Crosslinking of acrylic latex coatings with cycloaliphatic diepoxide

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Abstract

Acrylic thermosetting latexes were synthesized using methyl methacrylate (MMA) and butyl acrylate (BA) with methacrylic acid (MAA) or 2-hydroxyethyl methacrylate (HEMA). The MAA or HEMA was incorporated to provide the latexes with carboxyl or hydroxyl functionality, respectively. A cycloaliphatic diepoxide (3,4-epoxycyclohexyl methyl-$3',4'$-epoxycyclohexane carboxylate) was used to crosslink with hydroxyl or carboxyl functional latexes. The coatings were crosslinked as a function of temperature, time, and the amount of the crosslinker. The crosslinking reactions were monitored using differential scanning calorimeter, IR spectroscopy, and dynamic mechanical thermal analysis. The coatings properties were evaluated in terms of water absorption, gel content, pencil hardness, and pull-off adhesion. The morphology of the latex coatings was studied using atomic force microscopy. The spectroscopic and rheological data showed that the cycloaliphatic diepoxide effectively crosslinked both the hydroxyl and carboxyl functional latexes. Carboxyl latex coatings were more reactive than hydroxyl latex coatings. The water resistance, solvent resistance, pencil hardness, and pull-off adhesion improved with the crosslinking temperature, time, and the amount of the crosslinker. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Cycloaliphatic epoxides; Crosslinking reactions; Thermoset coatings

1. Introduction

Traditional solvent-borne low solid enamels are based on reactive oligomers/polymers which are crosslinked via baking [1]. The resultant coatings are a three dimensional crosslinked network, which exhibit excellent chemical resistance, and mechanical properties. They are widely used in high performance applications such as aircraft, and industrial maintenance coatings. The Clean Air Act of 1990 severely limited the amount of VOCs (volatile organic compounds) allowed to be emitted by the coatings industry. As a result, the coatings industry have been forced to develop environmentally friendly coatings with less or ultimately zero VOCs [2]. Water-borne, radiation cure, powder, and high solids coatings have been promising approaches to reduce the VOCs emitted from the coatings.

Latex and water-reducible coatings are the two major types of the water-borne coatings approaches. Of the two the dominant type of water-borne coating technology is latex. However, the film formation of the conventional latex coatings primarily relies on coalescence of thermoplastic polymeric particles to provide mechanical

properties, and chemical resistance [3]. Coalescence is a result of physical entanglement of polymeric molecules, and consequently it is not an adequate substitute for the chemical crosslinking. To improve the performance, crosslinking technology has been incorporated into latex coatings. Latexes can be functionalized to incorporate hydroxyl or carboxyl groups for crosslinking. For the hydroxyl functional latexes, amino resins and blocked isocyanates were the traditional crosslinkers [4–7]. Both crosslinkers are reactive towards hydroxyl groups. Usually, a high baking temperature (150–200°C) is required to crosslink the baking finishes currently used in industry.

In recent years, a number of crosslinkers and crosslinking technologies were developed for the carboxyl functional latexes. Typical crosslinkers are polycarbodiimides [8,9], polyaziridines [10,11], and polyoxazolines [12,13]. Under acidic conditions, these crosslinkers are very reactive towards carboxylic groups of the latexes resulting in formation of crosslink networks. Polycarbodiimides [8,9] can be aliphatic or aromatic. Aliphatic polycarbodiimides react faster than the aromatic counterparts with carboxyl groups. As a result, aliphatic polycarbodiimide latex crosslinking systems represent a storage stability problem. In contrast, aromatic polycarbodiimide latex coatings showed better storage stability, and in addition have lower toxicity.

Polyaziridines [10,11] are the most popular type of the

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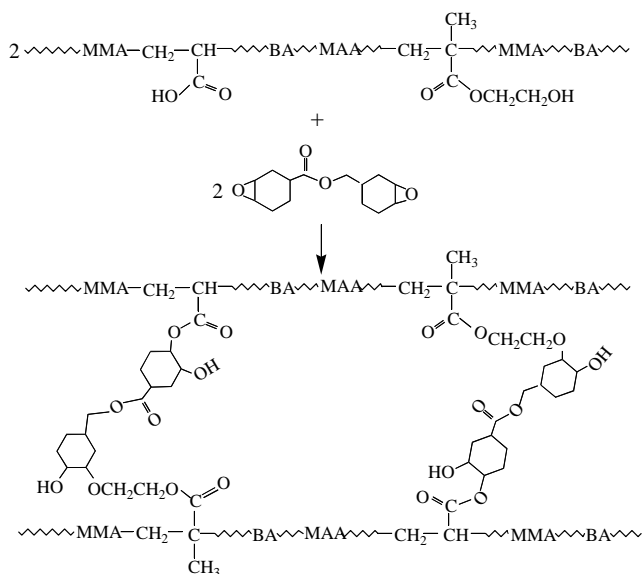
Scheme 1.

crosslinkers widely used in two component primers, topcoats, and other protective finishes. Polyaziridines are based on the ethyleneimine functionality. The crosslinking reactions of polyaziridines with carboxyl functional latexes are governed more by the availability of protons (acidity) than the temperature. Thus, pH of the coating system has been used to control the speed of the crosslinking. Coatings crosslinked with polyaziridines typically exhibit good adhesion, chemical resistance, and durability. However, polyaziridines are potential sensitizers, and have been shown to be possible mutagens according to the Ames test.

Polyoxazolines [12,13] are another type of carboxyl reactive crosslinkers. Oxazoline groups react with carboxylic groups or acid anhydrides resulting in the formation of amide ester linkages. The crosslinking reaction generally proceeds under an acidic condition, and an elevated temperature (80–100°C) is required for the crosslinking. It has also been shown that the coating formulations exhibit long pot-life and low toxicity. Typically, oxazoline groups are attached onto the latex polymer chains as pendant groups. The oxazoline functionalized latex is crosslinked with a carboxyl functional latex. However, the polymer–polymer interdiffusion and the rate of the crosslinking reaction must be carefully balanced.

Epoxides, especially phenyl glycidyl diepoxides, were also studied as alternative crosslinkers for water-borne coatings [14–18]. Since phenyl glycidyl epoxides are not soluble or miscible with water, they are typically emulsified in water and then incorporated into a water-borne coating with the aid of anionic or nonionic surfactant. In terms of the reactivity, phenyl glycidyl diepoxides react much faster with amines than hydroxyl and carboxyl functional compounds [19]. As a result, amines are typically used as the crosslinkers [14–16]. However, the coatings must be a two-component system, and the application is also limited

due to poor exterior weatherability. When hydroxyl and/or carboxyl functional latexes is crosslinked with the phenyl glycidyl epoxides, the crosslinking of the coating system required a much higher curing temperature (160–200°C) [17,18].

In addition, other crosslinkers or crosslinking technologies were also developed for the latex coating systems by Moles and Pollano [10,11,20,21]. Examples are glyoxals, metal chelating agents [10,11], and ethylene based oxidative crosslinking mechanisms [20,21]. Despite the number of crosslinkers or crosslinking technologies available for the latex coatings, the resultant coating systems always present environment or public health related problems or unsatisfactory coating properties.

