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Synthesis and characterization of cycloaliphatic diepoxide crosslinkable core–shell latexes

G. Teng, M.D. Soucek*

Department of Polymers and Coatings, North Dakota State University, Fargo, ND 58105, USA

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Abstract

New core–shell acrylic latexes designed for crosslinking with cycloaliphatic diepoxide were prepared. The core was prepared using methyl methacrylate, butyl acrylate, and 2-hydroxyethyl methacrylate. The shell contained methyl methacrylate, butyl acrylate, and methacrylic acid. A strong acid acrylate was incorporated into the shell to catalyze the crosslinking reactions, and provide freeze–thaw stability. The crosslinker was co-emulsified with the monomer and added during the latex preparation. The pot-life stability of epoxide was shown to be dependent on latex morphology, initiator system, and reaction conditions. The preparation of stable latex with minimum premature crosslinking required an ambient temperature shell polymerization via a redox initiator system under basic reaction conditions. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Core–shell latex; Methyl methacrylate; Cycloaliphatic diepoxide

1. Introduction

Solvent-borne coatings systems have been the predominant mode for coatings formulations for many years. However, due to environmental regulations there has been an impetus to formulate coatings without organic solvents. One of the most successful approaches to eliminate organic solvents in coatings is latex technology. Latex coatings can be inexpensive and environmentally benign, but suffer with respect to lack of hardness and solvent resistance. Recent studies have concluded that crosslinkable latex resins can afford a performance similar to solvent-borne thermosetting systems.

Although a number of crosslinkers have been developed for the carboxyl or hydroxyl functional latex resins [1–15], glycidyl and cycloaliphatic epoxides have been shown to have excellent weatherability, low resin viscosity, high reactivity, and low toxicity in comparison with the other crosslinkers. Epoxides can be catalyzed by acid, and two types of mechanisms (A-1 and A-2) have been proposed [16,17]. In A-1, the carbonium ion intermediates formation is the rate determining step. In A-2, the oxirane ring opening and new bond formation take place concurrently, and then the nucleophile attacks on the protonated epoxide. This nucleophilic attack is the rate-determined step [16,17].

Recently, cycloaliphatic diepoxide was reported as a suitable crosslinker for acrylic latex by Soucek and coworkers [11–15]. It was found that the reaction of cycloaliphatic epoxide followed the A-2 mode. As shown in Fig. 1, it was proposed that, the unprotonated epoxide is a *cis*-fused ring system, and the axial proton of the cyclohexyl structure prevents the nucleophilic from attacking the epoxide ring prior to the protonation via steric hindrance. Soucek and coworkers also reported that the carboxyl and hydroxyl functional latex resins were crosslinked with a cycloaliphatic epoxide as depicted in Schemes 1 and 2, respectively. The rate of the cycloaliphatic epoxide reaction with hydroxyl groups was found to be lower than with carboxyl groups. The crosslinking reactions were also affected by stoichiometry, pH, and temperature [6,11–15].

Latexes are typically prepared using a water-soluble free radical initiator. The free radical initiation can be catalyzed using a number of transition metal catalysts [30–37]. The stability of crosslinker and pre-mature crosslinking can be determined by the choice of initiator system. The redox system has reportedly been used in the presence of GMA or crosslinkable M-F latex resins [8]. Persulfate–bisulfite and persulfate–iron are two common redox initiator systems as shown in Scheme 3 [30–37]. For the latter, the presence of iron is detrimental to the corrosion resistance of latex-based products, and thus an investigation of persulfate–bisulfite redox system was of particular interest.

The modes of crosslinking in latex films can be classified

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* Corresponding author. Tel.: +1-701-231-8438; fax: +1-701-231-8439.
E-mail address: msoucek@plains.nodak.edu (M.D. Soucek).

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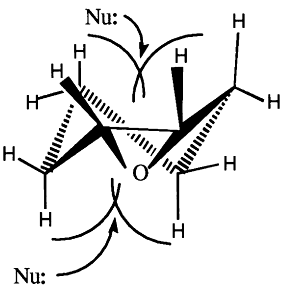
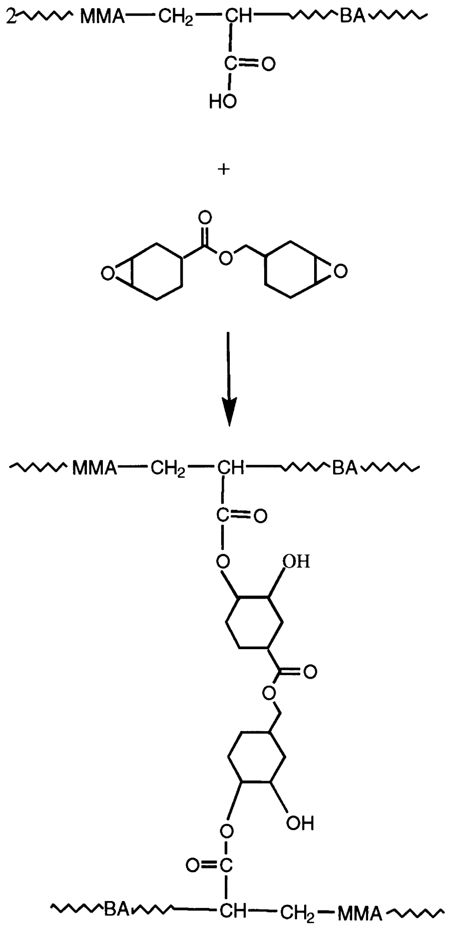
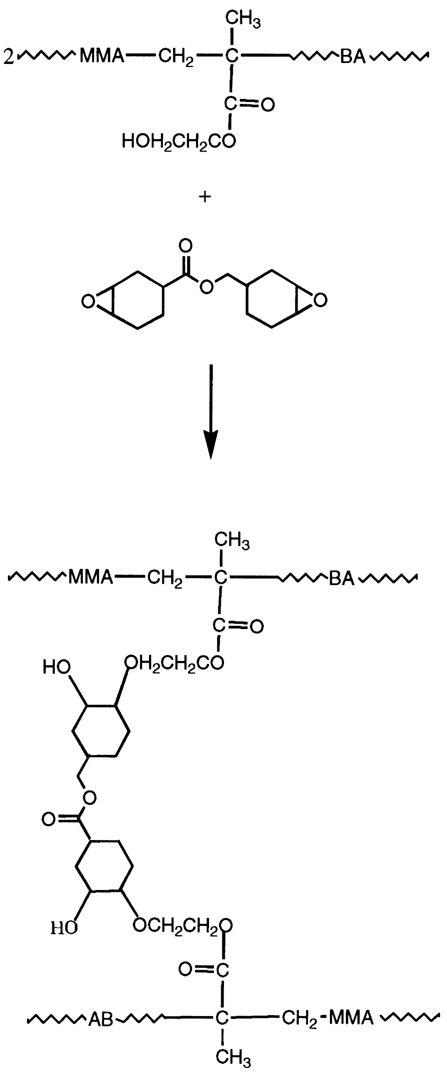


Fig. 1. Depiction of nucleophilic attack on oxirane ring of cycloaliphatic type epoxide.

into three types: homogeneous, inter-particle, and intra-particle, as shown in Fig. 2 [6]. In the homogenous crosslinking mode, the crosslink sites are statistically distributed throughout and between the polymer particles. For the inter-particle crosslinking mode, the crosslinking sites are on the particle surface. The intra-particle crosslinking mode is described as thermoplastic emulsion particles embedded in the matrix of crosslinked polymers. The crosslinking modes are determined principally by the method of cross-linker introduction and functional monomer feed into the system. Generally, when the crosslinker (such as glycidyl methacrylate) is added during the polymerization process, the film forms with the homogeneous crosslinking mode. However, the introduction of crosslinker into functionalized latexes preferentially yields the inter-particle crosslinking network.



