Effect of the Addition Mode of Cycloaliphatic Diepoxide on the Morphology and Film Properties of Crosslinkable Core-Shell Latex

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ABSTRACT: Core-shell latexes (LAs) designed for crosslinking with cycloaliphatic diepoxide were synthesized. The core contained methyl methacrylate (MMA), butyl acrylate (BA), and 2-hydroxyethyl methacrylate, and the shell was prepared with MMA, BA, and methacrylic acid. The crosslinker was coemulsified with the monomer and added during the LA preparation or after the polymerization either as an emulsion or in an organic solvent. The morphology of the LA was studied with atomic force microscopy and transmission electron microscopy. We used titration to establish the acid distribution. The water absorption and tensile and viscoelastic properties of the LA films were investigated as a function of the addition mode of the cycloaliphatic diepoxide crosslinker. The solution approach generally provided better mechanical properties than the emulsion approach, and the addition of epoxide during the polymerization lowered the water adsorption and hardness. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 245–257, 2003

Key words: crosslinking; coatings; mechanical properties

INTRODUCTION

Latex (LA) technology is one of most effective and successful vehicles for lowering the amount of volatile organic compounds.[1,2] The development of mechanical strength in traditional LA film results from the interdiffusion of the chain ends and segments and entanglements that cross particle boundaries. Without chemical bonding, the films generally suffer from poor solvent resistance and mechanical properties.[1] Many efforts have been made to develop a thermoset LA system in which functionalities such as carboxyl or hydroxyl groups are introduced during synthesis of the LA[3–7] and then are crosslinked with other resins via chemical bonding after the polymerization. This approach results in improved solvent resistance and elastic modulus. A variety of crosslinkers have been developed for thermoset LA systems.[3–7] Recently, cycloaliphatic diepoxide has been developed as a crosslinker for acrylic LA films by Soucek and coworkers.[7–13] Cycloaliphatic diepoxide can effectively crosslink with carboxyl or hydroxyl functional acrylic LAs, as shown in Schemes 1 and 2.

Significant progress has been made in the elucidation of the parameters that affect thermosetting LA properties, in particular crosslinking and interdiffu-

sion.[14–18] Zosel prepared a series of emulsion polymers containing butyl methacrylate and a bifunctional monomer (methallyl methacrylate) with particles ranging from uncrosslinked to highly crosslinked.[14,15] With the increase in crosslinking, the development of mechanical strength by interdiffusion and entanglement of chain was slowed. When the mean molecular mass between crosslinks became smaller than the entanglement length, interdiffusion and interparticle entanglement were impossible, and the film remained brittle on annealing. Winnik and coworkers[16] reported that fluorescence labeling and energy transfer measurement were used to obtain information on the relative rates of crosslinking and particle–polymer interdiffusion for a melamine–formaldehyde (M–F)-cured LA system. They discovered that the temperature and M–F resin location in the dry film before the onset of crosslinking had a significant effect on the development of the film properties.[16–18]

The homogeneous crosslinked polymer has been studied for many years, and the effects of crosslinking on the dynamic mechanical properties of the polymer have been well described.[14–16] Generally, the formation of a homogenous crosslinked network of LA film from dispersed particles seems unlikely. Two typical heterogeneous crosslinked networks modes, interparticle and intraparticle, can be utilized to classify crosslinked LA films, as shown in Figure 1. For the interparticle crosslink mode, the film forms from uncrosslinked particles across particle boundaries, and for the intraparticle crosslink mode, the crosslinking reaction occurs within the particle.[16] For epoxide-
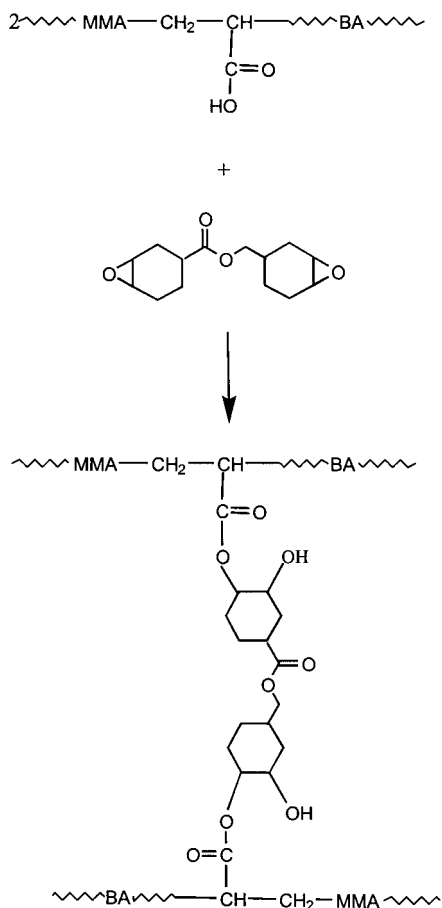
Scheme 1 Crosslinking reaction I.
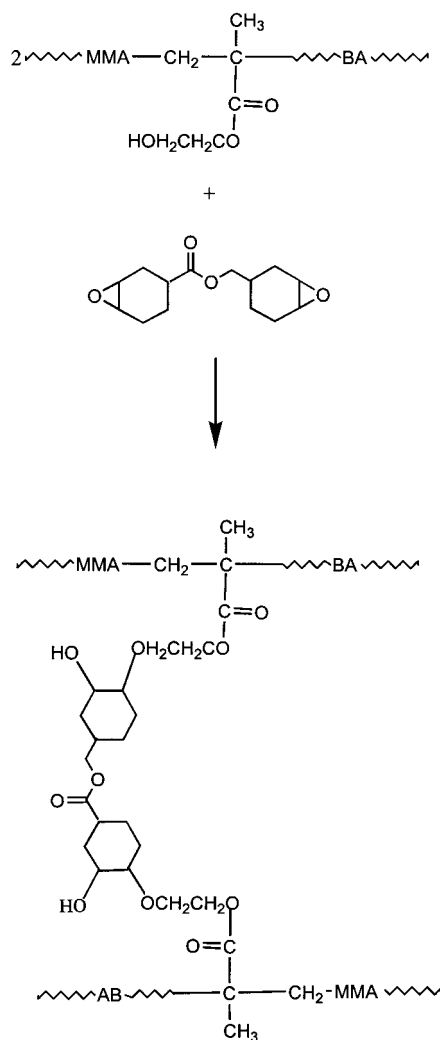
Scheme 2 Crosslinking reaction II.

based crosslinked LA systems, the epoxide is generally introduced after emulsion polymerization.[4,20–23] Epoxides can also be introduced during the polymerization.[4] However, gelation occurred when a low level of acrylic acid was present in LA particles.[4] Most recently, LAs consisting of a cycloaliphatic diepoxide and a hydroxyl functional monomer core and a carboxyl functional monomer shell (Fig. 2) have been prepared in the presence of cycloaliphatic diepoxide by a two-step emulsion polymerization.[25] The pot-life stability of the epoxide was dependent on LA morphology, the initiator system, and the reaction conditions. Stable LAs can be prepared with basic reaction conditions and ambient temperature for the shell polymerization.