All water-borne systems are expected to compete with traditional solvent-borne acrylic coating systems [4,22,23]. In the water-borne system, coatings were typically hydroxyl functionalized, and crosslinked with melamine–formaldehyde (MF) resins. The crosslinking was *trans*-etherification of the hydroxyl groups with the MF resins [22–25]. In addition to the concern of VOCs and formaldehyde, the coating system also presented acid-etching problems [22,23,25]. It may be due to the acid-catalyzed hydrolysis of the ether bonds [22,23]. Using the cycloaliphatic diepoxide as a crosslinker, water-borne systems using both carboxyl and hydroxyl functional acrylic latexes were crosslinked. Although the crosslinking of latexes also involved the formation of ether bonds, the steric hindrance inhibiting the hydrolysis of the ether bonds is much greater than the ether bonds of the MF crosslinked coating system [26–28]. As a result, the cycloaliphatic epoxide crosslinked coating system would be safer and be more weather-durable decreasing the acid-etching, which involved the MF resin crosslinked coating system.

The objective of this study was to develop a new type of environmentally friendly crosslinking technology for water-borne coating systems using cycloaliphatic diepoxides as the crosslinker. The proposed crosslinking reaction of the hydroxyl functional latex with cycloaliphatic diepoxide is shown in Scheme 1. Carboxyl or hydroxyl functional acrylic latexes were synthesized and used to crosslink with a cycloaliphatic diepoxide. The crosslinking reactions of the latexes with the diepoxide were studied spectroscopically. The mechanical properties of the crosslinked films are also reported herein.

2. Experimental

Methyl methacrylate (MMA), *n*-butyl acrylate (BA), methacrylic acid (MAA), 2-hydroxyethyl methacrylate (HEMA), ammonium persulfate, sodium bicarbonate, and ρ-toluenesulfonic acid (ρ-TsOH) were purchased from Aldrich. Defoamer Byk-035 was provided by BYK Chemie Company. Cycloaliphatic diepoxide (UVR-6105) and surfactants (Triton-200 and Tergital-XJ) were supplied by

Table 1
Synthesis of latexes (all the ingredient quantities are listed in g)

Latex	MMA	BA	HEMA	MAA	Ammonium persulfate	Triton-200	NaHCO$_3$
HO[a]	72.74	90.94	16.33	0.0	0.81	8.04	0.4
COOH	71.56	97.64	0.0	10.80	0.81	8.04	0.4

[a] The content of the hydroxyl and the carboxyl functional monomers of the two latexes are equivalent in moles (0.1256 mol).

Union Carbide Corporation. All materials were used without further purification.

Latex synthesis was carried out in a four neck fluted round bottom flask (500 mL). The purpose of using a fluted flask was to provide effective shearing and mixing of the reactor contents. The flask was also equipped with a mechanical stirrer and an overhead condenser. The stirring rate was kept constant at 200 rpm throughout the latex synthesis. The temperature of the flask was controlled using a thermostated water bath. Using the Fox equation [29], the glass transition temperature of latex polymers was designed to be at 0°C. The carboxyl or hydroxyl functional monomer content was designed to be at 6.0 and 9.1 wt% which is equivalent with respect to the average molecular weight functionality. The recipes for the synthesis of the hydroxyl or carboxyl functional latex are listed in Table 1.

The monomers were mixed and then slowly added into another fluted round bottom flask containing a stirred water solution (0.2 g NaHCO$_3$, 7.96 g Triton-200, and 96 g water) to obtain a monomer pre-emulsion. After the completion of the monomer-emulsification, the reactor was first charged with 77 g water, 14 g of the pre-emulsion, 8.1 g of the initiator solution (0.77 g (NH$_4$)S$_2$O$_8$, 35.0 g water), 0.2 g NaHCO$_3$, and 0.08 g Triton-200 at 80°C. The content was then heated at 80°C for 30 min. The remaining pre-emulsion was fed to the reactor over a period of 3.0 h using an addition pump (ISMATEC REGLO-100), and the initiator was added to the reactor concurrently with the monomer pre-emulsion feed at a constant rate using a Universal Syringe Pump (Valley Scientific Model 575). The polymerization was maintained at 80°C under nitrogen. After the addition of all the ingredients, the reaction mixture was heated for additional 2 h at 85°C to digest any residual monomers. Then, the reactor contents were cooled to 30–35°C and neutralized with ammonia to a pH of 8.5. The latex was stored in a glass container after filtration of the contents through a 300-mesh screen to remove any residual coagulum.

The cycloaliphatic diepoxide (UVR-6105) was emulsified using a mixture of anionic and non-ionic surfactants (Triton-200 and Tergital-XJ). The anionic surfactant (3.21 g) and non-ionic surfactant (1.35 g) were dissolved in deionized water (55.0 g) containing 0.1 g defoamer (Byk-035). Then, cycloaliphatic diepoxide (UVR 6105, 45.0 g) was slowly emulsified into the water solution at 60°C. A stoichiometric amount of the epoxide emulsion

(45.0% solids) was then added into the latexes. The hydroxyl functional latex coatings contained 0.6 wt% ammonia neutralized ρ-TsOH as the catalyst. To study the crosslinker effect on the coatings properties, 87.5 and 112.5% of the stoichiometric amount of the epoxide crosslinker were also added to formulate the latex coatings.

All the latex coatings were cast on glass or aluminum substrates using a drawdown bar (5 mil). The coatings cast on the glass substrates were used to provide crosslinked free films for water absorption and gel content measurements. The free coating samples were scraped off from the substrates using a razor blade. The coatings cast on the aluminum substrates were used to determine other coating properties after crosslinking. After the latex coalescence for 2 h, the latex coatings were crosslinked in an oven (Blue M Electronic B-3898Q). The crosslinking was performed as a function of baking temperature and time. Both the carboxyl and hydroxyl functional latexes were baked at 130, 150, and 170°C for 105 min. Based on the results of the crosslined films as a function of temperature, the crosslinking of the carboxyl functional latex was then studied at 130°C as a function of the baking time (60, 105, and 165 min). Similarly, the crosslinking of the hydroxyl functional latex was also studied at 170°C for 60, 105, and 165 min.