Scheme 1.



Scheme 2.

Reduction: $^{-}O_3S\text{-}O\text{-}O\text{-}SO_3^{-} + e^{-} \rightarrow SO_4^{2-} + SO_4^{-}\bullet$

$Cu^{2+} + e^{-} \rightarrow Cu^{+}$

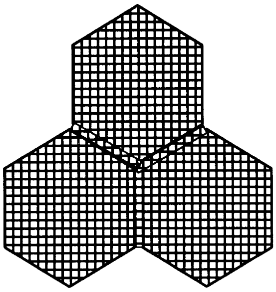
Oxidation: $SO_3^{2-} \rightarrow SO_3^{-} + e^{-}$

$Cu^{+} \rightarrow Cu^{2+} + e^{-}$

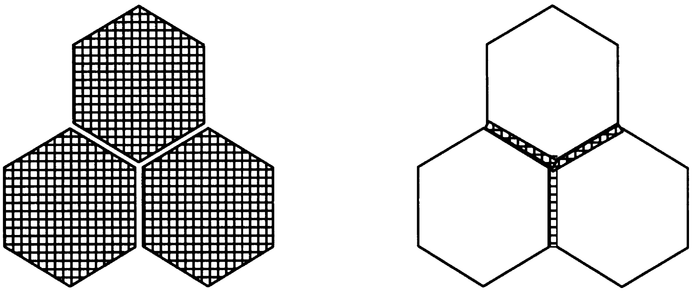
Net Reaction: $^{-}O_3S\text{-}O\text{-}O\text{-}SO_3^{-} + SO_3^{2-}$

$\rightarrow SO_4^{2-} + SO_4^{-}\bullet + SO_3^{-}$

Scheme 3.



Homogenous crosslink



Intraparticle crosslink

Interparticle crosslink

Fig. 2. Crosslink modes of latex.

In crosslinked latex coatings, epoxides generally are added to a previously prepared hydroxyl- or carboxyl-functional latex via emulsion or solution [19–29]. This has the potential to induce mechanical instability and non-uniform crosslinking due to the incompatibility of latex and epoxide. The surface treatment of epoxide functional latexes with carboxyl functional monomer or carboxyl functional latex with epoxide is another approach to introduce the epoxide [8]. In addition, epoxides such as glycidyl methacrylate have also been introduced during polymerization without significant loss of functionality. The introduction of the epoxide during polymerization is presumed to provide more homogenous films, but suffered from gelation when even low concentration of methacrylic acid (MAA) were included into the latex forumulation [7].

In this study, cycloaliphatic diepoxide crosslinkable latexes were prepared via free radical emulsion polymerization with and without a redox initiation system. The emulsion polymerization was also carried out under either acidic or basic condition. Core–shell latexes predominately of methyl methacrylate (MMA) and butyl acrylate (BA) were prepared with hydroxyl (2-hydroxyethyl methacrylate (HEMA)) and carboxyl (methacrylic acid) functional monomers. In one series of latexes, HEMA was formulated into the core and MAA into the shell; in a second series of latexes, MMA was formulated into the core and HEMA into the shell. It was attempted to add the diepoxide during the preparation of both the core and the shell of the various latexes. The morphology of the core–shell latexes was studied by preparing a separate latex with a polystyrene core and comparing with hydroxyl functionalized core via transmission electron microscopy (TEM) and acid distribution.

2. Experimental

2.1. Materials

All the materials were used without further purification. Cycloaliphatic diepoxide (UVR-6105) and surfactants (Triton-200 and Tergital-XJ) were supplied by Union Carbide Corporation, Danbury, CT. 2-Sulfoethyl methacrylate (SEM) was supplied by Hampshire Chemical Corporation, Waterloo, NY. MMA, BA, MAA, HEMA, ammonium persulfate, copper (II) sulfate, triethyl amine, and sodium bicarbonate were purchased from Aldrich, Milwaukee, WI. Ruthenium tetroxide (RuO_4) was purchased from Polyscience, Warrington, PA. Sodium bisulfite was purchased from Mallinckrodt Baker, Paris, KT. (Ethylenedinitrilo)-tetra-acetic acid tetrasodium salt (EDTATSS) was purchased from EM Science, Gibbstown, NJ.

2.2. General synthesis

Emulsion polymerization was effected in a 500 ml four-necked flask immersed in a constant temperature water bath and equipped with a mechanical stirrer, a reflux condenser, and a gas inlet. A Universal Syringe Pump (Valley Scientific Model 5754) and addition pump (ISMATEC REGLO-100)

Table 1
Recipes for the synthesis of hydroxyl functional homogeneous latex; entries in parentheses are formulations without or with epoxide, respectively

Components	Function	Weight (g)	Equivalent
BA	Monomer	78.98	0.62
MMA	Monomer	94.74	0.94
HEMA	Hydroxyl monomer	8.16	0.06
$NaHCO_3$	Buffer	0.2	–
Triton-200	Surfactant	(6.4 or 7)	–
Tergital-XJ	Surfactant	(1.6 or 1.2)	–
Deionized water	Solvent	96	–
Cycloaliphatic diepoxide	Crosslinker	0 or 15.89	(0 or 0.12)

were used to feed the catalyst and monomers into the reaction flask, respectively. When the polymerization was required to proceed under basic conditions, triethylamine was utilized to neutralize the monomer to pH 8.5, using pH paper as an indicator.

2.3. Homogenous latex preparation

(a) *BA–MMA–HEMA copolymer containing cycloaliphatic diepoxide.* The monomer mixture of BA, MMA, and HEMA, as shown in Table 1 was slowly added into a flask containing a stirring water solution of $NaHCO_3$ (0.20 g), Triton-200 (6.4 g), Tergital-XJ (1.6 g), and deionized water (96 g) to obtain a monomer pre-emulsion. An initiator solution was prepared by dissolving ammonium persulfate (0.88 g) in deionized water (40 g). The monomer pre-emulsion (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 contents were stirred for 0.5 h at 80°C bath temperature to form seed latex particles. The cycloaliphatic diepoxide (15.89 g), Triton-200 (0.56 g), Tergital-XJ (0.14 g), and water (20 g) were added slowly into a flask containing the remaining pre-emulsion (270.2 g) with continuous stirring.This mixture and initiator were concurrently added into the seed latex at a constant rate (1.5 mL/min) over a period of 3 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 2 h in order to digest all residual monomers.

(b) *BA–MMA–HEMA copolymer without cycloaliphatic diepoxide.* The same procedure as for the BA–MMA–HEMA copolymer containing cycloaliphatic diepoxide was used, without the addition of cycloaliphatic diepoxide. Table 1 outlines the specific formulation used.

