Morphology Development in Polychloroprene–Polystyrene Latex Interpenetrating Polymer Networks

R. P. BURFORD, C. D. VO

School of Chemical Engineering and Industrial Chemistry, The University of New South Wales, NSW, Australia 2052

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ABSTRACT: Latex interpenetrating polymer networks (LIPNs) have been prepared using a crosslinked polychloroprene latex as the seed emulsion, followed by the *in situ* polymerization of styrene, typically with a 10% divinyl benzene crosslinker. Polychloroprene-crosslinked polystyrene (XPS) ratios ranging from 70/30 to 40/60 were used, with the second monomer being added as a single aliquot rather than by "starvation" routes. The majority of the work has been conducted using the water-soluble persulfate initiator method, which entails lengthy (~ 6 h) polymerizations. To follow the development of microstructure, polymerizations were also stopped at 0.5, 1, and thence hourly intervals up to 6 h, so that any effect of time on shell and domains could be seen by transmission electron microscopy (TEM). Parallel studies using azo-bis(isobutyronitrile) (AIBN) as initiator at the same temperature were conducted. Products were also studied, after staining, by TEM. For the persulfate initiator, domain structures predominated for the 70/30 ratio, but polystyrene-rich shells are found in all cases, with increasing thickness as the chloroprene/styrene ratio was reduced. The styrene-rich products (i.e., 40/60 Neoprene/XPS ratio) appear to have larger unstained domains suggesting phase separation. For the AIBN-initiated styrene polymerization, shells are less evident, and where they exist, are both thinner and less continuously developed. Domain sizes are somewhat larger. This relatively hydrophobic initiator has caused polymerization predominately in the interior of each latex particle. The particle size distribution of the seed neoprene latex is broad and bimodal. As the LIPNs form, the larger diameter component increases and little evidence for fresh nucleation, in the form of small diameter particles, is seen. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 629-638, 1999

Key words: latex interpenetrating polymer networks; seeded emulsion polymerization; morphology; neoprene latex; polystyrene

INTRODUCTION

Latex interpenetrating polymer networks (LIPNs) are typically prepared by the sequential *in situ* polymerization of a second monomer diffused in a crosslinked "seed" latex. Generally, no significant additional surfactant is added in the second step, to avoid fresh nucleation of a second polymer latex,

Journal of Applied Polymer Science, Vol. 74, 629–638 (1999) © 1999 John Wiley & Sons, Inc. CCC 0021-8995/99/030629-10 which would lead to simple latex blends. The general features of LIPNs have been reviewed in both introductory¹ and specialized² monographs as well as encyclopedias.³ They have attributes of involving relatively simple synthetic routes combined with the potential to process the advantages of thermosets with those of thermoplastics. Two or more polymers can be combined leading either to moldable resins or to impact modifiers.

The formation of structure in latex IPNs has not been discussed in significant detail, even though related products such as those based on

Correspondence to: R. P. Burford. Contract grant sponsor: AUSAID.

natural rubber latex with poly(methyl methacrylate) have been disclosed for about a decade.⁴

LIPNs are mentioned, for example, in Blackley's three-volume treatises, but only constitute a few pages.⁵ The closely related work to that described in this paper, by Narkis et al.,^{6–8} is also lacking in mechanistic detail.

In contrast, substantially more has been done on seeded emulsion polymerization, and if one discounts the presence of crosslinking, the models developed may be appropriate. Lee and Rudin have given an overview of the technology in a 1992 paper,⁹ and a wide variation in core-shell and other structures are shown to be controlled by factors such as hydrophobicity/hydrophilicity, stage ratios, and control of phase volume by particle numbers and sizes. The paper shows the simple transition from cellular or domain twostage particle, to core shell, when second monomer amounts are increased, for a given polymer 1 particle size (Figure 9 in ref. 9). However, occluded polymer 2, together with a shell, is also possible at intermediate seed latex sizes. These, in Figure 10 of ref. 9, are coincidentally about the same as our Neoprene seed, i.e., of 400 nm diameter.