In this study, acrylic LA with hydroxyl-functionalized cores and carboxyl-functionalized shells was prepared via free-radical polymerization, and the epoxide was introduced into the LAs by three modes. In the first mode, the epoxide was added with the monomers during the synthesis of LA. In the second mode, the epoxide was dissolved in the solvent and then added after the LA was formed. In the third mode, the epoxide was emulsified separately and then formulated into the LA. LA film properties, including viscoelasticity, Tukon hardness, tensile properties, and water

adsorption, were evaluated as a function of the crosslinker addition mode. The morphologies of the core-shell LAs were also studied via transmission elec-
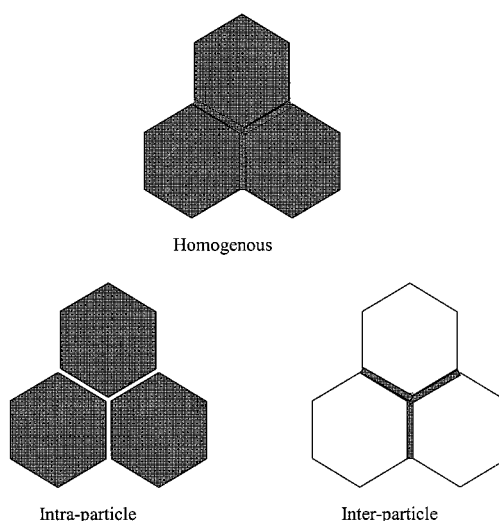

Homogenous

Intra-particle   Inter-particle
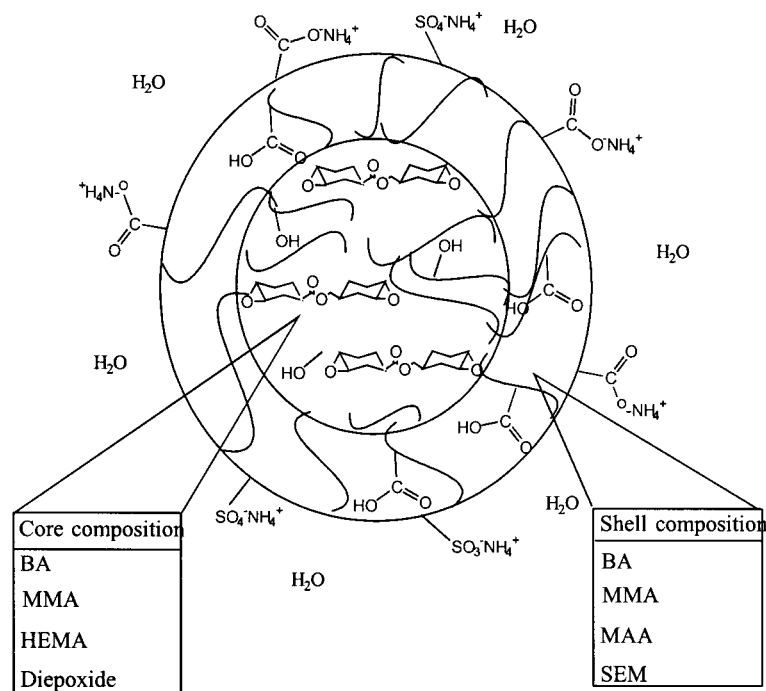
Figure 1 Crosslink mode of LA.

Figure 2 Cycloaliphatic diepoxide crosslinkable core-shell LA particle.

tron microscopy (TEM), atomic force microscopy (AFM), and acid titration.

EXPERIMENTAL

Materials

Methyl methacrylate (MMA), butyl acrylate (BA), methacrylic acid (MAA), 2-hydroxyethyl methacrylate (HEMA), ammonium persulfate, copper(II) sulfate, isopropanol, and sodium bicarbonate were purchased from Aldrich (Milwaukee, WI). Cycloaliphatic diepoxide (UVR-6105) and surfactants (Triton-200 and Tergital-XJ) were supplied by Dow/Union Carbide Corp. (Danbury, CT). 2-Sulfoethyl methacrylate (SEM) was supplied by Hampshire Chemical Corp. (Waterloo, NY). Ruthenium tetroxide (RuO_4) was purchased from Polyscience (Warrington, PA). Sodium bisulfite was purchased from Mallinckrodt Baker (Paris, KY). (Ethylenedinitrilo)tetra-acetic acid tetrasodium salt (EDTATSS) was purchased from EM Science (Gibbs-

town, NJ). All the materials were used without further purification.

LA synthesis

LA was prepared in a four-necked fluted round-bottomed flask (500 mL). The purpose of using a fluted flask was to provide effective shearing and mixing of the reaction contents. The flask was also equipped with a mechanical stirrer, a reflux condenser, and a gas inlet. We slowly added the monomer mixture of BA, MMA, and HEMA as shown in Table I to a flask containing a stirred solution of $NaHCO_3$ (0.1 g), Triton-200 (3.2 g), Tergital-XJ (0.8 g), and deionized water (48 g) to obtain a monomer preemulsion for the LA core. We prepared an initiator solution by dissolving ammonium persulfate (0.44 g) in deionized water (20 g). The monomer preemulsion (14 g) and initiator solution (8.1 g) were charged into the reaction flask with $NaHCO_3$ (0.2 g), and Triton-200 (0.08 g). The

TABLE I
Recipes for the Synthesis of Core LA ($T_g = 0°C$)

Component	Functionality	Weight (g)	Equivalent
BA	Monomer	44.24	0.35
MMA	Monomer	29.39	0.29
HEMA	Hydroxyl monomer	16.38	0.12
Cycloaliphatic diepoxide	Crosslinker	0 or 15.89	0 or 0.12
$NaHCO_3$	Buffer	0.1	—
Triton-200	Surfactant	3.2	—
Tergital-XJ	Surfactant	0.8	—
Water	Solvent	48	—

TABLE II
Recipes for the Synthesis of Shell LA ($T_g = 0°C$)

Component	Functionality	Weight (g)	Equivalent
BA	Monomer	51.31	0.40
MMA	Monomer	27.69	0.28
MAA	Carboxyl monomer	10.8	0.12
NaHCO$_3$	Buffer	0.1	—
Triton-200	Surfactant	3.2	—
Tergital-XJ	Surfactant	0.8	—
Water	Solvent	48	—
SEM	Strong acid monomer catalyst	0.571	0.003

contents were stirred for 0.5 h at 80°C to form seed LA particles. The cycloaliphatic diepoxide (15.89 g), Triton-200 (0.56 g), Tergital-XJ (0.14 g), and water (20 g) were added slowly to a flask containing the remaining preemulsion (128.1 g) with continuous stirring. This mixture and initiator were then fed to the reactor concurrently at a constant rate (1.4 mL/min) over a period of 1.5 h. The polymerization was maintained at 80°C under nitrogen. After the addition of all ingredients, the contents were heated at 80°C for an additional 1.5 h to digest all residual monomers.