Table 2
Recipes for the synthesis of homogenous carboxyl functional latex; entries in parentheses are formulations without or with epoxide, respectively

Components	Function	Weight (g)	Equivalent
BA	Monomer	86.5	0.68
MMA	Monomer	84.40	0.84
MAA	Carboxyl monomer	10.8	0.12
$NaHCO_3$	Buffer	0.2	–
Triton-200	Surfactant	(6.4 or 7)	–
Tergital-XJ	Surfactant	(1.6 or 1.8)	–
Deionized water	Solvent	48	–
Cycloaliphatic diepoxide	Crosslinker	0 or 15.89	(0 or 0.12)

Table 3
Recipes for the synthesis of hydroxyl functional core latex with MAA; entries in parentheses are formulations without or with epoxide, respectively

Components	Function	Weight (g)	Equivalent
BA	Monomer	39.49	0.31
MMA	Monomer	47.37	0.47
HEMA	Hydroxyl monomer	8.16	0.06
$NaHCO_3$	Buffer	0.1	–
Triton-200	Surfactant	(3.2 or 3.8)	–
Tergital-XJ	Surfactant	(0.8 or 1)	–
Deionized water	Solvent	48	–
Cycloaliphatic diepoxide	Crosslinker	0 or 15.89	(0 or 0.12)

(c) *BA–MMA–MAA copolymer containing cycloaliphatic diepoxide.* The same procedure as for the BA–MMA–HEMA copolymer containing cycloaliphatic diepoxide was used, using MMA replacing HEMA. Table 2 outlines the specific formulation used.

(d) *BA–MMA–MAA copolymer without cycloaliphatic diepoxide.* The same procedure as for the BA–MMA–MAA copolymer containing cycloaliphatic diepoxide was used, without the addition of cycloaliphatic diepoxide. Table 2 outlines the specific formulation used.

2.4. Core latex preparation

(a) *BA–MMA–HEMA copolymer containing cycloaliphatic diepoxide.* The monomer mixture of BA, MMA, and HEMA as shown in Table 3 was slowly added into a flask containing a stirring water 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 pre-emulsion for the latex core. An initiator solution was prepared by dissolving ammonium persulfate (0.44 g) in deionized water (20 g). The monomer pre-emulsion (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 contents were stirred for 0.5 h at 80°C bath temperature to form seed latex particles. The cycloaliphatic diepoxide (15.89 g), Triton-200 (0.56 g), Tergital-XJ (0.14 g), and water (20 g) were added slowly into a flask containing the remaining pre-emulsion (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 in order to digest all residual monomers.

(b) *BA–MMA–HEMA copolymer without cycloaliphatic diepoxide.* The same procedure as for the BA–MMA–HEMA copolymer containing cycloaliphatic diepoxide was used, without the addition of cycloaliphatic diepoxide. Table 3 outlines the specific formulation used.

Table 4
Recipes for the synthesis of hydroxyl functional core latex with styrene; entries in parentheses are formulations without or with epoxide, respectively

Components	Function	Weight (g)	Equivalent
BA	Monomer	39.68	0.31
MMA	Monomer	43.16	0.41
HEMA	Hydroxyl monomer	8.16	0.06
$NaHCO_3$	Buffer	0.1	–
Triton-200	Surfactant	(3.2 or 3.8)	–
Tergital-XJ	Surfactant	(0.8 or 1)	–
Deionized water	Solvent	48	–
Cycloaliphatic diepoxide	Crosslinker	0 or 15.89	(0 or 0.12)

(c) *BA–Styrene–HEMA copolymer containing cycloaliphatic diepoxide.* The same procedure as for the BA–MMA–HEMA copolymer containing cycloaliphatic diepoxide was used, using styrene instead of MAA. Table 4 outlines the specific formulation used.

(d) *BA–Styrene–HEMA copolymer without cycloaliphatic diepoxide.* The same procedure as for the BA–Styrene–HEMA copolymer without cycloaliphatic diepoxide was used, without the addition of cycloaliphatic diepoxide. Table 4 outlines the specific formulation used.

2.5. Shell latex preparation with thermal initiator

A solution of BA, MMA, and HEMA or MAA as shown in Tables 4 and 5 was slowly added into a flask containing a stirring water 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 pre-emulsion for the shell. A 5 wt% SEM aqueous solution was prepared by dissolving SEM (1 g) in deionized water (20 g). The initiator solution was prepared by dissolving ammonium persulfate (0.44 g) in deionized water (20 g). After core polymerization was complete, the reactor was charged with the initiator solution (6 g) for 2 min at 80°C. The pre-emulsion, the remaining initiator, 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 using a syringe pump. The polymerization was maintained at 80°C under nitrogen. After the addition of all ingredients, the contents were heated for an additional 2 h at 85°C to digest any residual monomers. The reactor was cooled to 30–35°C, and the reaction mixture was neutralized with ammonia (pH = 8.5). The latex was then filtered through a 300-mesh screen to remove any residual coagulum.

Table 5
Recipes for the synthesis of carboxyl functional shell latex

Components	Function	Weight (g)	Equivalent
BA	Monomer	43.25	0.34
MMA	Monomer	42.20	0.42
MAA	Carboxyl monomer	5.4	0.06
$NaHCO_3$	Buffer	0.1	–
Triton-200	Surfactant	3.2	–
Tergital-XJ	Surfactant	0.8	–
Deionized water	Solvent	48	–
SEM	Acid catalyst	0.0571	0.0003

2.6. Shell latex preparation with redox initiator

Procedure I. The same procedure as for the thermal-initiated shell polymerization was used except the redox-initiated system was used, and polymerization was carried out at room temperature (22°C). The redox initiator system consisted of oxidant and reductant, and the recipe was shown in the Table 6. The oxidant solution was prepared by dissolving ammonium persulfate in deionized water, and the reductant solution was prepared by dissolving EDTA, sodium bisulfite, and copper (II) sulfate in deionized water. Half of the reductant portion of the initiator solution was added two minutes 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.

Procedure II. The same method as Procedure I was used, except that the reductant solution was fed to the reactor concurrently at a constant rate (0.17 ml/min) over a period of 2 h.

2.7. Preparation and thermal stability investigation of epoxide emulsion

The cycloaliphatic diepoxide (UVR-6105) was emulsified using a mixture of anionic and non-ionic surfactants (Triton-200 and Tergital-XJ). The anionic surfactant (0.32 g) and non-ionic surfactant (0.14 g) were dissolved in deionized water (11 g). Then the cycloaliphatic diepoxide (9 g) was slowly emulsified into the water solution at 60°C. The emulsion was added into a 50 ml flask immersed in a constant temperature water bath and equipped with a mechanical stirrer, a reflux condenser, and a gas inlet. The content was heated at 80°C for 7.5 h.

2.8. Latex characterization

The ^1H NMR spectra were obtained on a JEOL 400 spectrometer in $CDCl_3$ at ambient temperature. Infrared (IR) spectra were obtained on a Nicolet Magna-IR 850 spectrometer. The IR spectra of dry latex film were recorded with dry air as the background. The particle size measurement was performed using dynamic light scattering (NICOMP 380). The morphology of the latex stained with ruthenium tetroxide (RuO_4) and phosphotungstic acid (PTA) was determined by TEM at CRSS-USDA Electron Spectroscopy Center, Fargo, ND. Acid distribution in the latex was determined using a method by Robertson [38]. A typical latex titration curve is indicated in Fig. 3. The surface acid was considered to be the acid reacted in the first second after base addition. The end-point of the sub-surface acid was determined by back titration with HCl after equilibration at high pH for 1 h. The acid distribution in the

Table 6
Redox initiator system

Formulation	Ammonium persulfate (g)	Sodium bisulfate (g)	Copper sulfate (g)	EDTATSS[a] (g)
I	4.47	2.01	0.72	1.44
II	2.79	0.05	0.07	0.14
III	0.44	0.22	0.22	0.22
IV	0.44	0.05	0.05	0.05

[a] Ethylenedinitrilo-tetra-acetic acid tetrasodium salt.

aqueous phase was further measured. The diluted latex (50 wt% in water) was separated using 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. The process was repeated three times. The acid concentration was determined by conductometric titration of 0.1 N NaOH solution.