The topic of seeded emulsion polymerization is reviewed in a chapter by Diomonie et al.¹⁰ This work begins with the Grancio and Williams coreshell model of 1970,^{11,12} which deviates from the previous homogeneous monomer swelling assumptions. The arguments, based on kinetics, morphology, and thermodynamic criteria, are then discussed, with recent attempts at resolving inherent conflicts being reviewed. For example, to explain large compositional differences between core and shell, different reaction loci are postulated.¹³ Napper has studied the case of seeded emulsion polymerization using water-soluble initiator and proposed a hypothesis to explain the development of a "core-shell" structure.¹⁴ The presence of surface-active oligomer radicals with polar initiator group at one end, which are formed by the propagation of potassium persulfate and monomer in aqueous phase, is the main factor resulting in the "encapsulation" process. This hypothesis was later supported by Vanderhoff's experimental data.¹⁵

Finally, one could consider homogeneous nucleation, for which many mechanisms exist. They include, for example, the "coagulative nucleation mechanism" of Gilbert and Napper¹⁶ and the "hydrophobic association" model of Pirma.^{17,18} However, in our view such systems have primary relevance in relation to the role of surfactant con-

centration, whereas in our case, no additional surfactant is added, and no evidence of increased small particle size latexes is found. We would assume that homogeneous nucleation independent of the seed is only remotely possible.

While it is becoming evident that the understanding of core-shell development in latexes is improving, there remain gaps in knowledge. In the case of crosslinked systems (for example, LIPNs), most work has been by the Narkis^{6,8} and Hourston groups,^{19,23} and the range of monomer is still rather limited.

In the present case, we have used a commercially available crosslinked polychloroprene latex (Neoprene A671) as the seed material, as not only is it of industrial importance, but it also has the attributes of low T_g compared with the second polymer, and the presence of unsaturation and heavy atom (chlorine) are both potential markers for electron microscopy. We now describe the structure and properties of LIPNs of varying Neoprene/XPS ratios.

EXPERIMENTAL

Materials and Polymerization

The LIPNs were made by performing a sequential, thermally initiated polymerization of styrene in a commercial polychloroprene emulsion. The "Neoprene 671A" latex supplied by DuPont Australia Pty. Ltd is well described in both the literature and in company brochures.^{24–26} Relevant properties are 59% w/v solids, a pH of 12.5, and a mixed anionic emulsifier comprising "potassium salts of disproportionate resin acid and polymerized potassium salts of alkyl naphthalene sulfonic acid." The stated average particle size is 0.21 μ m. Although the crosslink density is not precisely stated by DuPont, Figure 2 in Gelbert's paper²⁵ shows it to be at the high end of the gel content range, presumably due to high conversion manufacture.

The latex was diluted to about 13% solids content with distilled water and the pH was readjusted to above 12 using potassium hydroxide. After nitrogen gas purging (30 min) in a 250 mL stirred reactor, the inhibitor-free (alumina column) styrene monomer (Aldrich), and divinyl benzene (Aldrich, also alumina treated) were added, with the divinyl benzene (DVB) being 10% w/w relative to the styrene (see Table I). The mixture was stirred for 1.5 h at 75°C to encourage the diffusion of monomers through the seed latex.



Figure 1 Particle size distribution of latex Neoprene A671 and associated LIPNs.

The appropriate weight of potassium persulfate (1% relative to styrene and DVB) was then added as a 5 mL aqueous solution and the reaction allowed to proceed for 6 h, when conversion is quantitative, as shown by gravimetry.

A further polymerization at the ratio of 50/50: Neoprene/XPS and with persulfate initiator was conducted, during which about 3 mL of mixture was withdrawn at intervals of 0.5, 1, and thence hourly intervals, and then frozen to coagulate the latex, as recommended in Johnson's article,²⁴ to show changes in shell and domain development by transmission electron microscopy (TEM).

For azo-bis(isobutyronitrile) (AIBN), the polymerization was carried out under the same conditions as mentioned above, with the appropriate amount of AIBN (2% relative to monomer/ crosslinker) being dissolved in the styrene and DVB mixture prior to addition to the hot neoprene latex. The work to date has been limited to two polymer/monomer ratios for this type of initiator.



Figure 2 FESEM micrograph of 60/40 Neoprene/XPS LIPN.