A Differential Scanning Calorimeter (Perkin–Elmer DSC 7) was used to record the heat flow as a function of the temperature involved in the crosslinking of the latex coatings with cycloaliphatic epoxide. The DSC scanning was performed using 17–20 mg film samples with a 10°C/min heating rate. The IR (infrared) spectra of the coating samples were obtained on a Nicolet Magna-IR 850 spectrometer, and directly recorded on dry films using dry air as the background. The morphology of the latex coatings was obtained using an atomic force microscopy (AFM, Nano-Scope III). The viscoelasticity of the latex coatings as a function of the temperature was recorded using a Dynamic Mechanical Thermal Analysis instrument (Rheometric Scientific DMTA 3E). Dry coating films were cut into 10 × 30 mm^2. The scans were performed on the samples using a dynamic temperature ramp (3°C/min), a fixed oscillating frequency (1 Hz), and a controlled strain (0.5%). Then, the crosslinking density (XLD) of the samples was calculated according to Eq. (1) [30,31].

$$V_e = \frac{E'}{3RT} \qquad (1)$$

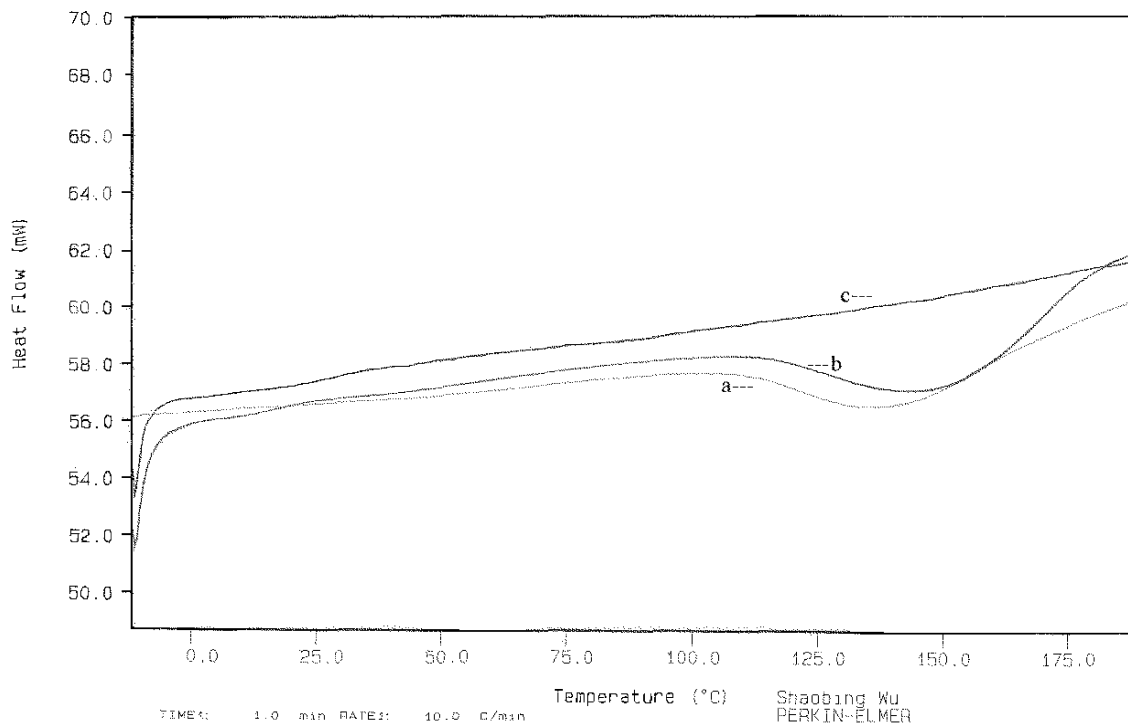where V_e is crosslink density, E' the elastic storage
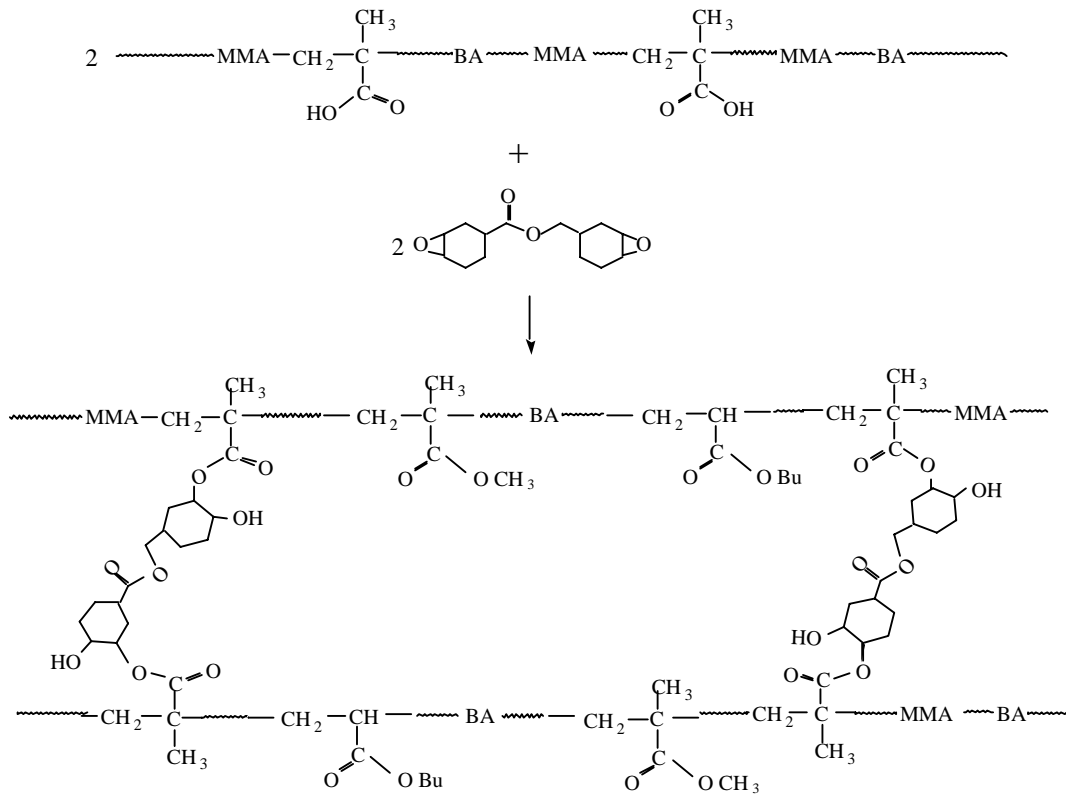
Scheme 2.