3. Results and discussion

The objective of this study is to develop latexes suitable for crosslinking with cycloaliphatic diepoxide. A number of factors have to be taken into account, including dispersion stability, pot life of the epoxide, morphology of the latex, particle size and distribution, core and shell dimension, and acid distribution. The dispersion stability of the latex particle is dependent on the monomers, type of initiator system, and surfactants. The morphology of core–shell latex particles is dependent on the choice of monomers and monomer feed sequence. The stability of glycidyl methylacrylate in latex system has been shown to be particularly dependent on initiation and pH [13–15,18,38–59]. As a consequence, to develop a new latex system for crosslinking with cycloaliphatic diepoxide, all of these factors were systematically varied in this study.

Several series of latexes were prepared under starved condition via free radical polymerization. Initially, the latexes were prepared using a thermal initiator (persulfate) with the hope to elucidate the influence of the sequence of monomer fed into the system upon the morphology and epoxide stability of the overall system. For comparison, a redox initiation system (persulfate–bisulfite–copper sulfate) was utilized for preparing latexes at ambient temperature. It was thought that initiation at ambient temperature could limit the mobility of the phase, and suppress the pre-mature reaction of the epoxide. Finally, the polymerization was conducted under basic conditions to identify the effect of pH on the reaction. The latexes were evaluated using NMR, IR, TEM, light scattering, and conductometric analysis.

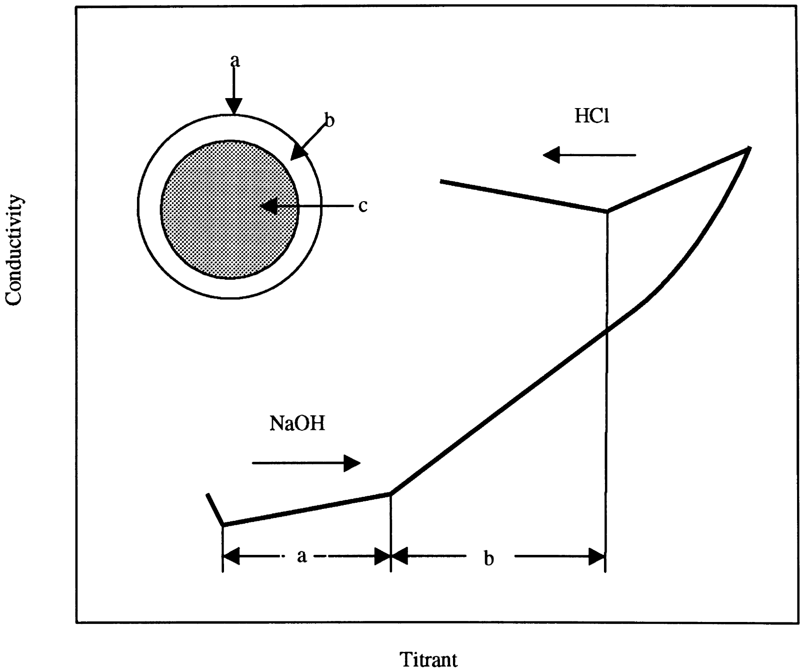


Fig. 3. Conductivity varied with titrant: (a) surface acid; (b) subsurface acid; (c) unneutralized acid.

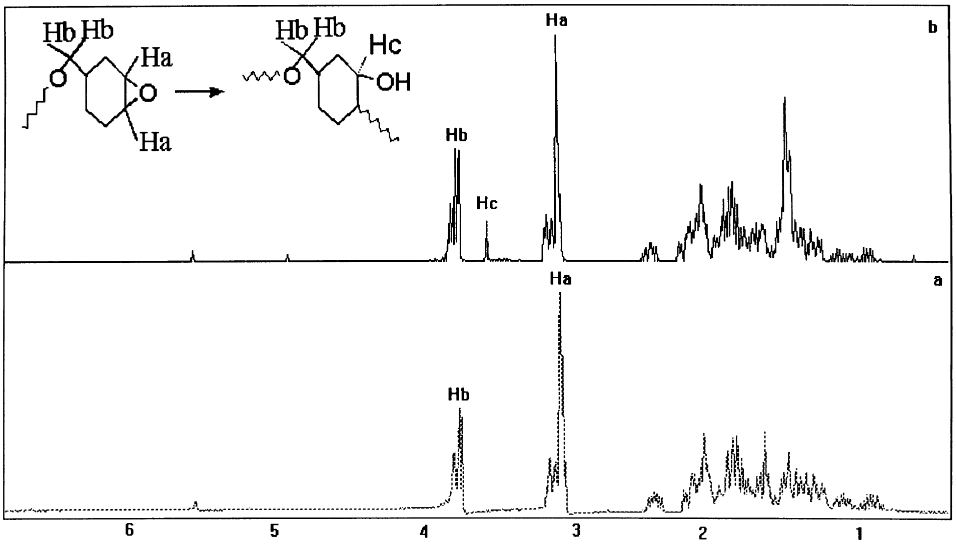


Fig. 4. ^{1}H NMR spectra oxirane ring in chloroform. (a) epoxide; (b) epoxide emulsion after heating at 80°C for 7.5 h.

3.1. Cycloaliphatic epoxide stability of thermally initiated latex systems

The influence of functional monomer composition, morphology of latex, and introduction method of crosslinker was investigated using a thermal initiation system. However, the first concern was the stability of the cycloaliphatic epoxide during the polymerization. Several epoxide reactions are possible: (1) esterification of the epoxide with the carboxyl group of MAA; (2) etherification of the epoxide with the hydroxyl group of HEMA or surfactants; (3) hydrolysis of the epoxide; and (4) homopolymerization of the epoxide. In this study, hydrolysis, possible reaction with surfactant, and homopolymerization were investigated.

The epoxide emulsion was prepared under the same reaction condition (80°C for 7.5 h) as the thermal-initiated polymerization. To monitor the conversion of cycloaliphatic diepoxide, ^{1}H NMR was used [11–15]. The relative concentration of the cycloaliphatic diepoxide versus the reacted epoxide in the epoxide emulsion system was calculated based on the integration values of protons a and c, as labeled in Fig. 4. After the epoxide emulsions was subjected to above reaction conditions, less than 10% of the epoxide charged was observed to react. This indicates that hydrolysis, homopolymerization, or esterification with surfactants was not the principal reactions during polymerization.

3.2. Homogenous latexes

Previous studies have been conducted to investigate homogenous latexes [11–15]. As a control for our study, two types of homogenous latexes were prepared via semi-continuous polymerization. One consisted of carboxyl functionalized monomer and the epoxide (see Table 2), and the other contained hydroxyl functionalized monomer and the epoxide (see Table 1). The epoxide was incorporated into the latex formulations after the seed preparation. When cycloaliphatic diepoxide was added during the polymerization of the carboxyl functional latex, gelation occurred. It was observed in the ^{1}H NMR spectra that all the epoxide groups were consumed during polymerization. From this spectral evidence, and the earlier control experiments, it was surmised that carboxyl groups react with the diepoxide to form ester. It was also assumed that significant levels of inter-particle crosslinking led to the gelation. In contrast, the hydroxyl-functionalized latex did not gel, and the epoxide group was observed (IR, and ^{1}H NMR) intact after the polymerization. However, the hydroxyl functionalized latex suffered with respect to coatings properties, and hydrolytic stability, as compared to the carboxyl functional latex coating system [11–15].

