Latex Interpenetrating Polymer Networks Based on High Styrene Resin

C. D. VO, R. P. BURFORD

Center for Applied Polymer Science, School of Chemical Engineering and Industrial Chemistry, The University of New South Wales, NSW 2052, Australia

Received 6 November 1998; accepted 26 February 1999

ABSTRACT: Latex interpenetrating polymer networks based on high styrene resin ("HSR300") as seed latex and polystyrene as the second polymer have been synthesized in different compositional ratios. The morphology of resultant materials was determined by field emission electron microscopy, atomic force microscopy, transmission electron microscopy, and by dynamic mechanical analysis. A polystyrene (PS) rich shell is observed in the latex particles. At higher second polymer ratios, a PS-rich shell can be resolved, but in general the majority of the polymer is incorporated as domains within each particle. The two crosslinked polymers are well intermeshed at the microscopic level, as reflected not only by morphology but also by single tan δ peaks in dynamic mechanical analysis (DMA) data. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 622–628, 1999

Key words: latex interpenetrating polymer networks; two-stage emulsion polymerization; high styrene resin

INTRODUCTION

Latex interpenetrating polymer networks (LIPNs) may be synthesized by two-stage emulsion polymerization in which seed latex of crosslinked polymer 1 is first prepared. Polymerization and crosslinking of monomer 2 takes place in the immediate presence of the seed latex.¹⁻⁶ Potential advantages of this family of polymers are simple synthesis methods and possible thermo-processing that is difficult for other crosslinked polymers. In addition, by using twostage emulsion polymerizations, one can generate various morphologies leading to different properties of resulting materials by carrying out the polymerization under different conditions.^{6–8}

LIPNs have been well documented for several decades.^{1–11} Narkis et al. have indicated for sty-

Correspondence to: R. P. Burford.

Contract grant sponsor: AUSAID.

Journal of Applied Polymer Science, Vol. 74, 622–628 (1999) © 1999 John Wiley & Sons, Inc. CCC 0021-8995/99/030622-07 rene-based LIPNs that the polymer network is formed within each latex particle, with sufficient protruding chains to enable binding during injection molding. Stiffer and potentially tougher materials from commodity monomers are therefore possible. In addition, solvent resistance of the resultant materials is improved significantly.⁶ Morphology of the resultant materials has been investigated by using several techniques.

Hourston and his coworkers have been successful in the preparation of a large number of LIPNs.^{8–11} They have reported that the mixing of the two components at the molecular level is found in different LIPN systems, as interpreted by the inward shift of glass transition temperatures (T_g s) corresponding to that of each polymer, the changes of tan δ magnitude in the intertransition region, as well as the width of the tan δ peak measured at half-peak height.^{8,9}

In Australia, Kemcor Pty. Ltd., produces a range of styrene butadiene copolymers by emulsion polymerization techniques. One member of this family,

Bound styrene (%)	85
T_{g} (°C)	69
Mean particle size (nm)	95
Solid content (%)	30

 Table I
 Properties of Latex HSR300

containing 15% butadiene and 85% styrene is known as "high styrene resin," (HSR300). The resins are colorless when molded. They are only moderately affected by aliphatic solvents but are sensitive to aromatic and chlorinated fluids. This category of resins finds application as a reinforcing agent in natural and synthetic rubbers in which the improvement in stiffness, hardness, abrasion resistance, and processing along with low specific gravity and good color are required.^{12,13} A synthetic rubber, under the code SBR1900, is made by blending HSR300 with conventional SBR emulsions having about 20% bound styrene. Here LIPNs are prepared, which are stiff, and so used formulations with high (>85%) bound styrene content. However, the 15% butadiene of the HSR300 not only serves to potentially toughen the product, but also to act as a marker when stained for electron microscope (EM) observation, thus allowing the development of structure to be followed.

In the present work, LIPNs having varying total styrene content are prepared by using a range of HSR/styrene, divinyl benzene (DVB) ratios. Properties of the LIPNs are characterized by dynamic light scattering, electron microscopy, and thermal analysis.

EXPERIMENTAL

Materials

Styrene was purchased from Aldrich (Milwaukee, WI). Divinyl benzene was supplied by Polysciences (Warrington, PA). They were freed of inhibitors by using basic activated aluminum oxide. Potassium persulphate ($K_2S_2O_8$) was used as the initiator. Sodium lauryl sulfate (SLS) was used as the stabilizer. Both were obtained from Ajax Chemicals, Sydney. Di-sodium hydrogen orthophosphate was used as a buffer (Merck, Kilsyth, Vic.).