Fig. 1. DSC data for the carboxyl functional latex coatings (MAA 15 wt%): (a) cycloaliphatic diepoxide with a stoichiometric amount of phthalic acid; (b) carboxyl latex film with a stoichiometric amount of cycloaliphatic diepoxide; (c) reheat of (b).
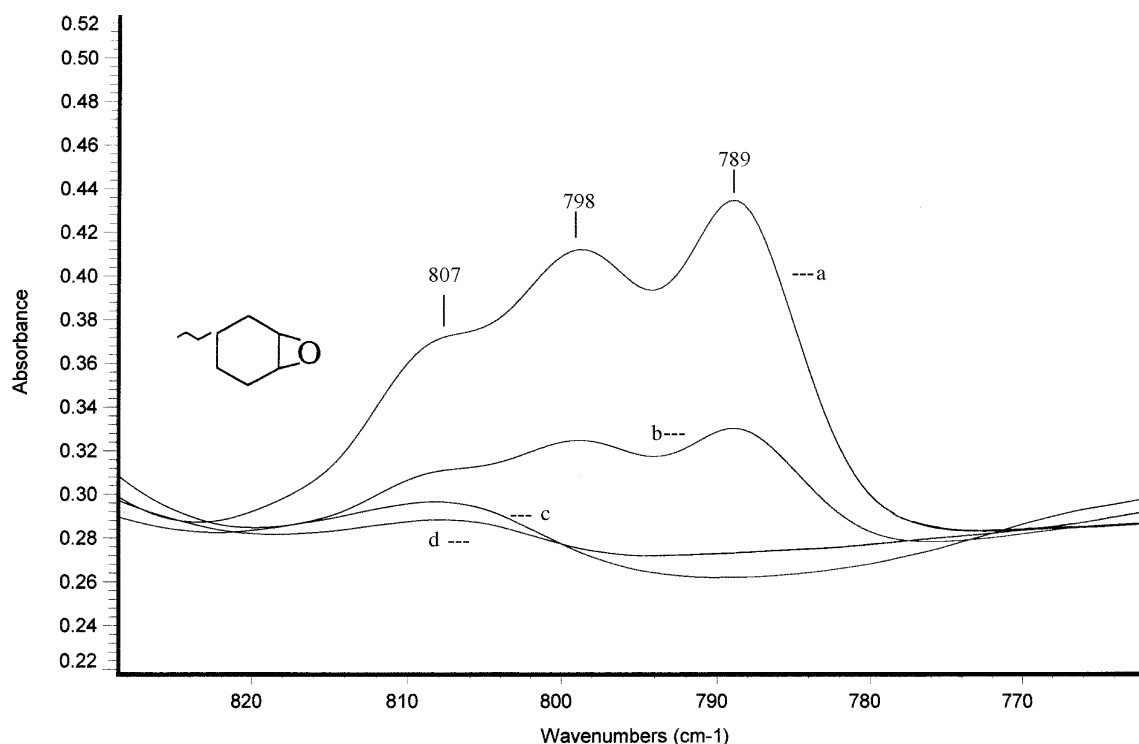
Fig. 2. IR spectra of the epoxy ring stretching of the carboxyl functional latex coatings as a function of curing temperatures: (a) latex film with a stoichiometric amount of the cycloaliphatic diepoxide cured at the ambient temperature; (b) latex film with a stoichiometric amount of cycloaliphatic diepoxide cured at 90°C for 30 min; (c) Latex film with a stoichiometric amount of cycloaliphatic diepoxide cured at 130°C for 30 min; (d) latex film without cycloaliphatic diepoxide.

modulus, R the ideal gas constant, and T is the temperature (K) at which the elastic modulus is taken. The elastic storage modulus of the coatings (E') was obtained on the rubbery plateau region at a temperature 50°C above the glass transition temperature. The gel content (ASTM D2765), water absorption (ASTM D3419), pencil hardness (ASTM D33363), and the pull-off adhesion (ASTM D4541) of the crosslinked coatings were measured 24 h after baking.

3. Results and discussion

Our previous model compound study indicated that hydroxyl and carboxyl groups react with cycloaliphatic epoxide [26–28]. The primary mode of the reactions was the direct oxirane ring opening by the hydroxyl or the carboxyl group. The reactions resulted in the formation of ether and ester bonds. To crosslink acrylic latexes with a cycloaliphatic diepoxide, model carboxyl or hydroxyl functional acrylic latexes were synthesized. The epoxide crosslinkable latex coatings were formulated with the model carboxyl or hydroxyl latexes and the cycloaliphatic diepoxide, and crosslinked as a function of either temperature or time. Both DSC and IR were used to study the crosslinking reactions as a function of temperature. The crosslink density was obtained from DMTA data. The distribution of the crosslinker before and after crosslinking was investigated using AFM. In addition, the crosslinked coatings were

also evaluated via water absorption, gel content, pencil hardness, and pull-off adhesion.

The crosslinking reaction of the carboxyl functional latex coatings with the cycloaliphatic diepoxide is depicted in Scheme 2. The crosslinking reaction was first monitored using DSC. The exotherm of the epoxide reaction(s) with carboxyl groups is illustrated in Fig. 1. The first scan depicts the exotherm of the diepoxide with phthalic acid. This exotherm was used to identify the formation of ester bonds. The onset temperature of the reaction was at 110°C, and the end temperature of the reaction was at 175°C. Fig. 1(b) shows the exotherm of the carboxyl functional latex with the cycloaliphatic diepoxide. The onset and end temperatures of the exotherm were approximately in the same range as the exotherm of the epoxide with phthalic acid. By analogy, it was assumed that the crosslinking reaction between the carboxyl functional latex and the diepoxide crosslinker was the exotherm depicted in the second scan. Fig. 1(c) represents the reheating of the crosslinked latex coating in the second scanning. No exotherm peak was observed in Fig. 1(c), indicating the completion of the crosslinking reaction of the carboxyl functional latex with the diepoxide in Fig. 1(b). Therefore, the crosslinking reaction of the carboxyl group with the cycloaliphatic diepoxide within the latex coating system occurred from 110 to 175°C.

The epoxide ring opening reaction with carboxyl groups within the carboxyl functional latex coatings was also monitored using IR. The disappearance of the epoxy ring was

Table 2
The conversion of the cycloaliphatic diepoxide into the crosslinks as a function of the cure temperature (30 min)

Carboxyl latex coating		Hydroxyl latex coating	
Temperature (°C)	Conversion (mol%)	Temperature (°C)	Conversion (mol%)
25	0	25	0
90	73.0	150	47.3
130	100.0	170	100.0

monitored via oxirane stretching at 807, 798, and 789 cm^{-1} [32]. The IR spectra monitoring the epoxy ring as a function of cure temperatures is shown in Fig. 2. The epoxy ring opening reaction is apparent in the decreasing intensity of the stretching bands at 807, 798, and 789 cm^{-1} as the cure temperature was increased from 25 to 130°C. In comparison with the IR spectrum of the latex film without the cross-linker (Fig. 2(d)), the IR spectrum of the latex cured at 130°C (Fig. 2(c)) did not show any absorption peaks in the oxirane region (807–789 cm^{-1}) indicating completion of the crosslinking reaction. Using the IR spectrum of the latex without the crosslinker as a reference, the conversion of the epoxide to the crosslinks as a function of the tempera-ture based on the intensity at 789 cm^{-1} was calculated, and is shown in Table 2. The increasing conversion with the cure temperature also suggests the completing of the crosslinking

reaction. The 100% conversion of the epoxide at 130°C also suggests the completion of the crosslinking reaction of the latex with the crosslinker.