3.3. Preparation of core–shell latexes

Two-stage latex preparation was attempted by introduction of both carboxyl and hydroxyl functional monomer within the same latex particle. By controlling the architecture of the latex particle, and the spatial position of the functional groups, it was hoped that a stable mixed functional latex could be prepared for crosslinking with cycloaliphatic epoxides. In a core–shell latex, the core is generally prepared with a relatively high glass transition temperature (T_g) compared to the shell to enhance mechanical properties [4]. In our study, however, the core and shell were formulated with the same T_g. It was anticipated that crosslinking would raise the overall T_g of the system, therefore a higher core T_g was not needed for improved mechanical properties. The epoxide was embedded into the core latex particles with less reactive hydroxyl functional monomer, and then carboxyl functional monomer and strong acid catalyst were added at the shell polymerization stage. Due to the differences in hydrophilicity, the strong acid groups are

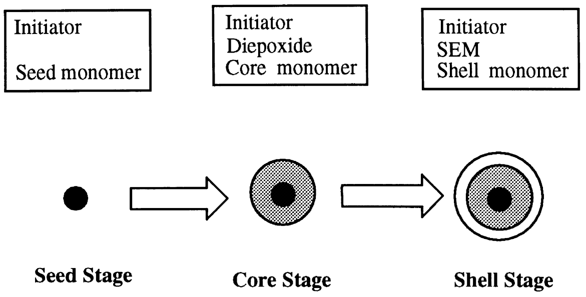


Fig. 5. Typical procedure of latex synthesis.

preferentially located near the surface of the latex shell, and the epoxide groups inside latex particles. Consequently the pre-crosslinking of the epoxide could be inhibited. Fig. 5 shows the concept of the proposed approach.

In addition to monomers BA, MMA, HEMA, and MAA as the representatives of monomers utilized in the latex coatings, styrene also was investigated to identify the core–shell structure of the latexes. The latex with hydroxyl functionality and the epoxide in the core (see Table 3), and carboxyl functionality and strong acid in the shell (see Table 5) was prepared by a seeded semi-continuous emulsion polymerization. After the synthesis, the latex was stable, but the epoxide groups were consumed. On the other hand, when cycloaliphatic diepoxide was added into the carboxyl functional core formulation, gelation occurred. By virtue of the lack of reactivity of the epoxide with water, surfactant or itself (homopolymerization) under latex preparation, it can be assumed that gelation was a result of pre-mature cross-linking with the hydroxyl and carboxyl functionality.

3.4. Redox-initiated polymerization

The investigation in the synthesis of latexes using thermal initiator demonstrated that the introduction of the epoxide into hydroxyl functional latex allowed for the production of latex with colloid and epoxide stability. However, when the carboxyl functional monomer was used in the core formulation containing the epoxide, all the epoxide was consumed during the polymerization. To overcome this problem, a combination of thermal and redox initiators was employed in the shell polymerization. The redox initiators allow a low polymerization temperature, which can aid in the stability of diepoxide.

The recipe of the ambient temperature redox initiator system consisting of persulfate, bisulfite, and copper sulfate is shown in Table 6 [54–56]. After the core latex with hydroxyl functionality and the epoxide (see Table 3) was prepared via thermal initiator, the synthesis of the shell (see Table 5) with carboxyl functionality and strong acid proceeded using redox initiator at ambient temperature. When the reductant portion (bisulfite) was added at a constant rate into the second stage polymerization using Formulation I, a high level of coagulum formation was observed. However, when the reducing portion (bisulfite) was added via a batch method. Coagulation was significantly diminished. This difference can be attributed to the effect of initiation rate on particle formation [48–50].

Although the batch addition of reductant can provide less coagulate coagulation, the latex particles were less uniform. A series of alternative latexes were made using a similar procedure, changing initiator composition. The particle size and distribution of latexes were evaluated via TEM and light scattering. At low concentration of initiator (Formulation II), low levels of coagulation were observed, but particle size was still not uniform as shown in Fig. 6. On the other hand, very low concentration of initiator (Formulation IV) led to a low polymer yield due to the inadequate radical formation suitable for initiation. The optimum formulation appeared to be Formulation III (intermediate), which provided a high yield, less coagulate, and uniform latex size and structure as shown in Fig. 7. In addition to particle size, the TEM data (Figs. 6 and 7) also showed latex particles which were spherical. The particle size of latexes was quantified by light scattering, and the results are shown in Table 7. The particle size of the core–shell latex is larger than that of the homogenous latex (see Table 2), since lower concentration of carboxyl functionalities are located near the latex particle surface.

The crosslinking reaction of epoxide with carboxyl groups as a function of initiation mode can be followed using FT-IR. As shown in Fig. 7, the oxirane ring of the cycloaliphatic diepoxide stretches appears at 803, 793, and 787 cm^{-1}. The intensities of these stretching frequencies decreased when the redox initiator was utilized. Thus the lower reaction temperature of the redox-initiated shell appeared to suppress the reactivity of the epoxide.

3.5. Polymerization pH and latex stability

The regulation of pH plays a significant role in the emulsion polymerization, depending on the formulation, and process conditions [57]. At low pH, the decomposition of persulfate initiator was accelerated, resulting in a reduction in the amount of free radical and monomer conversion. The pH also influences the pre-crosslink formation and hydrolysis of cycloaliphatic diepoxide during polymerization. A recent model compound study for crosslinking of acrylic latex with cycloaliphatic diepoxide reported that, as the pH of the media decreased, the rate of crosslinking reaction increased [13–15]. In an effort to enhance the stability of the epoxide, the emulsion polymerization under basic conditions was investigated. Amine (triethyl amine) was added to the latex formulation to regulate the pH of the emulsion. Initially, the homogenous latex was prepared with carboxyl functionality and the epoxide (see Table 2) under basic conditions. This attempt resulted in a high level of latex coagulation. To overcome this problem, the formulation and feed method was modified.