(b)

Figure 3 AFM micrographs: (a) Neprene A671; (b) 70/30: Neoprene/XPS LIPN.

For the persulfate-initiated polymerizations, it was found necessary to add soap (sodium lauryl sulfate) after the completion of the reaction, to avoid coagulation during storage.

Characterization

Particle Size Analysis

One or two droplets of each latex was diluted with 50 mL distilled water, transferred to a washed sample cell, and analyzed in a Malvern Autosizer 4700. Data were taken at an angle of 90° and at a temperature of 25°C.

Field Emission Scanning Electron Microscopy (FESEM)

For most LIPNs, the glass transition temperature was too low to allow preservation of latex morphology when subjected to high vacuum during chromium metal coating. However, for the 60/40: Neoprene/XPS LIPN, FESEM was suitable and the following conditions were used: a few droplets of the latex were dropped on a copper slide and left to dry. The dried polymer was coated with chromium using a Xenosput coater, prior to observation in a Hitachi S-900 unit.

Atomic Force Microscopy (AFM)

A few droplets of latex were transferred to a glass slide and left to be dried. This was mounted in a Digital Instruments Nanoscope IIIa Atomic Force Microscope. Tapping mode using an etched silicon probe ("TESP") was used.

Transmission Electron Microscopy

About 20 mg of the finely divided dried powder was initially treated with a few drops of a 2%



Figure 4 AFM micrograph of 60/40: Neoprene/XPS LIPN.

aqueous OsO_4 solution for 24h at 25°C. Surplus staining solution was removed by distilled water washing, and the blacken particles were embedded in epoxy resin (Spurr's resin) and set over 12 h in stub molds. Postcuring was then undertaken for 24 h at 60°C and the hard blocks were then trimmed prior to sectioning at room temperature using a Reichert Ultracut ultramicrotome. The sections were collected on 300 mesh copper grids and reimmersed in a 2% aqueous OsO_4 solution for 0.5 h, rewashed, and dried.

Samples were examined using a Hitachi H-7000 transmission electron microscope operated at 10 kV and images were recorded using conventional film techniques.

RESULTS AND DISCUSSION

Particle Size Distribution

The primary focus to date have been on persulfate initiated polymerizations. The particle size distributions of latex samples drawn from the reactor after 6 h at 75°C are shown for varying Neoprene/ XPS ratios in Figure 1.

From the trace of the Neoprene itself, it can be seen that while the first peak is around 0.21 μ m, consistent with the nominal DuPont specification, there is a significant larger particle population that might arise from micelle coalescence in storage. During the subsequent conversion to the LIPN, this larger particle size shoulder (about 0.4 μ m) increases, while the 0.21 μ m peak remains essentially unaltered. At Neoprene/XPS ratios of 70/30, 60/40, and 50/50, the distribution is clearly bimodal, with the 0.4 μ m peak overtaking the smaller one. It is noted that no evidence of further nucleation to give small particles is found. The number of very large (>0.6 μ m diameter) latex particles is not significant. The initial broad par-



Figure 5 AFM micrograph of 50/50: Neoprene/XPS LIPN.

ticle size distribution indicated by this method is also shown in both the AFM and TEM micrographs below.

The growth associated with the second polymerization appears to be confined to the larger latex particles in the seed emulsion.

Particle Morphology by FESEM and AFM

Initial attempts at obtaining useful images by FESEM were unsuccessful. The Neoprene latex was found after vacuum coating to be featureless, due to coalescence at room temperature (the polymer T_g was determined by DSC to be -41° C). Similarly, latexes with high neoprene contents had poorly revealed structural features, but at an XPS content of 40%, globular structures are resolvable (Fig. 2).

