym. Sci., Polym. Lett. Ed.*, **20**, 45 (1982).
9. M. Okubo, S. Yamaguchi, and T. Matsumoto, *J. Appl. Polym. Sci.*, **31**, 1075 (1986).
10. V. L. Dimonie, M. S. El-Aasser, A. Klein, and J. W. Vanderhoff, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 2197, (1984).
11. L. W. Morgan, *J. Appl. Polym. Sci.*, **27**, 2033 (1982).
12. D. I. Lee and T. Ishikawa, *J. Polym. Sci., Polym. Chem. Ed.*, **21**, 147 (1983).
13. D. I. Lee, T. Kawamura, and E. F. Stevens, *NATO ASI Ser., Ser. E. (Future Dir. Polm. Colloids.)*, **138**, 47 (1987).
14. S. Muroi, H. Hashimoto, and K. Hosoi, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 1365 (1984).
15. M. Narkis, Y. Talmon, and M. S. Silverstein, *Polymer*, **26**, 1359, (1985).
16. M. S. Silverstein, Y. Talmon, and M. Narkis, *Polymer*, **30**, 416, (1989).
17. D. J. Hourston, R. Satgurunathan, and H. C. Varma, *J. Appl. Polym. Sci.*, **34**, 901, (1987).

Received December 20, 1994

Accepted May 8, 1995