The crosslinking reaction of the hydroxyl functional latex coatings with the cycloaliphatic diepoxide is shown in Scheme 3. Similarly, the crosslinking reaction was studied using DSC and IR. The exotherm of the epoxide reaction with hydroxyl groups monitored by DSC is depicted in Fig. 3. Fig. 3(a) shows the exotherm of the diepoxide with 0.6 wt% TsOH. The exotherm at the onset temperature 245°C suggested an acid-catalyzed homopolymerization of the cycloaliphatic epoxide. The second scan depicts the exotherm of the acid catalyzed (0.6 wt% TsOH) reaction of cycloaliphatic epoxide with a stoichiometric amount of caprolactone diol. The exotherm depicted in Fig. 3(b) suggests that an acid-catalyzed crosslinking reaction occurs
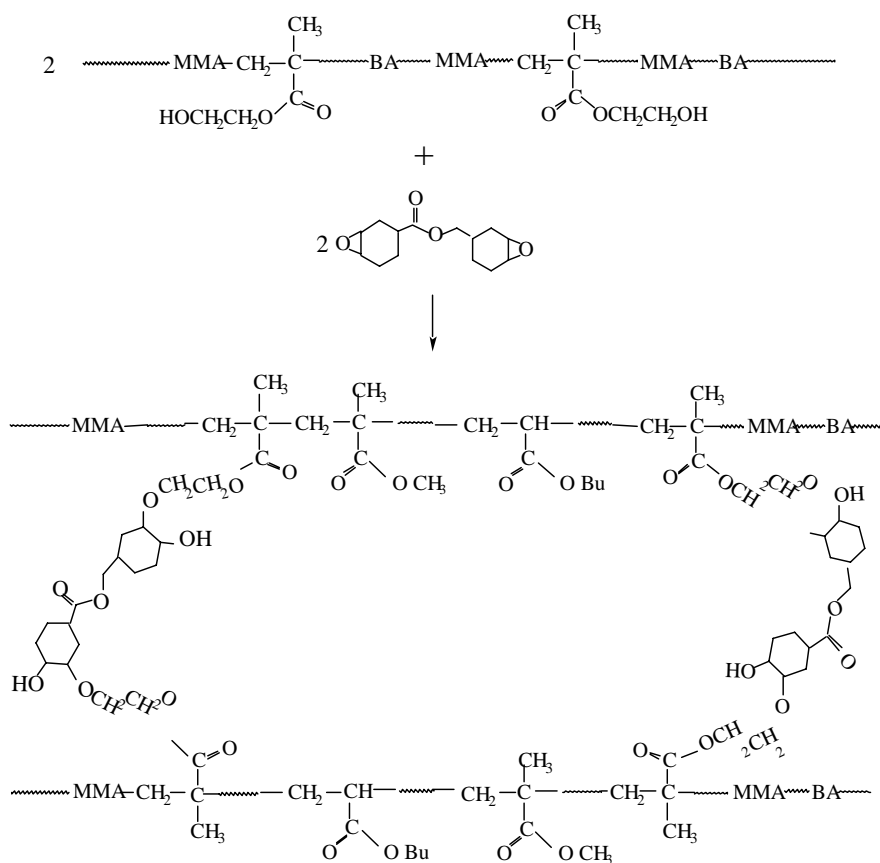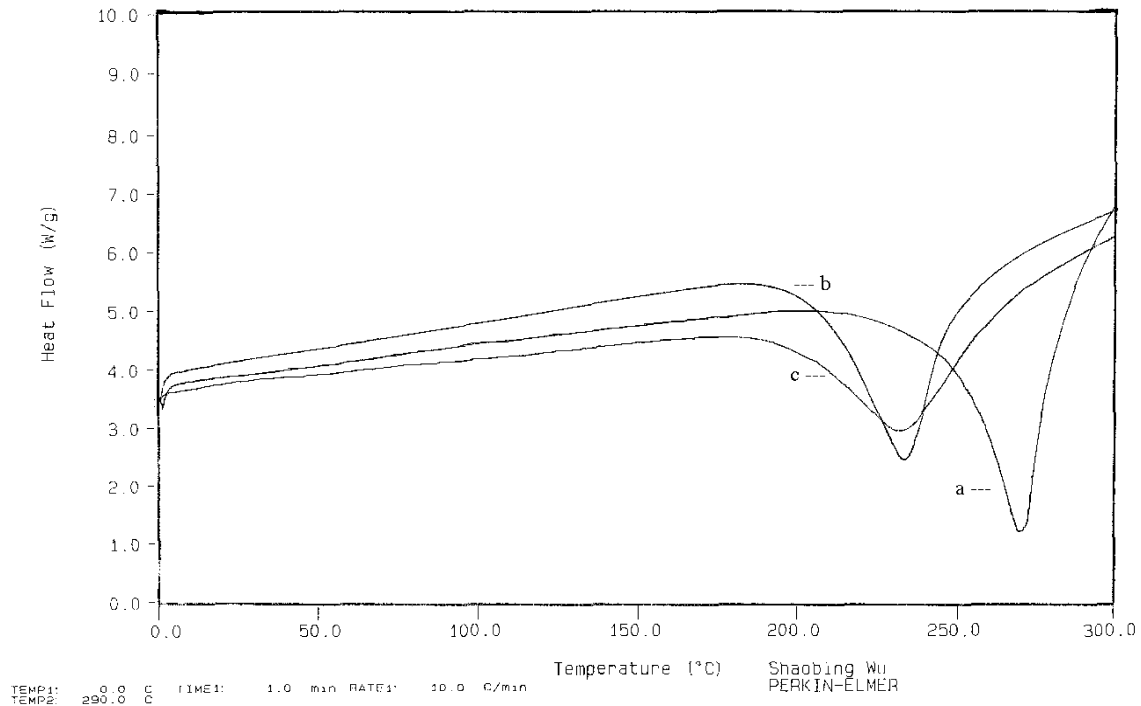

Scheme 3.

Fig. 3. DSC data for hydroxyl functional latex coatings (HEMA 22.7 wt%): (a) cycloaliphatic diepoxide with 0.6 wt% TsOH; (b) cycloaliphatic diepoxide with a stoichiometric amount of caprolactone diol (Tone 0201) and 0.6 wt%; (c) latex film with a stoichiometric amount of cycloaliphatic diepoxide and 0.6 wt% TsOH.
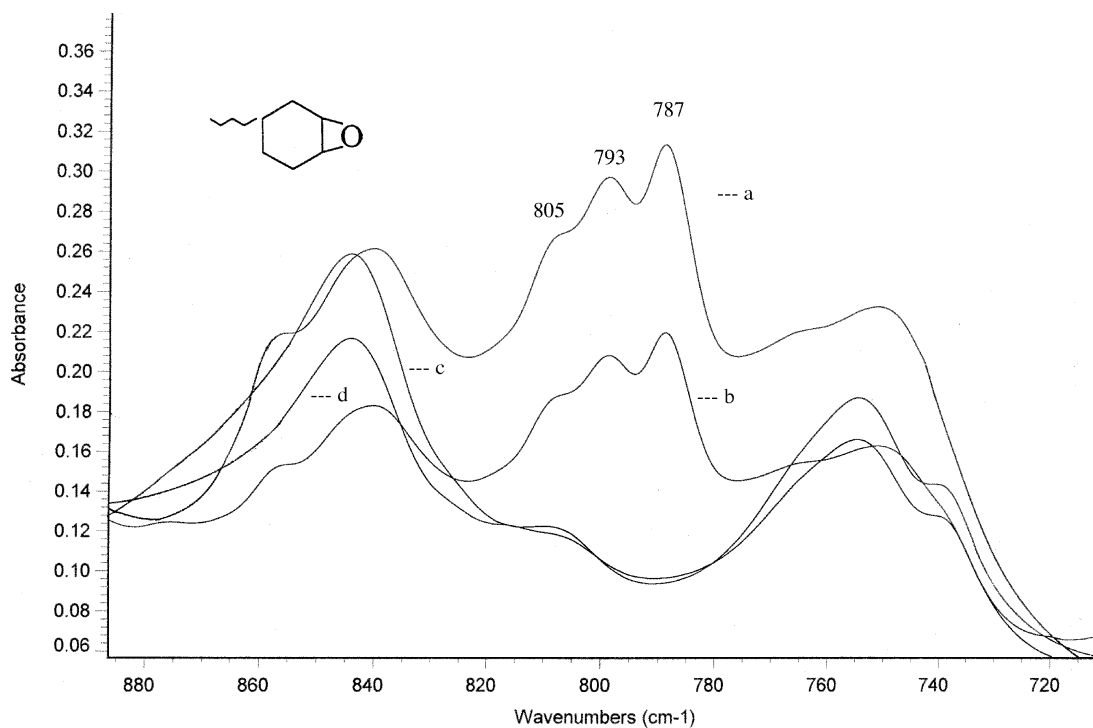