We have found that AFM leads to less risk of artifacts, as metallization and vacuum exposure are

 Table I
 Typical Formulations for LIPNs Based on Neoprene A671

	$K_2S_2O_8$					AIBN		
	80/20	70/30	60/40	50/50	40/60	70/30	60/40	50/50
Neoprene latex (13%) (g)	100	100	100	100	100	100	100	100
Styrene (g)	2.95	5.06	7.87	11.81	17.72	5.05	7.87	11.81
DVB (55%) (g)	0.53	0.92	1.43	2.14	3.22	0.92	1.43	2.14
Initiator (g)	0.03	0.05	0.08	1.13	0.19	0.11	0.17	0.26
H_2O to dissolve initiator (g)	5	5	5	5	5	0	0	0
Surfactant (g)	0	0	0	0	0.15	0	0	0



Figure 6 TEM micrograph of 70/30: Neoprene/XPS LIPN using potassium persulfate initiator.

both avoided, and it is more convenient. Again, however, the 100% Neoprene and 70/30:Neoprene/polychloroprene-crosslinked polystyrene (XPS) IPN are featureless (Fig. 3a and b), while the higher XPS LIPNs show retention of the latex particulate shape. That for the 60/40: Neoprene/XPS (Fig. 4) is in fact very similar to the corresponding FESEM image (Fig. 2). The higher ratios (50/50 and 40/60): Neoprene/XPS) LIPNs show development of large particles, consistent with the PSD data in Figure 1. In all cases, there is a broad range of particle sizes in the AMF images, and the diameters themselves correlate well with the particle size analysis data. The success with both FESEM and AFM methods at higher XPS contents reflects an increase in surface hardness and thermal resistance. Some evidence for fusion of two larger particles can be found, as indicated by large, "peach-shaped" objects in the 70/30 LIPN and in occasional very large particles, as seen in Figure 5, for the 50/50 LIPN.

Phase Morphology by TEM

Ratio of Seed Latex Polymer to Added Monomer

The widest range of Neoprene to polystyrene products was formed using potassium persulfate initiator, as indicated in Table I. At a fixed polymerization time of 6 h, latex particles were collected from products of the four ratios 70/30 through 40/60 Neoprene/XPS (in all cases 10% DVB was used, relative to styrene). Electron micrographs of the stained and embedded products are shown in Figures 6–9, from which the following comments are made. First, in all cases a dappled internal structure ("cellular" structure or "domains") exists, indicating phase separation at the molecular level. However, the domains are small (~ 20 nm) and the texture generally is rather uniform across most of the particle inte-



Figure 7 TEM micrograph of 60/40: Neoprene/XPS LIPN using potassium persulfate initiator.



Figure 8 TEM micrograph of 50/50: Neoprene/XPS LIPN using potassium persulfate initiator.

rior, indicating uniform composition at the macroscopic (>0.1 μ m) level. The structure is consistent with a genuine IPN, in that there appears to be component co-continuity and the individual phases are less than 50 nm in diameter and so meet Narkis' criteria.⁸ The 70/30 LIPN shows virtually no shell, with only patchy areas <10 m diameter appearing in Figure 6. The absence of a hard shell also explains the difficulty in retention of the particulate structure when using AFM at room temperature for this product.

As the XPS content increases, the thickness of the shell also increases as found in Figures 7–9. The latter two have an interior cellular structure completely encased in (non-stained) XPS, with a thickness of about 30-50 nm. The domain size



Figure 9 TEM micrograph of 40/60: Neoprene/XPS LIPN using potassium persulfate initiator.



Figure 10 TEM micrograph of 60/40: Neoprene/XPS LIPN using AIBN initiator.

also appears to increase slightly with XPS content up to the 50/50 ratio, while for the 40/60 LIPN the XPS- rich domains are somewhat larger (20-50nm). The overall structure of these particles fits the model shown in Figure 1 (for hydrophilic seed, full IPN, XPA/XPS) in the Nemirovski, Silverstein, and Narkis paper.⁸

Polymerization Using AIBN Initiator

From a practical viewpoint, several classes of initiator are found to be useful. The initial study, using the water-soluble persulfate initiator, is simple and well understood, although for many monomers persulfate initiators are not used due to their rather high temperature (compared with redox systems). A second issue is that initiators,



Figure 11 TEM micrograph of 50/50: Neoprene/XPS LIPN using AIBN initiator.



(a)



(b)



which are hydrophobic, may lead to products with differing and potentially superior microstructures. We therefore used an AIBN initiator system with particular attention to development of domain structures, as reaction loci have been shown to be affected by initiator type.²⁷

As a simple comparison, ratios of 60/40 and 50/50 seed polymer to second polymer were used. The conditions were otherwise essentially the same with respect to time and temperature (Table I) as for the persulfate experiments.