High styrene resin latex (HSR300) was supplied by Kemcor (Altona, Vic.). Some of the properties of this latex are summarized in Table I.

Preparation of LIPNs

LIPNs were prepared by seeded emulsion polymerization techniques. The diluted HSR latex was charged in a stirred 250-ml glass flask, and purged with nitrogen for 30 min. A mixture of styrene and divinyl benzene was added to the seed latex and stirred under nitrogen for 1.5 h. After heating to 75°C, potassium persulphate solution was added. After monomers were added to the seed latex, a stabilizer solution was added to the seed latex, a stabilizer solution was added to the reactor every hour with level of surfactant below its critical micelle concentration (CMC). The reaction was carried out at 75°C for 6 h to allow the polymerization to be completed. Typical formulations are shown in Table II.

	-					
	1% DVB			10% DVB		
HSR solid/XPS	8/2	7/3	6/4	8/2	7/3	6/4
HSR latex (30%) (g)	100	100	100	100	100	100
Styrene (g)	7.4	12.7	19.8	6.8	11.7	18.2
DVB (50%) (g)	0.14	0.25	0.39	1.36	2.32	3.63
$K_{2}S_{2}O_{8}(g)$	0.11	0.19	0.3	0.11	0.19	0.30
Buffer (g)	0.50	0.50	0.50	0.50	0.50	0.50
$H_2O^a(g)$	10.0	10.0	10.0	10.0	10.0	10.0
SLS (g)	0.15	0.25	0.40	0.15	0.25	0.40
Buffer (g)	0.50	1.00	1.50	0.50	1.00	1.50
$H_2O^b(g)$	10.0	20.0	30.0	10.0	20.0	30.0

Table II General Recipe for LIPNs Based on HSR300

^a Water to dissolve initiator and buffer.

^b Water to dissolve surfactant and buffer.

Characterization of the Latexes

Particle Size and PSD

Latex average particle size and particle size distributions (PSD) were investigated by using a Malvern Instruments Autosizer 4700. The instrument was stabilized for at least half an hour before using. One drop of latex was diluted to about 50 ml. The sample cell was washed carefully with distilled water, diluted latex, and finally filled again with diluted latex.

Latex Particle Morphology

Two microscopic methods were used to observe the particle morphology of the LIPNs, Field Emission Electron Microscopy (FESEM) and Atomic Force Microscopy (AFM).

For FESEM, one drop of the latex was dropped on a copper slide and left to dry. The dried powder was coated with chromium using a Xenosput (Dynanvac, Sydney) coater prior to observation in a Hitachi S-900 unit (Tokyo, Japan).

For AFM, latex drops were placed on a glass slide and dried at room temperature. The sample was examined using a Nanoscope IIIa AFM (Digital Instruments, Santa Barbara, CA), using tapping mode.

Phase Morphology

The latex was dried to obtain a powder and stained with 2% aqueous osmium tetroxide solution for 24 h. The blackened powder was washed with distilled water to remove surplus reagent, dried, and embedded in epoxy resin for 12 h. The plastic mold was heated (65° C for 12 h) to fully cure the epoxy resin. The resulting block was trimmed and ultra-microtomed to produce sections of 60–90-nm thickness. The sections were restained with 2% aqueous osmium tetroxide solution for 1 h before washing with distilled water. Sections were examined using a Hitachi H-7000 TEM (Hitachi, Tokyo, Japan) to record phase structures/morphology.

Tg

Latex was coagulated using a hot 10% alum solution. The coagulated powder then was washed with distilled water to remove surfactant residues. The powder was oven dried before being fused at 230°C under pressure to form DMA test bars. The T_{g} s of the polymers were examined using a TA Instruments (New Castle, DE) Model



Figure 1 Particle size distribution of HSR300 latex and associated LIPNs with 10% DVB in the XPS.

983 DMA operating in resonant frequency mode and a heating rate of 10°C/min.

RESULTS AND DISCUSSION

Particle Size and Particle Size Distribution

The polydispersities of latex HSR300 and LIPNs as obtained using the Autosizer 4700 are shown in Figure 1. The equipment used provides data as a z average. The broad particle size distribution of the HSR300 latex is replicated for all associated LIPNs.

