ELSEVIER

Polymer 41 (2000) 81–92

polymer

Synthesis of model acrylic latexes for crosslinking with cycloaliphatic diepoxides

S. Wu, J.D. Jorgensen, M.D. Soucek*

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

Received 8 June 1998; received in revised form 9 February 1999; accepted 12 February 1999

Abstract

Two model acrylic latex systems were synthesized. One latex system was carboxyl functional, and prepared using methyl methacrylate (MMA) and butyl acrylate (BA) with methacrylic acid (MAA). The second latex system was hydroxyl functional, and prepared using MMA and BA with 2-hydroxyethyl methacrylate (HEMA). Both the resultant latexes were crosslinked with a cycloaliphatic diepoxide (3,4-epoxycyclohexyl methyl-3′,4′-epoxycyclohexane carboxylate). Dynamic mechanical thermal analysis (DMTA) and differential scanning calorimeter (DSC) were used to study the rheological and thermal properties of the crosslinked coatings. The film properties of the crosslinked latexes were evaluated in terms of water absorption, gel content, Tukon hardness, pull-off adhesion, and hydrolytic stability. The increase in the latex carboxyl or hydroxyl functionality and glass transition temperature resulted in enhancement of the overall film properties. However, a balance of the crosslink density and the glass transition temperature was necessary for good adhesion. In addition, the carboxyl functional acrylic latexes displayed better overall properties than the hydroxyl functional acrylic latexes, and the polarity and steric hindrance of the ester crosslinks may play important functions in the observed properties. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Cycloaliphatic epoxides; Crosslinking reactions; Thermoset coatings

1. Introduction

Melamine–formaldehyde crosslinked coating systems are the major type of the coatings used for automotive topcoats [1]. In the automotive coating systems, acrylic and polyester polyols were the primary binders, and they were crosslinked with melamine–formaldehyde (MF) resins [2]. Typically, the MF resins are synthesized using melamine, formaldehyde, and an alcohol or a mixture of alcohols [3]. Two steps are involved in the synthesis of MF resins. In the first step, melamine and formaldehyde react together via a base-catalyzed methylolation. In the second step, the methyloated product(s) react with an alcohol or a mixture of alcohols via an acid-catalyzed etherification.

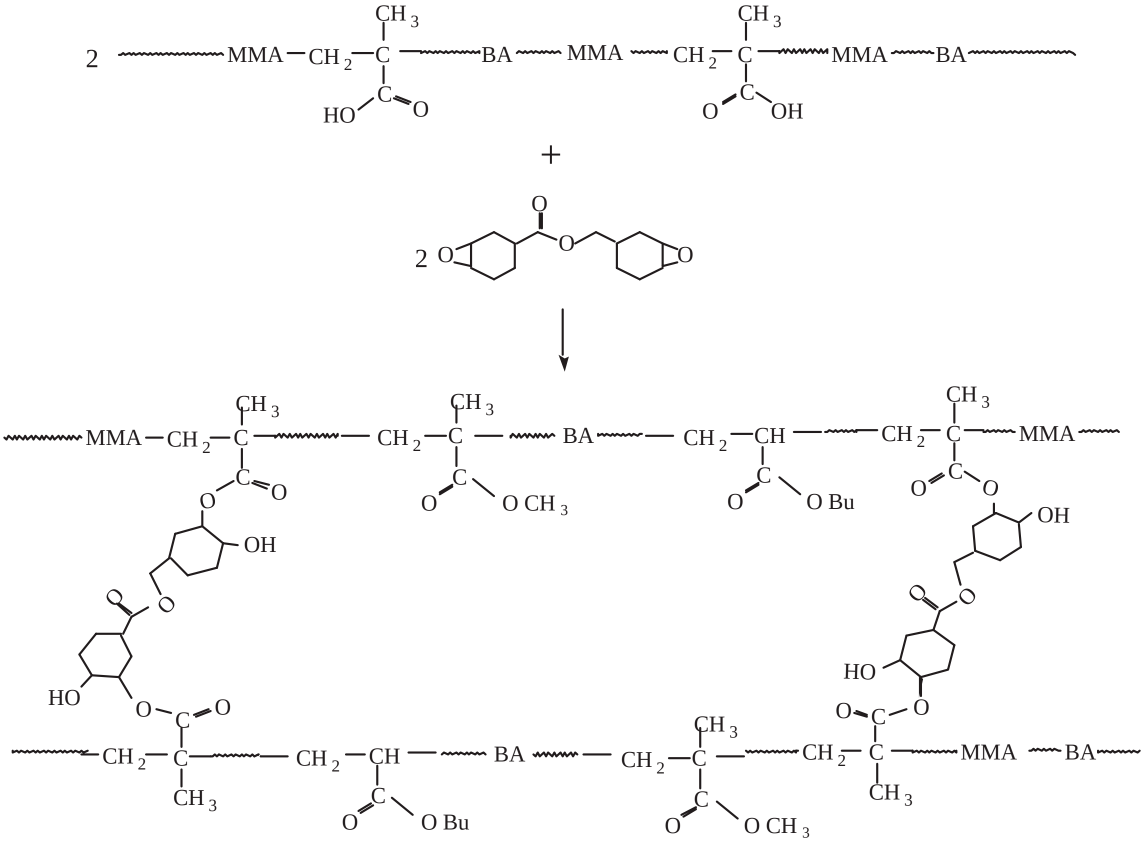
To decrease the viscosity of MF resins, their synthesis requires high degrees of methylolation and etherification [4,5]. As a consequence, the crosslinked coatings also display high hydrolytic stability. However, the water solubility of the resultant MF resins is low. To overcome the low water solubility and improve the miscibility with the coating binder(s), water-miscible organic solvents must be used in the coating formulations [3,6]. As a consequence, the levels of volatile organic compounds (VOCs) are high. In addition, problems of the evolution of formaldehyde during the crosslinking and acid-rain etching of the cured coatings were also observed [7].