Fig. 4. IR spectra of the epoxy ring stretching of the hydroxyl functional latex coatings as a function of curing temperatures: (a) latex film with a stoichiometric amount of the cycloaliphatic diepoxide at ambient temperature; (b) latex film with a stoichiometric amount of cycloaliphatic diepoxide cured at 150°C for 30 min; (c) latex film with a stoichiometric amount of cycloaliphatic diepoxide cured at 170°C for 30 min; (d) latex film without cycloaliphatic diepoxide.
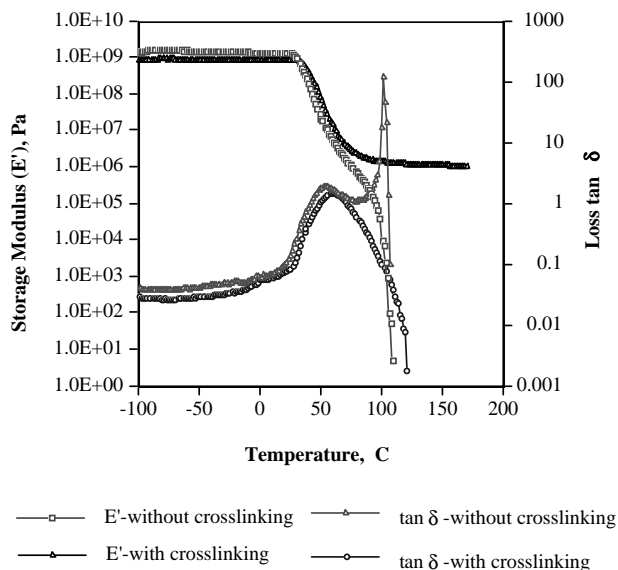
Fig. 5. Storage modulus (E') and loss tangent δ of the carboxyl functional latex coatings as a function of the temperature and crosslinker.

between the cycloaliphatic epoxide and hydroxyl functional latex (Fig. 3(c)).

The epoxy ring opening reaction with a hydroxyl functional latex was also monitored using IR absorptions at 807, 798, and 789 cm^{-1} [32]. The IR spectra as a function of the cure temperature is shown in Fig. 4. Similar to the crosslinking of the carboxyl functional latex, the intensity of the stretching bands at 807, 798, and 789 cm^{-1} decreased as the cure temperature was increased from 25 to 170°C. In comparison with the IR spectrum of the latex film without the crosslinker (Fig. 4(d)), the IR spectrum of the latex cured
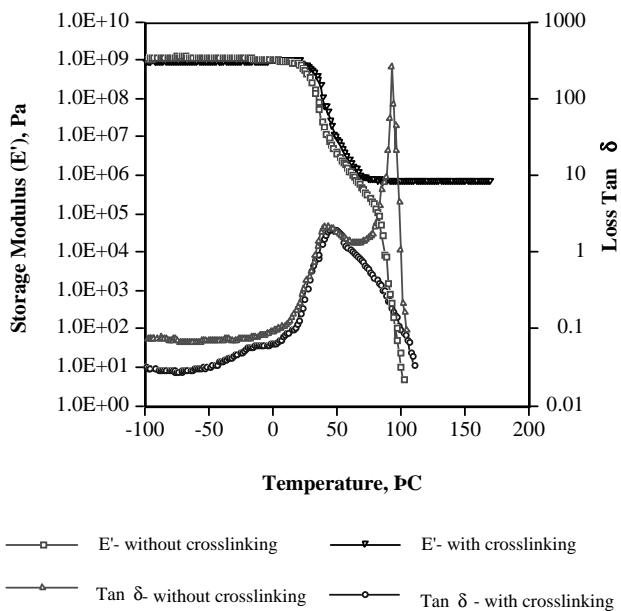

Fig. 6. Storage modulus (E') and loss tangent (δ) of the hydroxyl functional latex coatings as a function of temperature and crosslinker.

at 170°C (Fig. 4(c)) did not show any absorption band in the range of 807–789 cm^{-1} indicating the completion of the crosslinking reaction. Again, the epoxy conversion (789 cm^{-1} in comparison with the latex without the crosslinker is enhanced (Table 2). This also suggests that the crosslinking reaction increases with the cure temperature. However, the crosslinking reaction at 150°C afforded only 47.3% epoxy conversion. In comparison with the carboxyl functional latex (Fig. 3), a higher crosslinking temperature was required for the hydroxyl functional latex. This higher crosslinking temperature was also consistent with the DSC results.

The storage modulus (E') and loss tangent (δ) of the crosslinked latex films as a function of temperature were studied using DMTA. Figs. 5 and 6 show the DMTA scans of the uncrosslinked and the crosslinked latex coatings as a function of temperature. Without the cycloaliphatic diepoxide crosslinker, the storage modulus for both the carboxyl and hydroxyl coatings did not show a rubbery plateau region after their respective glass transitions. In contrast, the latex coatings crosslinked with the cycloaliphatic diepoxide exhibited a rubbery plateau region after the glass transition. These rubbery plateau regions indicated the existence of effective crosslinking networks [30,31]. In addition, the uncrosslinked coatings displayed two peaks in the loss tangent (δ) above room temperature indicating the glass and viscous-fluid transitions of uncrosslinked polymeric materials [33]. The crosslinked coatings showed only one peak of the loss tangent (δ) representing the glass transition for the crosslinked coatings.

The coating properties of the crosslinked latex films were studied in terms of the water absorption, gel content, pencil hardness, and pull-off adhesion. These data were further used to evaluate the crosslinking of the coatings. Table 3 shows the properties of the crosslinked carboxyl functional latex coatings as a function of crosslinking temperature. In comparison with the coating at 25°C without crosslinker, the water absorption of the crosslinked coatings decreased substantially, while the gel content, pencil hardness, and pull-off adhesion of the coatings increased. The decreased water absorption was due to the formation of ester bonds which reduced the polarity of the crosslinked coating (Scheme 2). The increased gel content was due to the crosslinked network, which had lower entropy and was difficult to dissolve in the solvent. The increased adhesion may be attributable to the epoxy ring opening resulting in a hydroxyl group, which promotes interfacial adhesion. Thus, the significant changes in coating properties can be attributed to the effect of the crosslinking.