As can be seen from Figure 1, the shape of the curves representing the PSD of the LIPNs remains essentially constant. The curves shift to a higher particle size when the ratio of second polymer to the seed latex is increased. This is because the loci of the second polymerization are mainly on the seed latex particles and no significant new nucleation was generated during the second polymerization stage. This conclusion is confirmed later when TEM was used to investigate the phase morphology of latex particles. No particles with homogeneous crosslinked polystyrene (XPS) composition are found. The added surfactant was below the CMC. The role of the added surfactant is mainly to stabilize the latex during the reaction by absorbing on the surface of the latex particles rather than contributing to the formation of new nucleation. This is the primary criterion to ensure interpenetrating polymer networks formed in each latex particle.

Particle Morphology by FESEM and AFM

Particle morphologies of HSR300 and associated LIPNs examined by FESEM and AFM are shown in Figures 2 and 3, respectively. The scanning



(a)

(b)



(c)

Figure 2 FESEM micrographs (a), latex HSR300; (b), LIPN 80/20 HSR/XPS (10% DVB); (c), LIPN 70/30 HSR/XPS (10% DVB).

electron micrographs confirm the broad particle size distribution of HSR300 and associated LIPNs. The HSR, with only 15% butadiene, can retain its shape under vacuum during sample preparation. As the LIPNs have even less butadiene, individual particles are clearly visible, and have sizes consistent with the data obtained by Autosizer 4700.

Phase Morphology by TEM

HSR300 is stated by Kemcor to be prepared at high temperature ($>50^{\circ}$ C). This product was

found to be crosslinked, as evidenced by insolubility in various aromatic solvents. Full interpenetrating polymer networks could be obtained by introduction of a second polymer network of styrene crosslinked with DVB. In theory, styrene should dissolve well in a copolymer of styrene and butadiene. A homogeneous distribution of styrene in the HSR300 seed latex particle is expected. This is particularly expected, as the bound styrene content of HSR300 is very high.

The HSR contains ${\approx}15\%$ unconjugated butadiene and so has adequate unsaturation to stain







(d)



Figure 3 AFM micrographs (a), latex HSR300; (b), LIPN 80/20 HSR (10% DVB); (c), LIPN 70/30 HSR/XPS (10% DVB); (d), LIPN 80/20 HSR/XPS (1% DVB); (e), LIPN 70/30 HSR/XPS (1% DVB); (f), LIPN 60/40 HSR/XPS (1% DVB).

with OsO_4 , and in principle be resolved from the conjugated second PS. The sizes of particles of about 100 nm shown in transmission electron microscope (TEM) micrographs (Fig. 4) are in good agreement with our other experimental data. Lighter shells were seen, indicating the presence of second polymer. However, it is difficult to determine by TEM whether interwoven networks occur in such areas.

An XPS rich shell indicating that a fraction of the second polymer has phase separated was

formed on the seed latex particle (Fig. 4). The thickness of XPS is not distributed evenly, either for a given particle, or from one particle to another. This suggests that the styrene polymerization is not uniform. At the same ratio, LIPNs with higher DVB content show XPS rich outer layers more clearly than their counterpart with a lower DVB content.

The presence of the XPS rich shell could be attributed to the slow diffusion of monomer 2 into the glassy seed latex and the rapid increase





Figure 5 tan δ vs. temperature plot of HSR300 and associated IPNs.

shape of latex particle under processing conditions.

T_g

Initially DSC was used to measure T_{g} s for the various LIPNs, but rather weak and broad signals made interpretation ambiguous. DMA is a preferred method as large sample sizes give strong signals, and additional mechanical data is provided. For simplicity, the tan δ is only shown in Figure 5 (the E' is typically 2.5 to 2.7 GPa at 20°C).

As can be seen in Figure 5, only a single broad T_g could be observed in all cases. The width of tan δ of the IPNs at its half peak height is larger than that of HSR. Spreads in polymer composition, a broad molecular weight distribution, grafting, and possible surfactant residues are all probable contributing factors.

The T_{g} s for the HSR is in broad agreement with the nominal specification, if using the formula cited on page 189 of Morton's book.¹⁴

For the LIPNs, no separate T_g for the second polymer is found but an increase in T_g occurs. This suggests that some grafting may have occurred. In any event, the two polymers are rather miscible, with phase separation only appearing to occur at the nm level, as seen in Figure 4.^{15,16} The tan δ traces are broader as the HSR/XPS ratio is increased, indicating an increase in phase separation.