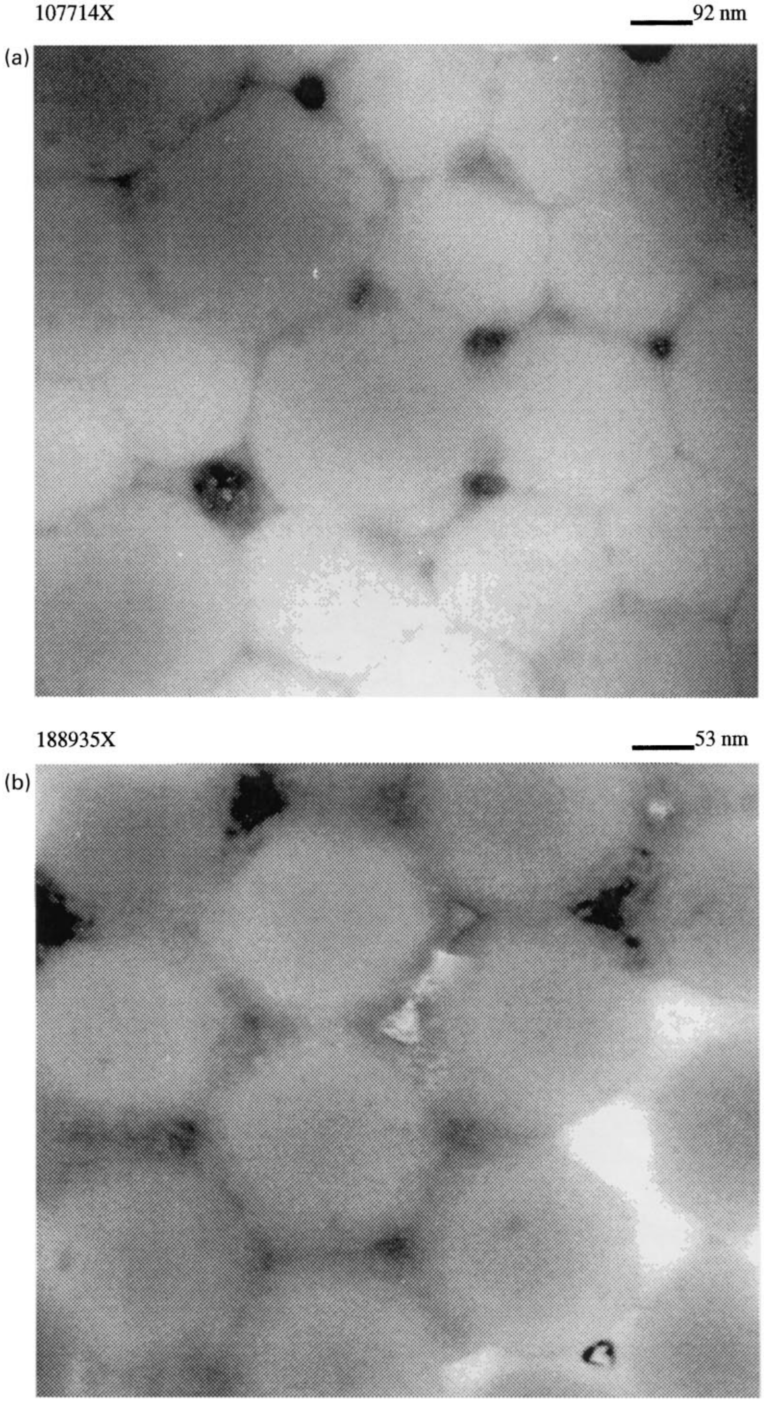


Fig. 6. TEM of: (a) core–shell latex made with high concentration of mixed initiator (Formulation II in redox system); (b) latex made with normal concentration of mixed initiator (Formulation III with redox system).

When the core–shell latex polymerization (see Tables 3 and 5) was carried out under basic condition using the thermal initiator, the hydroxyl functionalized core latex remained stable. However, a large amount of coagulation occurred after shell polymerization. In comparison, the same core–shell formulation with a mixed initiator for the shell polymerization at ambient temperature resulted in no observable coagulation. The thermal-initiated core–shell latexes prepared under acidic conditions were also stable (see Table 8). Thus, the stability of latex dispersion and crosslinking was found to be a function of pH, functionality, and initiation mode. The latexes remained stable under one of following three conditions: (1) the absence of carboxyl functional monomer; (2) redox initiation; (3) the absence of neutralization (low pH).

Temperature can play an important role on the stability of

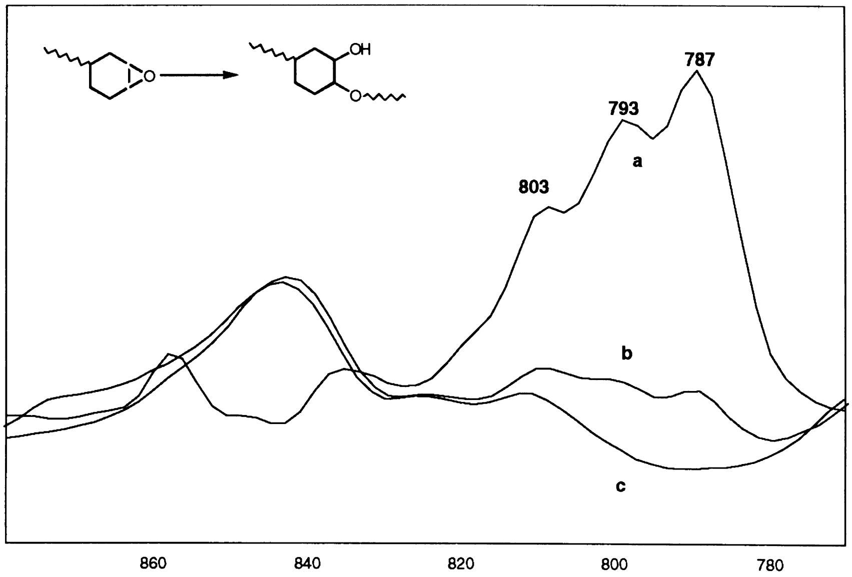


Fig. 7. IR spectra of oxirane ring: (a) epoxide; (b) core–shell latex containing epoxide with redox initiators; (c) core–shell latex containing epoxide with thermal initiator.

the latex. For the batch process, a higher concentration of initiator can be produced via elevated reaction temperature, providing low molecular weight polymers. The resultant small latex particles were less stable than that of larger latex particle. However, in the case of the semi-continuous process, polymerization proceeded under starved conditions, and uniform particle size is prone to form [58]. The role of temperature on the stability of the latex probably principally reflects on the movement of particles. The increase of temperature can induce extended Brownian motion, and as a consequence the dispersion stability decreases [18,59]. Additionally, the stability of the epoxide was monitored by FT-IR. Results in Fig. 7a and Table 9 show that basic conditions stabilize the epoxide during polymerization.

3.6. Morphology

A number of morphologies of two-stage latex particles have been reported [42–47], such as core–shell, raspberry-like, sandwich-like, acorn-like, inverted, and octopus ocellatus-like. The thermodynamic forces and kinetics of morphological development of latex determine the final structure. From the homogenous latex system and preliminary core–shell latex experiments, it was clear that the optimum core–shell latex model for the stability of both the epoxide and latex was a hydroxyl functionalized core, and carboxyl functionalized shell. In this system, the hydrophilic shell polymer–aqueous interphase would be more energetically favorable than polymer–aqueous interphase with the hydrophobic core [42–47], and thus it has a lower free energy for core–shell morphology than the inverted morphology. The morphology of the core–shell latex was evaluated by TEM.

In order to distinguish the core and shell via staining, styrene was introduced into the latex formulation. The latex was prepared with styrene and hydroxyl functionality in the core (see Table 4) and carboxyl functionality in the shell (see Table 5). The resultant latex was then stained with RuO_4, and analyzed using TEM as shown in Fig. 8a and b. Spherical latex particles and a significant contrast between core and shell in the stained latex were observed, suggesting that styrene was confined within the interior of the latex. This is clear evidence for the formation of the core–shell structure. Since the glass transition temperature of both styrene and MMA is approximately the same, and both core–shell latexes were formed under starved conditions, the latex based on MMA was postulated to have a core–shell structure as shown in Fig. 9.