The crosslink density data also reflected the effect of the crosslinking. In addition, the coating properties of the water absorption, gel content, and pencil hardness appeared to be improved with increasing crosslinking temperature from 130 to 170°C due to the increased crosslink density. The decrease in the adhesion with the temperature may also be

Table 3
Physical properties of crosslinked carboxyl functional latex coatings as a function of curing temperatures

Temperature (°C)[a]	Water absorption (wt%)	Gel content (wt%)	Pencil hardness	Pull-off adhesion (lb/in.^{2})	XLD (mol/cm^3 × 10^4)[b]
25[c]	223.4	10.3	3B	50	–
130	32.6	92.8	2B	400	1.36
150	32.0	93.1	2B	360	1.37
170	28.4	93.5	B	320	1.39

[a] All Samples were cured for 105 min.
[b] XLD: crosslink density.
[c] The coating was not crosslinked with the cycloaliphatic diepoxide, and was used as a control.

Table 4
Physical properties of crosslinked hydroxyl functional latex coatings as a function of curing temperatures

Temperature (°C)[a]	Water absorption (wt%)	Gel content (wt%)	Pencil hardness	Pull-off adhesion (lb/in.^{2})	XLD (mol/cm^3 × 10^4)[b]
25[c]	214.3	30.9	4B	60	–
130	181.0	65.0	6B	250	0.41
150	153.8	84.0	5B	260	0.67
170	38.5	91.6	3B	300	1.34

[a] All Samples were cured for 105 min.
[b] XLD: crosslink density.
[c] The coating was not crosslinked with the cycloaliphatic diepoxide, and was used as a control.

Table 5
Physical properties of crosslinked carboxyl functional latex coatings as a function of curing times at 130°C

Time (min)	Water absorption (wt%)	Gel content (wt%)	Pencil hardness	Pull-off adhesion (lb/in.^{2})	XLD (mol/cm^3 × 10^4)[a]
0[b]	223.4	10.3	3B	50	–
60	56.3	89.3	3B	425	1.15
105	32.6	92.8	2B	400	1.36
165	25.4	93.4	2B	380	1.38

[a] XLD: crosslink density.
[b] The coating was not crosslinked with the cycloaliphatic diepoxide, and was used as a control.

due to the increased crosslink density that made the coating less flexible. However, the changes in the coating properties and the crosslink density above 130°C were relatively small. These results suggest that a temperature of 130°C was reasonable for the crosslinking of the carboxyl functional latex coatings with cycloaliphatic epoxide, which was also consistent with both DSC and IR data.

The water absorption, gel content, pencil hardness, and pull-off adhesion of the crosslinked hydroxyl functional latex coatings as a function of the crosslinking temperatures are shown in Table 4. The crosslinked coatings exhibited lower water absorption, higher gel content, higher adhesion than the coating without crosslinker. In addition, the water absorption decreased while the gel content, pencil hardness, and the pull-off adhesion of the coatings increased as the crosslinking temperature was increased. The pencil hardness was lower for the coatings crosslinked at a lower temperature (150°C) than the uncrosslinked coatings. This may be attributable to the presence of a significant amount of uncrosslinked cycloaliphatic diepoxide in the coatings.

The unreacted cycloaliphatic diepoxide plastisized the coatings lowering the glass transition temperature and consequently decreasing the hardness. In contrast with the carboxyl functional latex coatings, the crosslink density of the hydroxyl functional latex coatings dramatically increased with increasing crosslinking temperature. Evidently, a maximum crosslink density for the hydroxyl functional latex coatings, which was comparable to the carboxyl functional latex coatings, was only obtained at 170°C. This suggested that a higher crosslinking temperature (170°C) was required for the hydroxyl functional latex coatings with cycloaliphatic epoxide than the carboxyl functional latex coatings for a same time. These results were also collaborated by both DSC and IR data.

In comparison with the crosslinked carboxyl latex coatings, the crosslinked hydroxyl latex coatings showed higher water absorption, and lower pencil hardness, and pull-off adhesion, and gel content. These trends may be due to the fact that the reactivity of the hydroxyl group with cycloaliphatic epoxide is lower than the carboxyl group

Table 6
Physical properties of crosslinked hydroxyl functional latex coatings as a function of curing times at 170°C

Time (min)	Water absorption (wt%)	Gel content (wt%)	Pencil hardness	Pull-off adhesion (lb/in.^{2})	XLD (mol/cm$^3 \times 10^4$)[a]
0[b]	214.3	30.9	4B	60	–
60	89.4	78.9	6B	280	0.91
105	38.5	91.6	4B	300	1.34
165	30.1	92.1	3B	250	1.39

[a] XLD: crosslink density.
[b] The coating was not crosslinked with the cycloaliphatic diepoxide, and was used as a control.

Table 7
Physical properties of crosslinked carboxyl functional latex coatings as a function of the crosslinker at 130°C for 105 min

Crosslinker content (%)[a]	Water absorption (wt%)	Gel content (wt%)	Pencil hardness	Pull-off adhesion (lb/in.^{2})
87.5	55.21	89.5	2B	360
100	32.56	92.8	2B	400
112.5	29.79	92.5	B	500

[a] Based on the stoichiometric amount.

Table 8
Physical properties of crosslinked hydroxyl functional latex coatings as a function of the crosslinker at 170°C for 105 min

Crosslinker content (%)[a]	Water absorption (wt%)	Gel content (wt%)	Pencil hardness	Pull-off adhesion (lb/in.^{2})
87.5	62.7	83.1	5B	180
100	38.5	91.6	3B	300
112.5	23.6	93.2	2B	420

[a] Based on the stoichiometric amount.

[26–28]. Consequently, a higher crosslinking temperature was required for the hydroxyl functional latex coatings with cycloaliphatic epoxide (Figs. 1 and 2). In addition, the lower polarity and higher flexibility of the ether crosslinks (Scheme 3) in comparison with the ester crosslinks (Scheme 2) probably also contribute to the differences in the coating properties.

The water absorption, gel content, pencil hardness, and pull-off adhesion of the crosslinked carboxyl functional latex coatings as a function of the crosslinking time is shown in Table 5. The water absorption decreased, and the gel content and pencil hardness of the coating systematically increased with the time, indicating improved crosslinking of the coating with cycloaliphatic epoxide. The crosslink density of the coatings also revealed this trend. The pull-off adhesion, however, reduced as the crosslinking was increased. This may be attributable to the increased crosslink density, which decreased the flexibility of the coating and consequently made the coating more brittle. Based on the data, the changes in the water absorption, gel content, and pencil hardness from 105 to 165 min cure time were relatively small indicating that a cure schedule at 130°C from 60 to 105 min can allow to achieve adequate crosslinking.

The water absorption, gel content, pencil hardness, and pull-off adhesion of the crosslinked hydroxyl functional latex coatings as a function of the crosslinking time is shown in Table 6. Similarly, the water absorption of the coating decreased significantly with the cure time while the gel content and pencil hardness of the coating increased. The pull-off adhesion increased until 105 min. The decrease in the adhesion after 165 min may be due to the increased crosslinking which resulted in less flexible coating as previously stated. The crosslink density of the coating systematically increased with time as indicated by the DMTA data.