For the shell polymerization, a redox-initiated system was used, and polymerization was carried out at a lower temperature (40°C). The redox initiator system consisted of an oxidant and a reductant. We slowly added a mixture of BA, MMA, and MAA, as shown in Table II, to a flask containing a stirred solution of NaHCO$_3$ (0.1 g), Triton-200 (3.2 g), Tergital-XJ (0.8 g), and deionized water (48 g) to obtain a monomer preemulsion for the shell. We prepared a 5 wt % SEM aqueous solution by dissolving SEM (1 g) in deionized water (20 g). We prepared the oxidant solution by dissolving ammonium persulfate (0.44 g) in deionized water (20 g), and we prepared the reductant solution by dissolving EDTATSS (0.22 g), sodium bisulfite (0.22 g), and copper(II) sulfate (0.22 g) in deionized water (920 g). After the core polymerization was complete, the reactor was charged with the ammonium persulfate solution (6 g) for 2 min at 40°C. The preemulsion, remaining ammonium persulfate solution, and SEM (11.42 g) were then added to the reactor concurrently at a constant rate (1.2 mL/min) over a period of 2 h with a syringe pump. Half of the reductant portion of the initiator solution was added 2 min before the oxidative portion of the initiator solution. The second half of the reductant portion of the initiator solution was added after the reaction mixture was stirred for 1 h. The polymerization was maintained at 40°C under nitrogen. After the addition of all ingredients, the contents were heated for an additional 2 h at 40°C to digest any residual monomer. The content was then filtered through a 300-mesh screen to remove any residual coagulum. The particle size measurement was conducted on diluted LA with dynamic light scattering (NICOMP 380, Santa Barbara, CA), and av-

erage size and relative and standard deviation of the LA particles are reported.

Film preparation and characterization

The morphologies of the LA and LA films were determined by AFM (Digital Instruments, NanoScope IIIa) and by TEM (Jeol JSM 6300V) at the CRSS-USDA Electron Spectroscopy Center (Fargo, ND). AFM measurements were conducted on the dried LA film. The diluted LA (5% in water) was put on a 300-mesh grid coated with formvaf support film, and then, the excess was removed with filter paper. After drying for 1 min, the solution was stained with 1% phosphotungstic acid (pH 6.8) for 30 s and dried up with filter paper. We further stained the solution with RuO$_4$ by placing a drop on and removing it immediately. Finally, the specimen was evaluated by TEM. The particle size measurement was performed with dynamic light scattering (NICOMP 380).

Acid distribution in the LA was determined with a method by Robertson.[25,26] The surface acid was considered to be the acid reacted in the first second after base addition. The acid concentration was determined by conductometric titration with 0.1N NaOH solution. Subsurface acid was determined by back titration with HCl after equilibration at high pH for 1 h. The acid content in the aqueous phase was also measured with the same method after separation of the diluted LA (50 wt % in water) with a J2-21 Beckman ultracentrifuge (Beckman Instruments Inc., Richmond, CA). The diluted LA (50 wt % in water) was separated with a J2-21 Beckman ultracentrifuge to obtain a clear serum. Deionized water was used to dilute the serum (10 wt % in water). The AG-501-X8 resin, twice the weight of the serum, was added to the diluted serum. The mixture was stirred at room temperature for 3 h, and the resin was removed by vacuum filtration. This process was repeated three times.

The cycloaliphatic diepoxide (UVR-6105) was emulsified with a mixture of anionic and nonionic surfactants (Triton-200 and Tergital-XJ). The anionic surfactant (0.32 g) and nonionic surfactant (0.14 g) were dissolved in deionized water (11 g). The cycloaliphatic diepoxide (9 g) was slowly added into the water so-
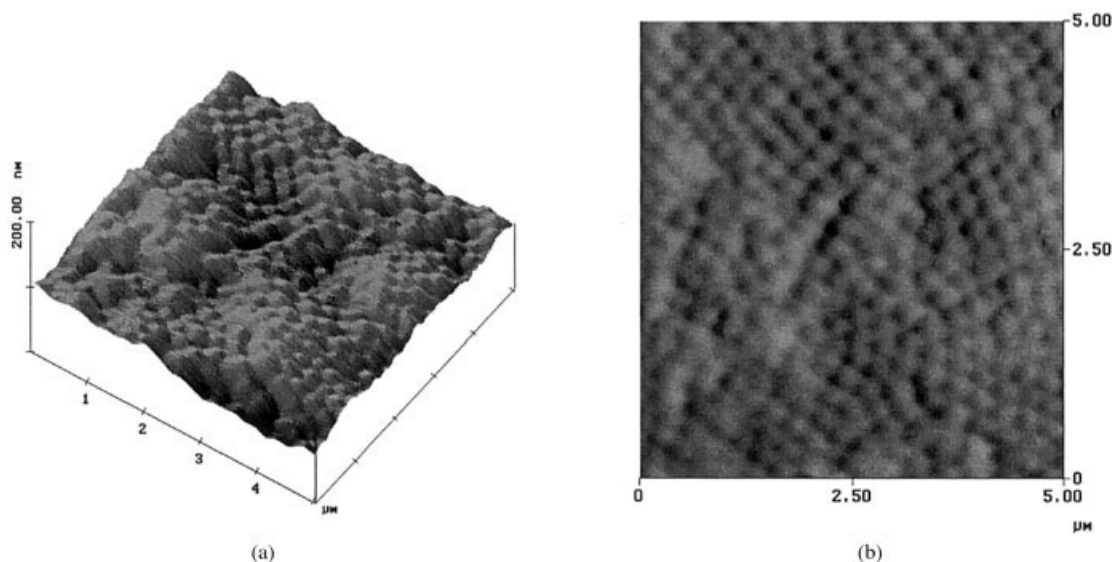
Figure 3 AFM images of the surface of LA film without epoxide: (a) height image and (b) phase image.

lution at 60°C to form an emulsion. The epoxide (5 g) was dissolved in isopropanol (5 g). Then, water (5 g) was added dropwise to this stirred solution. The epoxide emulsion or solution was added into the LA over 5 min. The formulations were cast at 8-mm wet thickness on the steel or glass substrate. After coalescence for 3 h, the LA coatings were cured at 170°C for 1 h and stored at ambient temperature for 48 h.