The two aspects to be considered are development of shell structure and the distribution and size of domains within each particle. At the 60/40: Neoprene/XPS ratio, no evidence of a shell structure was found throughout the product, with an example TEM being shown in Figure 10. In comparison with the corresponding persulfate system, domain sizes appear to be now somewhat larger than those shown in Figure 7. Factors that influence domain development and size include the rate of diffusion of initiator into the hydrophobic seed latex, which will be much higher for the AIBN than for the persulfate. The rate of polymerization, on the basis of Shahip's data,^{28,29} will be higher for persulfate for styrene than for AIBN under the same conditions. In fact, to endeavor to obtain similar structures, twice the level of AIBN relative to persulfate was used.

At the 60/40 Neoprene/XPS ratio, two main differences in structure from the persulfate system were noted. In Figure 10, no shell is seen and the domain size is larger, although exact quantification is complex due to the semicontinuous nature of the XPS phase. It is in any event larger than that in Figure 7 and is about 25–35 nm in diameter.

A plausible mechanism is that the AIBN rapidly diffuses into the seed latex, and promotes homopolymerization of the styrene, the carrier solvent. The development of the second phase in this way suggests that grafting is not substantial, again consistent with the partitioning of the AIBN within the styrene phase, rather than the more polarized neoprene seed.

A TEM micrograph of the 50/50: Neoprene/XPS LIPN using AIBN is shown in Figure 11 and two differences from Figure 10 are noted. Most dramatically, a shell is evident, although it is neither

Figure 12 TEM micrographs of 50/50: Neoprene/XPS LIPN using potassium persulfate initiator: (a) 30 min after adding initiator, (b) 2 h after adding initiator, and (c) 3 h after adding initiator.

continuous nor as thick as that found for the persulfate analogue (Fig. 8). It appears that the shell is thicker and continuous for the smaller particles' outer layer of micelle. The domain size has also increased and the uniformity of styrenerich cells appears to have decreased. Although there is clearly some subjectivity in interpretation of the micrographs, partly due to variation in print development, we believe there are several "shades of gray" indicating styrene dominant (light regions), neoprene dominant (dark regions), and intermediate interpenetrated zones. These may well exist in the persulfate analogs, but because of smaller dimensions, they are less easy to resolve.

The micrographs for all ratios reflect the broad particle distribution obtained by the Autosizer as shown in Figure 1. At the same seed/monomer ratios, there does not appear to be a dramatic shift in latex particle size distribution.

Polymerization Time Studies

As seen above, the major trend is in the development of shell vs. domain structures in products, with persulfate leading to small domains/thick shells and with AIBN leading to thin shells and large domains. One variable, which might influence the development of morphology, is polymerization time. We varied this for the persulfate system, from 0.5 to 6 h. The TEM images for the 50/50 system, shown in Figure 12a-c, indicate that shells form rapidly and that particle size and domain size do not alter significantly with time.

A plausible mechanism for the development of structure can be based upon the work of Roe and Frisch, as reported in Blackley's recent treatise.^{30,31}

CONCLUSION

Latex interpenetrating polymer networks with varying compositional ratios of polychloroprene to polystyrene have been prepared. The formation of fresh nuclei during the second polymerization has been controlled and the latexes obtained have been found stable during storage. The replication of a broad particle size distribution of commercial latex Neoprene A671 has been seen in the associated LIPNs.

It is noted that type of initiator contributed significantly in the morphology development of the LIPNs. For the water-soluble initiator ($K_2S_2O_8$), domain structures predominated for 70/30:Neoprene/ XPS, whereas polystyrene-rich shells and domain structures have been found in 60/40: Neoprene/XPS and lower ratios of Neoprene/XPS. Phase separation has been observed in styrene rich IPNs (e.g., 40/60: Neoprene/XPS). For the oil-soluble initiator (AIBN), larger domain sizes have been found in all cases, with thinner and less continuous shells for the 50/50 ratio. The different hydrophobic nature of the employed initiators leading to the difference reaction loci is the main factor for the observed morphologies.

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