The stoichiometry of the cycloaliphatic epoxide crosslinker to the carboxyl or hydroxyl functionality of the latex coatings also affected the crosslinking and the coating properties. Tables 7 and 8 show the coating properties as a function of the crosslinker based on the percentage of the stoichiometric amount required for the latex carboxyl or hydroxyl functionality, respectively. As the addition of the crosslinker was increased, the water absorption of the coating decreased. In addition, the gel content, pencil hardness, and the pull-off adhesion also increased systematically as a function of the crosslinker concentration. The enhancement in the coating properties of the hydroxyl functional latex

Table 9
Weight loss of the cycloaliphatic epoxide as a function of temperature (TGA)

Temperature (°C)	Weight loss (wt%)	Temperature (°C)	Weight loss (wt%)
100	0.00	150	1.70
105	0.02	155	2.22
110	0.07	160	2.86
115	0.13	165	3.60
120	0.22	170	4.47
125	0.33	175	5.57
130	0.49	180	6.83
135	0.68	185	8.34
140	0.95	190	10.23
145	1.26	195	12.36

coatings as a function of the crosslinker loading was greater than the carboxyl functional latex coatings. The greater enhancement in the coating properties suggested that the crosslinking of the hydroxyl functional latex coatings was more dependent on the amount of the crosslinker than the carboxyl functional latex coatings.

Table 9 shows the weight loss of the cycloaliphatic diepoxide as a function of the temperature. The weight loss percentage of the crosslinker increased with the increasing temperature. The crosslinker lost 0.49 wt% at 130°C and 4.47 wt% at 170°C. The significant weight loss (31.46 wt%) occurred at 250°C which was close to the boiling point of the cycloaliphatic diepoxide (258°C at 760 mm Hg) [34]. Thus, the greater dependence of the hydroxyl functional latex coatings on the content of the cycloaliphatic diepoxide may also be due to the greater weight loss of the crosslinker at 170°C.

The AFM was used to study the morphology of the uncrosslinked and crosslinked latex coatings. Figs. 7 and 8 show the AFM images of the carboxyl latex coatings before and after curing with the cycloaliphatic diepoxide, respectively. In Fig. 7, the white regions around the latex particles indicate the location of the cycloaliphatic epoxide crosslinker before the crosslinking, and the latex particles were about 190–200 nm in diameter. After crosslinking, the white regions between the latex particles disappeared (Fig. 8), and the neighboring latex particles merged to become larger particles (230–250 nm). This indicates that the cycloaliphatic diepoxide diffuses into latex particles before the crosslinking reaction takes place.

The crosslinking of carboxyl and hydroxyl functional acrylic latexes with a cycloaliphatic diepoxide was elucidated using DSC, IR, DMTA, and AFM spectroscopy. The DSC thermograms were used to establish the onset
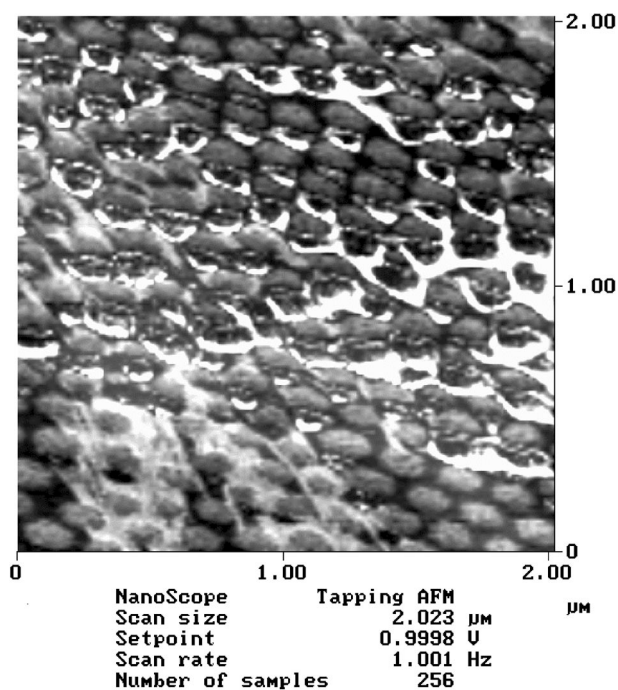

Fig. 7. Morphology of the carboxyl functional latex coating with the cycloaliphatic diepoxide before crosslinking using atomic force microscopy.
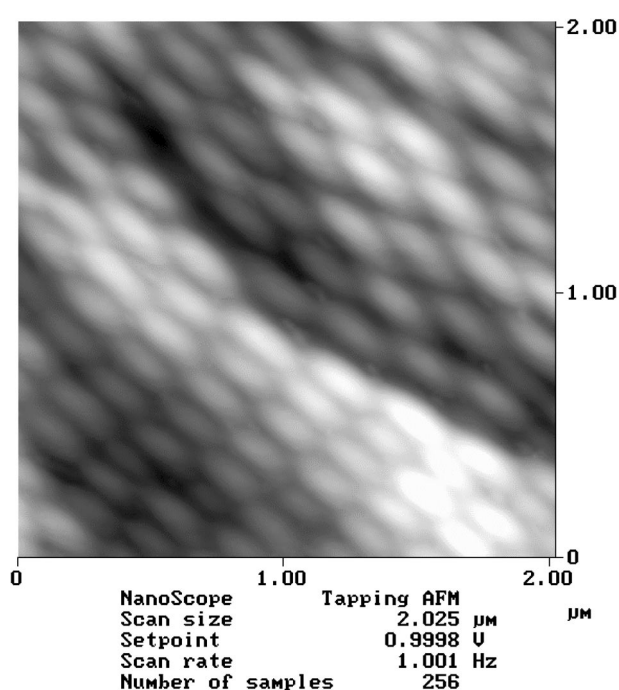

Fig. 8. Morphology of the carboxyl functional latex coating with the cycloaliphatic diepoxide after crosslinking using atomic force microscopy.

temperature of the crosslinking reactions. The loss of epoxide, and concomitant growth in ester or ether bond absorption observed in the IR data collaborated the crosslinking reactions of the carboxyl or hydroxyl groups, respectively. The substantially different viscoelastic properties from the DMTA, such as the occurrence of the elastic rubbery plateaus after the crosslinking of the coatings, clearly confirmed the effect of the crosslinking reactions between the latexes and the crosslinker. The AFM images visually revealed the interaction of the crosslinker with the latex particles before and after baking also providing indirect information on the crosslinking. In addition, the significant increase in the gel content, pencil hardness, and pull-off adhesion and the decrease in the water absorption of the coatings with the crosslinking temperature and time also showed the effects of the epoxy crosslinking on the coating properties.

4. Conclusion

The cycloaliphatic diepoxide crosslinked carboxyl or hydroxyl functional acrylic latexes. The carboxyl functional acrylic latexes were more reactive than the hydroxyl functional acrylic latexes with the cycloaliphatic epoxide, and consequently exhibited better coating properties. The crosslinking reactions and the crosslinked coating properties were also influenced by the crosslinking temperature, and the amount of the crosslinker used. The crosslinking of the carboxyl functional latex coatings with cycloaliphatic diepoxide was completed at 130°C, whereas effective crosslinking of the hydroxyl functional latex coatings required a higher temperature (170°C). The addition of excess crosslinker to both the carboxyl and the hydroxyl latex coatings was favorable for the overall enhanced coatings properties.

Acknowledgements

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