The films over steel panels were tested for Tukon hardness (ASTM D 1474-85). After removing the films over glass panels with a razor blade, we used an Instron universal tester (Canton, MA) (model 1000) to evaluate tensile properties (ASTM D 2370) and water adsorption (ASTM D 3419). We used a crosshead speed of 2 mm/min to determine tensile modulus, tensile strength, and strain at break. Pneumatically actuated 1-in. grips with a steel face were used for clamping the specimens. At least 10 samples were tested for each composition, and average values are reported. The test samples were 8 cm long and 1.7 cm wide. The viscoelasticity of the LA as a function of temperature was recorded with a dynamic mechanical thermal analysis (DMTA) instrument (Rheometric Scientific, Piscataway, NJ). The films were cut into 10 × 30 mm samples. The scans were performed on the samples with a dynamic temperature ramp (3°C/min), a fixed oscillating frequency (1 Hz), and a controlled strain (0.5%). Crosslink density was calculated with the following equation:[36–41]

$$E' = 3 \nu_e RT \ (T \gg T_g) \qquad (1)$$

where ν_e is the number of moles of elastically effective network chains per cubic meter of film, T_g is the glass-transition temperature from DMTA where maximum tan δ was obtained, and E' is the tensile storage mod-

ulus when the measured temperature was 50°C higher than the T_g of the LA films.

RESULTS AND DISCUSSION

The objective of this study was to develop LAs suitable for crosslinking with cycloaliphatic diepoxide and to investigate the effect of the introduction mode of the crosslinking agent into the LA on the morphology and properties of the LA film. The acrylic LAs were prepared with seeded semicontinuous emulsion polymerization. Carboxyl functional groups and a strong acid catalyst were added in the shell and hydroxyl groups in the core. The concentration of hydroxyl or carboxyl functionality was equivalent for all the LAs, and T_g's of both the core and shell were formulated to be the same (0°C) via the Fox equation.[1] In comparison with the previous study,[25] an LA with a greater number of functional groups and lower T_g was designed to formulate an LA without any additives, such as thickener, and to distinguish the influence of the introduction of the epoxide on film properties clearly.

Preliminary findings showed that when all of the epoxide (1 : 1 stoichiometric amount with the crosslinkable functionality) was added during the polymerization, the LA was unstable. Thus, two alternative approaches were taken. In the first approach, LA with half of the epoxide incorporated during the core polymerization (LAE) was prepared. The rest of the epoxide was added into the LA by a solution or emulsion method after the polymerization. In the second approach, no epoxide was introduced during the polymerization of LA, and all of the epoxide was introduced into the LA again via solution or emulsion. With addition of the epoxide and organic solvent (iso-
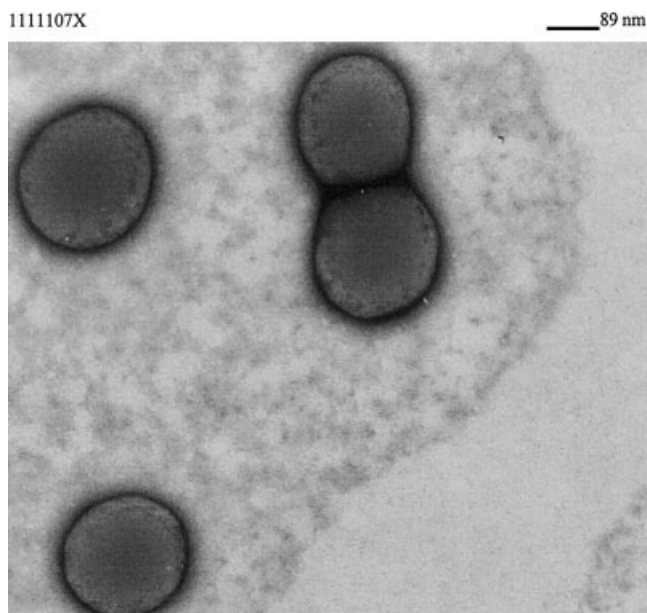
1111107X   ____89 nm

Figure 4 TEM of LA prepared in the absence of the epoxide (LA).

propanol), the LA particles may swell. However, the change of particle size is very limited even when all of the epoxide or solvent has been completely adsorbed. In an effort to identify the influence of the introduction method of crosslinker on the morphology, film properties, and crosslinking mode, the LAs and the films were evaluated in terms of morphology, tensile properties, dynamic mechanical thermal properties, and water adsorption.

Morphology

Development of LA particles

A large number of two-stage LA particle structures have been reported,[33] including core-shell and inverted LAs, depending on the thermodynamic forces and kinetics of the morphological development of the LA.[27] In this system, a high level of carboxyl functional monomer (MAA) was added during the shell polymerization. MAA has high water solubility and tends to produce new particles in the water phase. In addition, the higher acid concentration can enhance the crosslinking reaction of the epoxide with acid groups. Accordingly, monitoring the particle size, par-
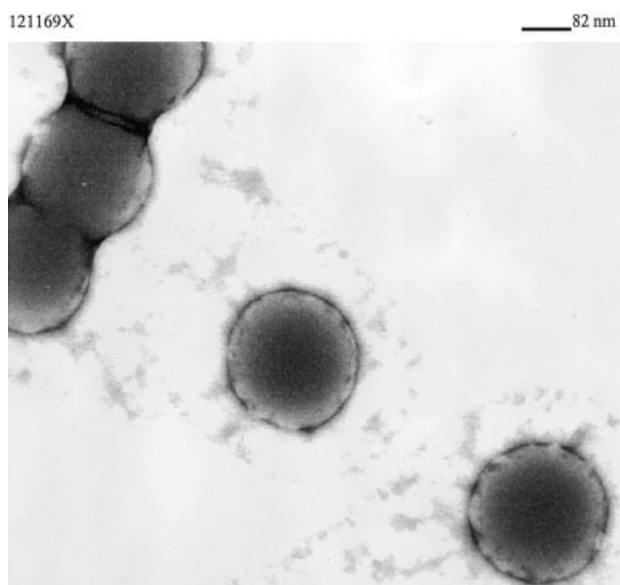
121169X   ____82 nm

Figure 5 TEM of LAE.

ticle size distribution, and particle shape of LA during the course of polymerization was critical.

The topography of the LA particles was examined by AFM, as shown in Figure 3. A well-ordered, close-packed structure of individual particles was observed. The nominal particle dimension from AFM was consistent with that of individual LA particles measured by transition electron microscopy (TEM; see Fig. 4). The particle size and particle size deviation of the core-shell LA were evaluated by light scattering, and the results are shown in Table III. LAs exhibited a general increase in particle size during the course of polymerization, from 99 ± 25 (seed), 206 ± 12 (seed/core), to 258 ± 25 nm (seed/core/shell). With the assumption of no secondary nucleation, the diameters of seed/core and seed/core/shell LA particles were calculated to be 214 and 267 nm, respectively, which were very close to the values measured by light scattering. As a consequence, the secondary was presumed negligible.