The T_g increase with styrene content is shown in Figure 6 for the LIPNs. The HSR alone has a T_g of 69°C. At the same HSR/XPS ratio, the LIPNs with 10% DVB show a higher T_g than their counterparts containing 1% DVB. The presence of higher DVB crosslinker decreases the mobility of polymer chains therefore increasing T_g .



(a)

(b)

Figure 4 TEM micrographs of LIPNs based on HSR300 (a), 60/40 HSR/XPS 1% DVB; (b), 60/40 HSR/XPS 10% DVB.

of the viscosity on the surface of the seed particle during the polymerization of styrene and DVB. Under the conditions of the polymerization, chains in the seed latex are nominally below or near the T_g and so monomer diffusion may be slow and non-Fickian conditions are possible. Some initial grafting at the surface is also likely.

The morphology is consistent with the model proposed by Narkis and coworkers.⁶ It corresponds to the system in which second polymer is miscible with the first polymer and no difference in hydrophilicity exists. Outer layers of the second stage polymer could be observed.

The presence of harder XPS on the outer layer of a latex particle enhances the retention of the



Figure 6 Dependence of T_g on styrene content of LIPNs based on HSR300 latex.

CONCLUSIONS

The synthesis and characterization of LIPNs based on commercial HSR300 and crosslinked polystyrene has been accomplished in different compositional ratios. The formation of new nucleation during the second polymerization has been controlled and the LIPNs have been found stable. An XPS rich shell can be resolved along with majority of XPS domains within each latex particle. A single broad T_g observed in the IPNs suggests that the two crosslinked polymers are well interwoven at the microscopic level. The resulting materials should be stiffer and have better solvent resistance than the HSR300.

The authors are grateful for help from M. Dickson, H. Liang, V.Piegerova, P. Marks, and B. Wolpensinger (electron microscopy); J. Starling (particle size analysis); and D. Forster and L. Muratore (thermal analysis). Financial support from AUSAID for C. D. V. is also recognized.

REFERENCES

- Sperling, L. H. Polymeric Multicomponent Materials; Wiley-Interscience: New York, 1997.
- 2. Sperling, L. H. Interpenetrating Polymer Networks and Related Materials; Plenum: New York, 1981.
- Hu, R.; Dimonie, V. L.; El-Aasser, M. S.; Pearson, R. A.; Sperling, L. H.; Hiltner, A.; Mylonakis, S. G. J Appl Polym Sci 1995, 58, 375.
- Silverstein, M. S.; Narkis, M. In Interpenetrating Polymer Networks; Klempner, D.; Sperling, L. H.; Utraki, L. A., Eds.; American Chemical Society: Washington, DC, 1994; Chapter 17, p. 1353.
- Silverstein, M. S.; Narkis, M. J Appl Polym Sci 1987, 33, 2529.
- Nemirovski, N.; Silverstein, M. S.; Narkis, M. Polym Adv Tech 1996, 7, 247.
- Silverstein, M. S.; Narkis, M. Polym Eng Sci 1989, 29, 824.
- 8. Hourston, D. J.; Satgurunathan, R. J Appl Polym Sci 1984, 29, 2969.
- 9. Hourston, D. J.; Satgurunathan, R.; Varma, H. J Appl Polym Sci 1986, 31, 1955.
- Hourston, D. J.; Satgurunathan, R.; Varma, H. J Appl Polym Sci 1987, 33, 215.
- Hourston, D. J.; Satgurunathan, R.; Varma, H. J Appl Polym Sci 1987, 34, 901.
- 12. Babbit, R. The Vanderbilt Rubber Handbook; R. T. Vanderbilt Company, Inc.: Norwalk, CT, 1978.
- Blow, C. M.; Hepburn, C. Rubber Technology and Manufacture, 2nd ed.; Butterworth Scientific: London, 1982.
- Morton, M. Rubber and Technology, 2nd ed.; Van Nostrand Reinhold Company: New York, 1973.
- Burford, R. P.; Zhang, F.; Vo, C. D. Proc Second Int Sem Polym Sci Technol, Tehran, Nov 3–5, 1997, 654.
- Vo, C. D.; Burford, R. P. 37th IUPAC Int Symp Macro, Gold Coast, July 12–17, 1998, 513.