Table 7
Particle size of latex

Latex type	Epoxide	Initiator	Particle size (nm)	Standard deviation (nm)
Homogenous	No	Thermal	238.8	18.2
Core/shell	No	Thermal	250.7	20.3
Core/shell	Yes	Thermal	252.0	28.2
Core/shell	Yes	Mixed	241.3	30.4

Table 8
Coagulate of latex

Latex type	Neutralization	Shell initiator	Coagulate
Homogenous	Yes	Thermal	Yes[a]
Core/Shell	Yes	Thermal	Yes
Core/shell	No	Thermal	No[b]
Core/shell	No	Redox	No
Core/shell	Yes	Redox	No

[a] 0.5 wt% or less of coagulates presented in latex.
[b] High level of coagulates presented.

3.7. Core and shell dimension

In latex design, especially for latexes containing carboxyl group, the expansion characteristic of latex particle is of particular importance. The expansion of latex particles depends on the concentration and frequency of acid group in the particle, T_g of latex, and pH of mixture. Particle-sedimentation in a centrifugal field and diluted suspension viscometer have been previously utilized to elucidate the expansion [48–50]. However, no study on the expansion of the core and shell portions of the latex has been reported. A method to identify such expansion has been proposed. The expansion of particles with styrene in the core can be evaluated using TEM data. For this system:

$$W_c = V_c D_c = \frac{4}{3}\pi R_c^3 D_c \qquad (1)$$

$$W_s = V_s D_s = \frac{4}{3}\pi((R_c + L_s)^3 - R_c^3)D_s \qquad (2)$$

where W_c, V_c, D_c, and R_c represent the weight, volume, density, and radius of the latex core, respectively. W_s, V_s, D_s, and L_s represent the weight, volume, density, and thickness of the shell, respectively. The core and shell were formulated to have to be equal weight percentage by mass.

$$\frac{4}{3}\pi R_c^3 D_c = \frac{4}{3}\pi((R_c + L_s)^3 - R_c^3)D_s \qquad (3)$$

Thus, the simplification of Eq. (3) yields:

$$\frac{L_s}{R_c} = \left(\frac{D_c}{D_s} + 1\right)^{1/3} - 1 \qquad (4)$$

Since the carboxyl-functionality is more hydrophilic than the hydroxyl- functionality, added in the second stage, the density of shell latex particles should be lower than that of the core.

Table 9
Stability of epoxide in latex

Latex type	Neutralization	Shell initiator	Epoxide stability[a]
Homogenous	No	Thermal	No[b]
Core/shell	No	Thermal	No
Core/shell	Yes	Thermal	Yes[c]
Core/shell	No	Redox	Yes
Core/shell	Yes	Redox	Yes

[a] 1 of equivalent ratio of epoxide to functional monomer.
[b] Epoxide disappeared.
[c] Epoxide remained.

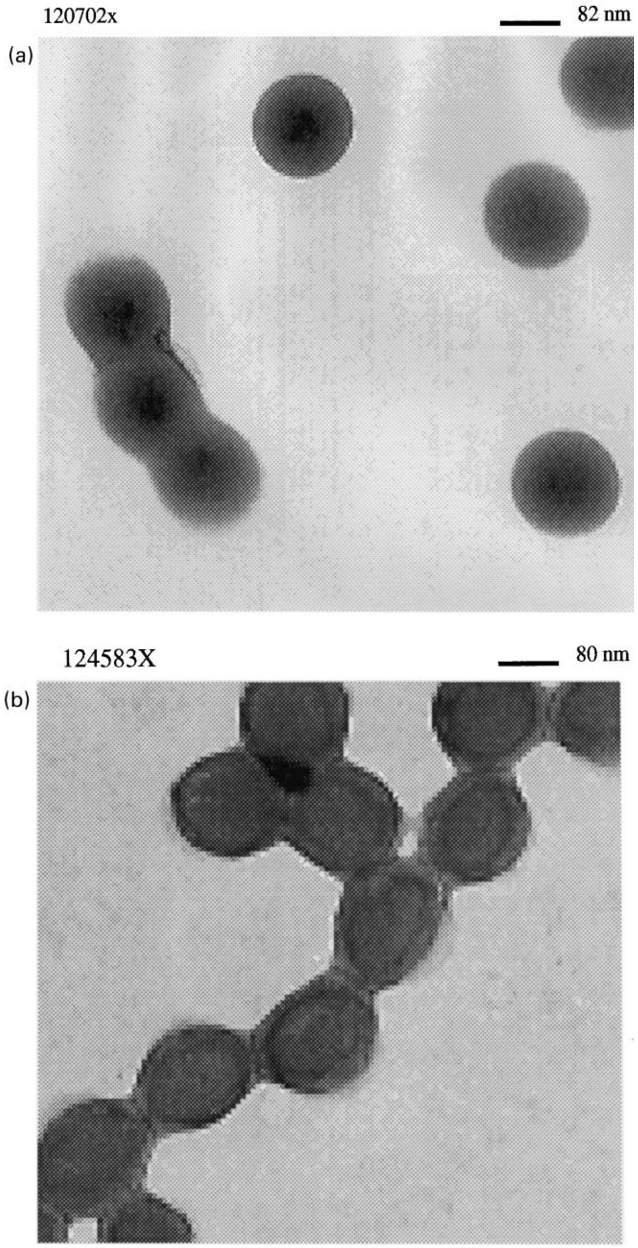


Fig. 8. TEM of latex containing styrene (a) without RuO_4; (b) with RuO_4.

$$D_c > D_s \qquad (5)$$

The substitution in Eq. (4) yields:

$$\frac{L_s}{R_c} < (2)^{1/3} - 1 = 0.26 \qquad (6)$$

Since hydrophobicity and rigidity of styrene restrict diffusion, and starved condition promote homogeneity for both the core and shell, it is presumed that R_c is constant [58]. A relative expansion of latex particles can be predicted in terms of the ratio between core and shell dimension, and comparison with 0.26. Based on the TEM data in Fig. 8a, the

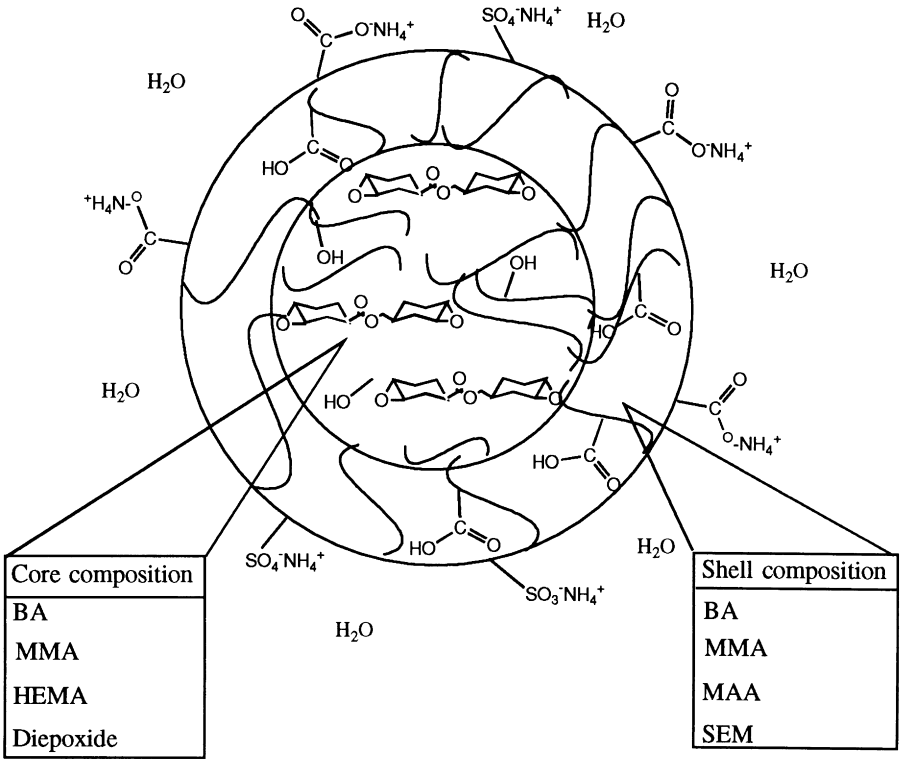


Fig. 9. Depiction of crosslinkable cycloaliphatic diepoxide core–shell latex.

ratio between the core and shell dimension of the latex is 0.51, almost twice that of 0.26, suggesting that a greater shell expansion than expected occurred. In addition, the introduction of styrene in the core provides a potential means of elucidating the expansion behavior of latex particles in depth.