Unlike the particle size of the LA, the relative deviation experienced a rise–fall pattern during the course of synthesis. In the seed stage, monomer, initiator, surfactant, and water were added at the outset of a batch emulsion polymerization, and thus, particle nucleation and growth proceeded simultaneously.[28] By

TABLE III
LA Particle Size

LA type	Epoxide	Particle size (nm)	Relative deviation (%)	Standard deviation (nm)
Seed	Both	99	0.27	25
Seed/core	No	206	0.059	12
Seed/core/shell	No	258	0.082	25
Seed/core	Yes	206	0.075	15
Seed/core/shell	Yes	266	0.10	27

TABLE IV
Acid Distribution in LA

Location	Content
Surface acid (Meq/m^2)	0.0082
Fraction of total acid charged (%)	87
Subsurface acid (Meq/m^2)	0.0012
Fraction of total acid charged (%)	13
Total titratable acid (Meq/m^2)	0.0094
Fraction of total acid charged (%)	100

use of a seed LA as one of the reactants, the particle nucleation could be eliminated for the following stages, and accordingly, LA seed had the highest relative deviation. Additionally, the LA prepared in the presence of the epoxide had a uniform particle structure with a predicted diameter.

Functional group location

In an effort to prepare a thermoset LA film, we incorporated two types of functionalities, the carboxyl group and the hydroxyl group, into the LA system as crosslinking sites. In addition, carboxylic acid monomers contained in emulsion polymers can improve the colloid stability and yield a separate membrane phase, which can inhibit or retard LA interdiffussion.[29–35] Unlike the carboxyl group, the hydroxyl-functionalized LA was stable in high levels of hydroxyl-functional monomers. The identification of functionality locus is particularly critical for the LA film behavior, depending on the crosslinking reaction and interdiffusion.[29] The emulsion polymerization could be assumed to proceed under starve conditions, and accordingly, the monomer distribution could be assumed to be uniform for every stage of polymeriza-
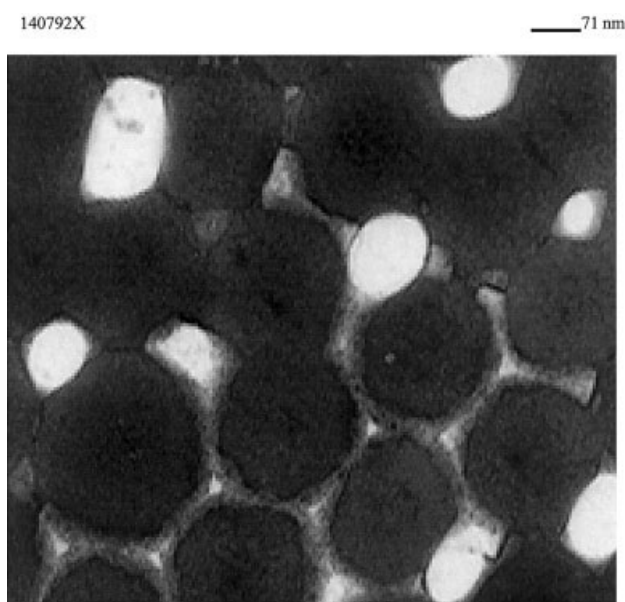

Figure 7 TEM of LA with emulsified epoxide.

tion. For the LA containing two functional groups prepared via two-stage semicontinuous free-radical emulsion polymerization, if one functional group could be located, the distribution of other functional groups added at different stages could be deduced. Acid distribution of LA was previously evaluated with acid content titration,[26] and this technique was chosen to elucidate the LA structure in this study.

The acid groups could be in four loci: (1) the aqueous phase, (2) the LA particle surface, (3) the LA particle subsurface, and (4) the unneutralized LA particle layer. The acid distribution in the resultant LAs was determined by conductometric titration with a
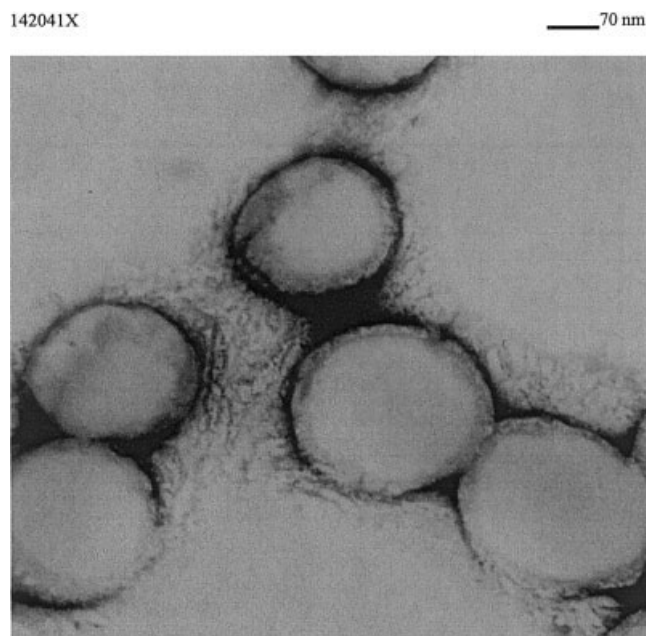

Figure 6 TEM of the epoxide emulsion.

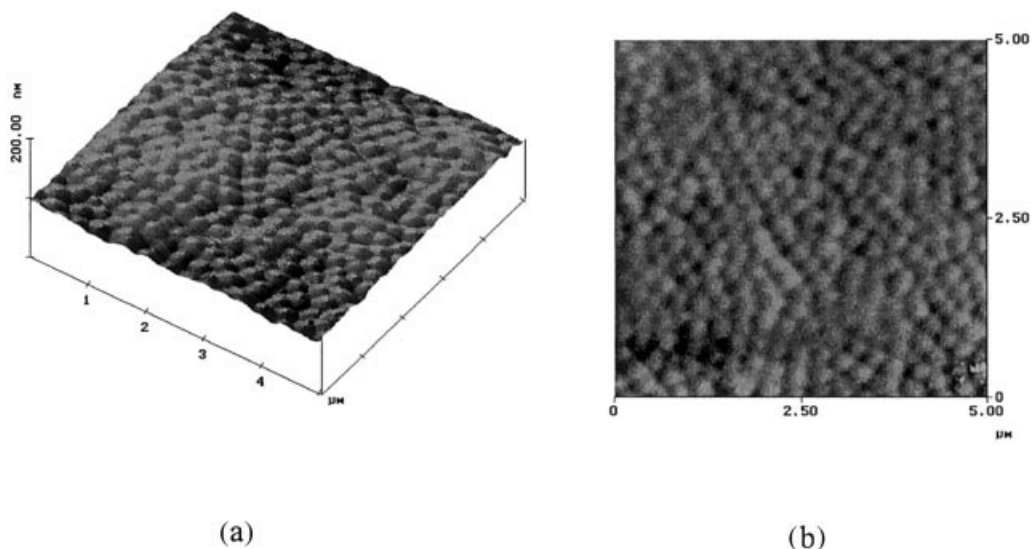**Figure 8** LA with epoxide solution.

Figure 9 AFM images of the surface of the film made from LA with epoxide solution: (a) height image and (b) phase image.

base; the results are shown in Table IV. There was no acid in the aqueous phase, indicating that the polymerization process was complete. Poly(methacrylic acid) is more polar; its presence at the polymer–water interface was strongly favored. A majority of the carboxyl groups were located at the LA particle surface (87%) and subsurface (13%), indicating the formation of a core-shell structure. These results were comparable to a previous study with a similar LA.[25]

Epoxide location

In thermoset LA systems, the crosslinker location within dry films can play a critical role in interdiffusion and in the crosslinking reaction within the LA film and, accordingly, the LA behaviors.[16] When the epoxide is transported into an LA dispersion system, it can be located in the aqueous phase, at the interface between water and the emulsion polymer, or within the emulsion polymer, depending on the chemical similarities between the polymer, the crosslinker, and water.[36,37] Unfortunately, the dye used (RuO_4) could not positively identify the epoxide. In this study, we used TEM and AFM to attempt to elucidate the location of the crosslinker in the LA.

Three types of LA samples were examined by TEM, as shown in Figures 6–8. For the epoxide emulsion, light domains could be observed (see Fig. 6). These domains were postulated to represent the epoxide phase. The light gray (in contrast) domains in Figure 7 for the LA with emulsified epoxide were presumed to be the emulsified epoxide phase, and the large dark
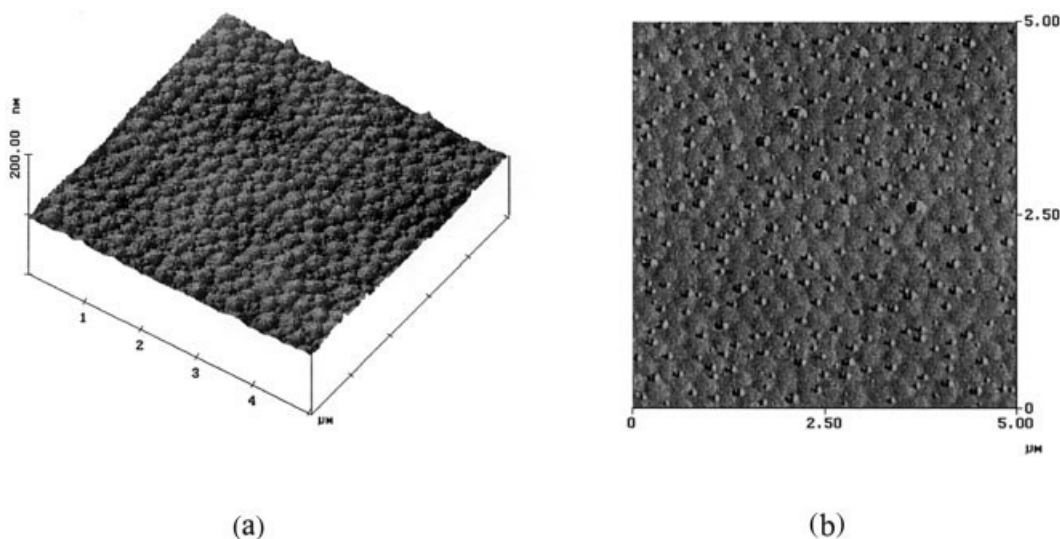

Figure 10 AFM images of the surface of the film made from LA with epoxide emulsion: (a) height image and (b) phase image.

TABLE V
DMTA Data of LA

LA	T_g (°C)	Storage modulus $\times 10^{-6}$ (Pa)	Crosslink density (mol/m³)
LA	54	1.24	152
LA + epoxide emulsion[a]	66	3.35	393
LA + epoxide solution[a]	69	3.58	424
LAE	66	1.96	232
LAE + epoxide emulsion[b]	69	2.98	346
LAE + epoxide solution[b]	72	3.33	390

[a] Equivalent of epoxide.
[b] Addition of 1/2 equivalent.

spherical particles were assumed to be the LA particles. However, the LA added with epoxide solution exhibited a different morphology (see Fig. 8). In this case, only a gray ring around the LA particle could be observed, probably resulting from the solvent and epoxide adsorbed on the LA particle surface.

The distribution of the epoxide within the dry film based on LA (LA) was examined further with AFM. Like the LA film (see Fig. 3), the film prepared from LA with epoxide solution showed a well-ordered close-packed structure in Figure 9. The film prepared from LA with the emulsified epoxide did not exhibit a close-packed array (Fig. 10). Smaller domains were trapped in the interstitial spaces between the LA particles. These domains were postulated to be the emulsified epoxide. The results of TEM and AFM suggested that the emulsified epoxide was isolated from the LA particles, whereas dissolved epoxide was adsorbed on the surface of the LA particles.

Mechanical properties and water adsorption

The dynamic mechanical behaviors of thermosetting LA films are strongly influenced by the number of elastic crosslinks.[38] The temperature dependence of storage modulus, loss modulus, and loss tangent (δ) were evaluated with DMTA, and the results and the calculated crosslink densities[39] are shown in Table V. Without the cycloaliphatic diepoxide crosslinking, the storage modulus for the LA showed a rubbery plateau. The rubber plateau region could be attributed to the formation of effective crosslinking networks through the esterificaion of carboxyl acid and hydroxyl groups attached to the LA. In comparison with the LA film without the cycloaliphatic diepoxide, the films with the epoxide exhibited higher crosslink densities because the epoxide crosslinking further suppressed the polymer flow and made the films more elastic. Interestingly, although the introduction of the epoxide after polymerization offered identical composition for all the LA formulas, the epoxide crosslinked LA films prepared from the LA showed higher crosslink densities than those prepared from LAE. T_g, derived from the loss tangent, was generally in good agreement with crosslink density data.