3.8. Acid distribution

Carboxylic acid monomers such as MMA are usually included in emulsion polymerization to enhance the colloid stability. The carboxyl groups can also function as crosslinking sites in thermosetting films. Moreover, the inclusion of carboxylic groups also has a profound impact on the rheological and adhesion behavior of latexes [51–53]. Acid groups are likely to be present in four loci: (1) water phase; (2) particle surface; (3) subsurface layer; (4) unneutralized layer. The type of acid monomer, reaction courses, pH of the reaction mixture, T_g of the latex, and hydrophilicity of the comonomer are principal parameters affecting the acid distribution. Various methods were utilized to synthesize and analyze the latexes, and thus the substantial discrepancies of tested results were reported [38–41].

Table 10
Acid distribution in latex (ND, no present detectable amount)

Latex	MMA based	Styrene based
Diameter of latex particle (nm)	250.7	233.7
Surface acid		
Meq/m^2	0.00146	0.00129
Fraction of total acid charged (%)	24.87	23.07
Subsurface acid		
Meq/m^2	0.00450	0.00292
Fraction of total acid charged (%)	70.09	51.90
Total titratable acid		
Meq/m^2	0.00596	0.00421
Fraction of total acid charged (%)	94.96	74.97
Soluble acid	ND	ND

Two latexes were prepared, one with MMA and hydroxyl-functionality in the core, the other with styrene and hydroxyl-functionality in the core, and both having carboxyl functionality in the shell. The latexes were then neutralized and dialyzed or purified using a centrifugal field, ion exchange resins, and filtration, depending on the characteristic of acid groups. The acid distribution in resultant latexes was determined by conductometric titration of the base as shown in Table 10. No acid was observed in the in water phase, suggesting that the polymerization process was complete. There were similar values in surface acid for both the styrene and MMA core latexes, again suggesting the validity of the same core–shell architecture for both latexes.

However, unlike the surface acid, the total titratable acid concentration varied with latex compositions. A higher acid value was observed for the MMA-based latex. The substitution of styrene from MMA in the core had a significant effect on the acid distribution of the core–shell latex. It is well known that the acid distribution of latexes varies considerably with the shift of styrene to MAA [48–50].

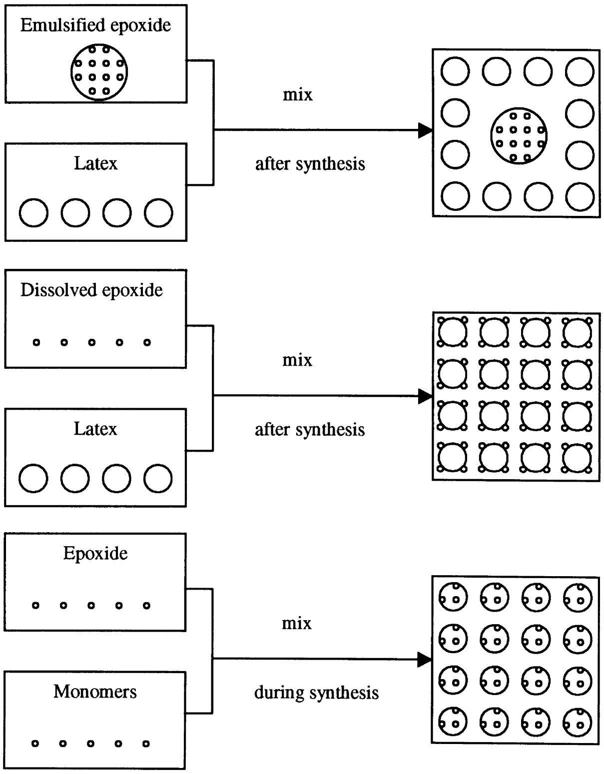


Fig. 10. Addition modes of epoxide into latex.

This difference can be attributed to the immigration ability of the monomers. In comparison with acrylic polymers, the polymer containing styrene is more rigid owing to the presence of the bulky benzene ring, and as a consequence, the movement of acid toward the particle surface is restricted. In the preparation of the core–shell latex, styrene was added prior to the addition of acid functional monomers, and thus the lowered subsurface acid concentration implies that diffusion between the core and the shell of the latex occurred.

It is postulated that, only the outer part of the shell latex particle could be permeated by sodium ion in such a diluted latex dispersion since the carboxyl-functional groups are preferentially located near the particle surface. In the end usage of the latex, the crosslinkers face a greater challenge. It has relatively bulky dimensions, and diffuses in very viscous conditions. Additionally, the carboxyl membrane and crosslinking of the epoxide during the cure process can limit the extent of polymer inter-diffusion and crosslinking. In this case, the optimization of the addition mode of crosslinker is more significant in determining of the type of crosslinked network.

The synthesis of the epoxide crosslinkable latex is of practical significance. In comparison with previous studies [19,20,23], the polymerization was carried out at ambient temperature, and the formulation consisted of a higher solid content and lower concentration of initiator. For epoxide crosslinked latex coatings, three structures appear to form prior to the latex coalescence, as shown in Fig. 10. In the previous study, hydroxyl or carboxyl functionalized latexes were shown to crosslink with the cycloaliphatic diepoxide [13–15]. The addition of the epoxide during the polymerization has potential to form a more homogeneous crosslink network. The incorporation of both carboxyl and hydroxyl functionalities into the latex formulation can provide a synergistic effect of general coating properties, hydrolytic stability, and concentration limit. Preliminary evidence for the crosslinking of mixed hydroxyl–carboxyl functionalized core–shell latexes has been reported [60], and a more completed manuscript is in preparation [61]. In traditional epoxide water-borne coatings, amines function as the crosslinker, not stabilizer, and thus the latex suffers with respect to stability problem. In contrast, this system can be stabilized using the amine due to the low reactivity of the amine toward cycloaliphatic diepoxide. This appears to provide a potential means to lower cost and improve durability.

4. Conclusions

The crosslinkable latex could be prepared in the presence of epoxide by a two-step core–shell emulsion polymerization. The pot-life stability of epoxide was shown to be dependent on latex morphology, initiator system, and reaction condition. In comparison with the thermal initiation system, the application of a persulfate–bisulfite–copper sulfate redox initiation system afforded adequate initiation rates at a much lower temperature, minimizing the reactivity of the epoxide toward the functional monomers. When amine was added into the latex formulations, the stability of epoxide was enhanced. The core–shell latex was most stable when the epoxide and hydroxyl functionalities were in the core and carboxyl functionality was in the shell. In addition, the acid distribution and TEM data indicated a core–shell structure.

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