The effect of the introduction mode of the epoxide was also investigated in terms of hardness and tensile properties. As shown in Figure 11, the Tukon hardness of films based on LA increased with the introduction of the epoxide. For the LAE-based films, an increase in Tukon hardness was observed for the introduction of epoxide solution but not for the emulsion approach. Overall, the postaddition of the epoxide after LA formulation resulted in higher hardness values. The stress–strain behaviors of the cured LA films are shown in Figures 12–14. The tensile modulus followed a similar trend as the Tukon hardness for the crosslinked LA and LAE LAs. The incorporation of the epoxide improved the tensile moduli of films, and it could be interpreted that the solution approach resulted in tensile moduli higher than the emulsion approach. Unlike the tensile modulus, elongation at
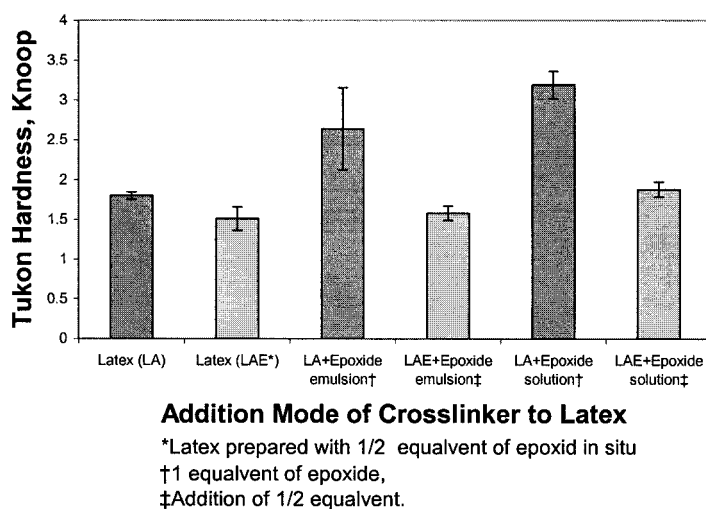

Figure 11 Tukon hardness of cured films as a function of the introduction mode of the epoxide.
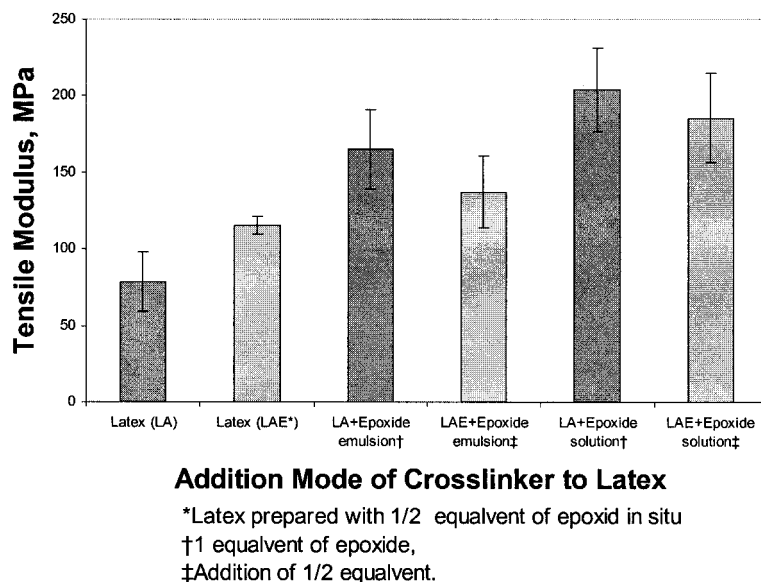
Figure 12 Tensile modulus of cured films as a function of the introduction mode of the epoxide.

break decreased with the introduction of the epoxide, and the solution approach resulted in the lowest elongation at break. The tensile strengths of the coatings were within experimental error.

The effect of the introduction mode of the epoxide on LA film was further verified in terms of water adsorption. As is well known, the curing process of an LA film can suppress the number of elastically effective chains and can accordingly limit water adsorption by the LA film.[41–42] However, the influence of crosslinking sites on the water adsorption of a thermoset LA system has not been reported. In Figure 15, it is shown that when the epoxide was added during polymerization, a lower water adsorption was observed.

General discussion

The dependence of the mechanical properties of LA films on the introduction mode of the cycloaliphatic
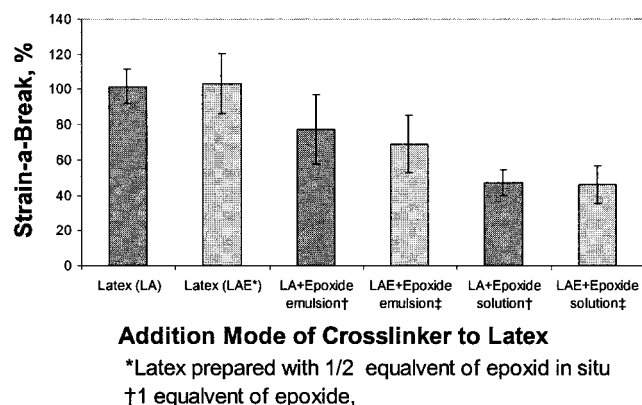

Figure 13 Strain at break of cured films as a function of the introduction mode of the epoxide.

diepoxide into LA was demonstrated in this study. There were differences in hardness, tensile moduli, strain at break, and dynamic mechanical properties between the modes of epoxide addition. The hardness, tensile modulus, and crosslink density for solution approaches were always higher than for the emulsion approaches. In contrast, the latter yielded a higher elongation at break. These variations could be attributed to the influence of the introduction mode on the film formation process. Film formation is a competitive process of interdiffusion and retardation. A very specific situation is expected for films prepared from LA with a high concentration of hydrophilic groups (COOH). In such cases, a separate phase forms (known as the *membrane phase*), which inhibits or retards LA interdiffusion, depending on acid concentration and the structure of the LA.[29] Moreover, the crosslinking and functionality can act as barriers during the curing process to limit the extent of polymer interdiffusion and extended crosslink reaction.[14–18]

The distribution of the crosslinker plays a critical role in the formation of a crosslinked network (see Fig. 16). When the epoxide solution was prepared, the addition of excess water gave rise to a cloudy solution, indicating a phase separation. From this observation, the epoxide, with a low water solubility of 0.02% at 25°C, was expected to be unstable in the aqueous phase. However, a clear solution formed when the epoxide was mixed with acrylic monomers. With stirring, the epoxide was likely to adsorb to the LA particle surface or move into the LA particle because of the similarity between the epoxide and the emulsion polymer. In contrast, when the epoxide was introduced into the LA with the emulsion approach, the emulsified epoxide was stable in the aqueous phase. Accordingly, the emulsified epoxide tended to remain
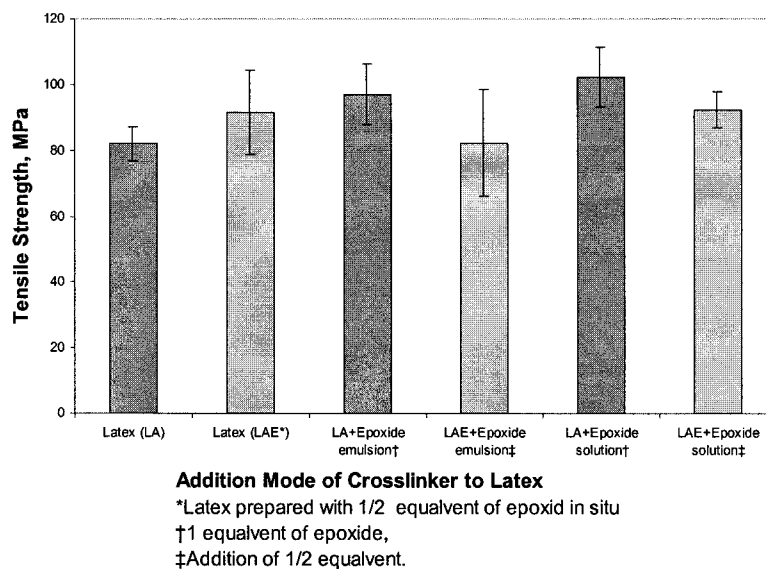
Figure 14 Tensile strength of cured films as a function of the introduction mode of the epoxide.

isolated from the LA particles. The solvent dissolved epoxide was more likely to be adsorbed on the surface of LA particles, and part of the epoxide was probably pulled into the LA particles, resulting in a more even distribution of the epoxide in the latter. In addition, adding the organic solvent to the LA formulation suppressed the T_g and lowered the resistance for polymer and epoxide diffusion, although the interdiffusion and entanglement that predominantly affected the development of mechanical properties took place after coalescence.[14,15] As a consequence, one would expect that an evenly distributed crosslinked network would yield a higher value of hardness, tensile modulus, and crosslink density than that observed for the LA/solvent system. Our investigations of the morphology and properties of LA and LA films confirmed the previous hypothesis.

In comparison with the thermoset LA film prepared from LAE, two differences were observed for films based on LA without the epoxide. One was higher hardness, and the other was a slightly higher crosslink density. These differences could be attributed to more intraparticle crosslinking because half of the epoxide was within the particle, and intraparticle crosslinking occurred during the cure process, resulting in a harder core, restricting particle interdiffusion.

For an LA of the same composition, the formation of a rigid polymer at the shell stage could improve the film modulus more effectively than the formation of a hard polymer at the core stage.[41] It was also reported that shell crosslinking played a more important role in the improvement of the storage modulus than the same volume of core crosslinking.[44] As a result, intraparticle crosslinking was expected to make a smaller
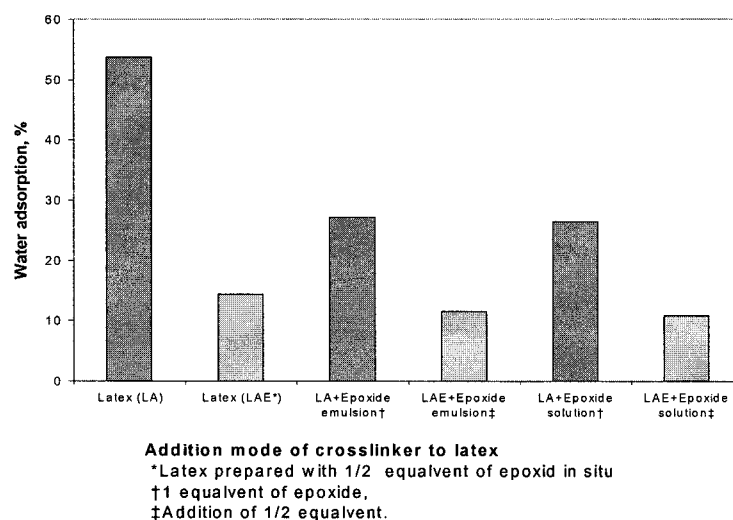

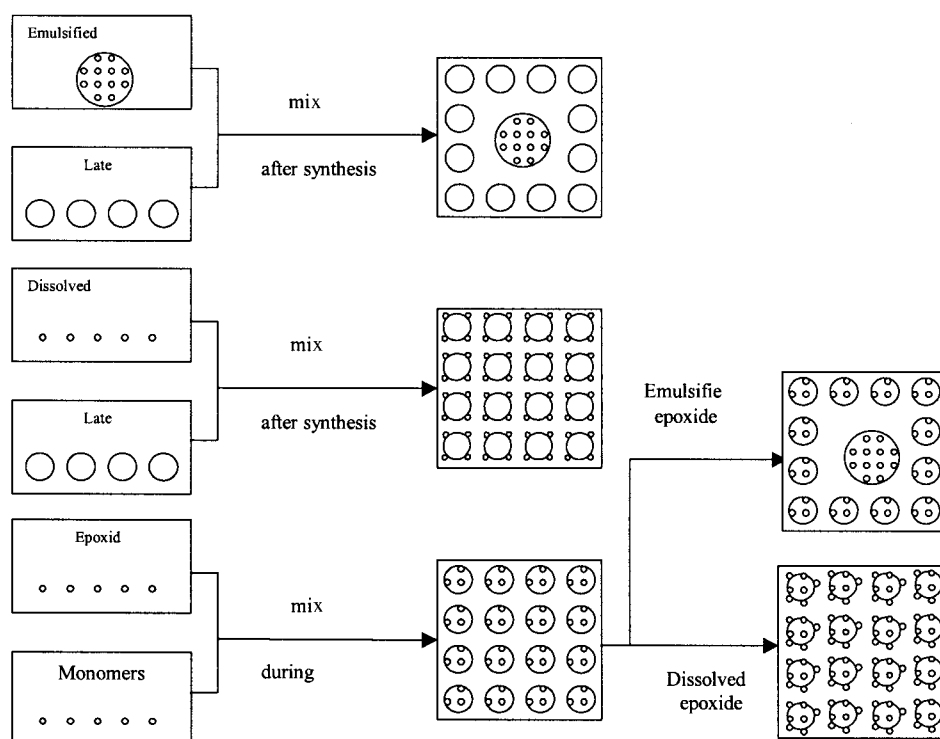**Figure 15** Effect of the introduction mode on the water adsorption of LA films.

Figure 16 Proposed effect of the introduction modes of crosslinker on the epoxide distribution within LA.

contribution to the build-up of crosslink density of LA films, and accordingly, the films based on LAE exhibited slightly lower crosslink densities. Intraparticle crosslinking, especially before LA coalescence, will inhibit or retard the interdiffusion, lowering the surface sensitive properties, such as hardness.[45–47] The LA film prepared from LAE combined intraparticle and interparticle crosslinking, but in the LA film based on LA without expoxide, intraparticle crosslinking was expected to be less significant. As a consequence, the former offered a more homogeneous film that restricted chain mobility of the polymer and suppressed water adsorption of the LA films.

CONCLUSIONS

Cycloaliphatic diepoxide crosslinkable core-shell carboxyl and hydroxyl-functional acrylic LAs were successfully synthesized. The addition modes of the epoxide had an effect on the epoxide location and thermomechanical properties of the cured LA films. The solution method generally provided high hardness and tensile modulus, postulated to be caused by the formation of a more uniform crosslinked network. When the epoxide was added during synthesis of the LA, a significant decrease in water adsorption and hardness was observed, suggesting the presence of a higher level of intraparticle crosslink network.

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