As the pressure to reduce VOCs in coatings continuously mounts, many efforts have been made to develop new crosslinking systems which can overcome those problems in the melamine crosslinking systems [8–13]. As a result, a number of new crosslinkers were developed. Examples of the new crosslinkers include carbodiimides [8,9], arziridines [10,11], and oxazolines [12,13]. However, these crosslinking systems also present more or less environmental, public health related problems or unsatisfactory coating properties. In searching for an environmentally more friendly crosslinking technology, we first studied the crosslinking reactions of carboxyl and hydroxyl acrylic latex polymers with cycloaliphatic epoxide using acetic acid, methanol, and cyclohexene oxide as the model compounds [14–16]. Both the reactions of acetic acid and methanol with cyclohexene oxide are acid catalyzed. The reaction of acetic acid with cyclohexene oxide exhibits higher rate constants and lower activation energies than methanol with cyclohexene

---

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

0032-3861/00/$ - see front matter © 1999 Elsevier Science Ltd. All rights reserved.
PII: S0032-3861(99)00158-5



Scheme 1. Crosslinking reaction of the carboxyl functional latex with cycloaliphatic diepoxide.

oxide. The formation of the primary ester and ether products are the two major modes of the reactions.

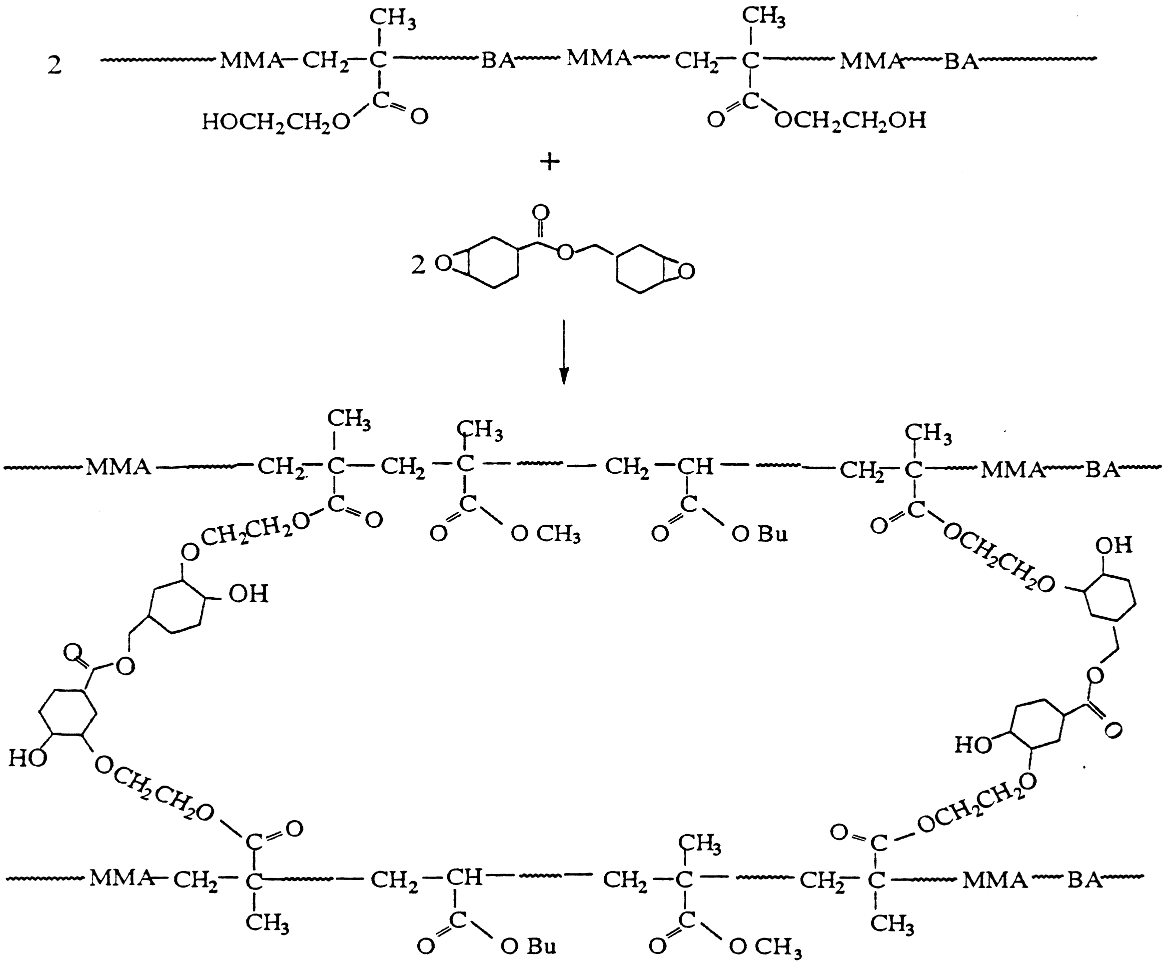
Based on the model compound study, we also reported the crosslinking of model carboxyl and hydroxyl functional acrylic latex coatings with a cycloaliphatic diepoxide [17–19]. The cycloaliphatic diepoxide effectively crosslinked with carboxyl or hydroxyl functional acrylic latexes. The crosslinking reactions are shown in Schemes 1 and 2. The crosslinking of hydroxyl functional latexes required an acid catalyst, whereas the crosslinking of carboxyl functional latexes did not necessarily need an external acid. The water resistance, solvent resistance, pencil hardness, and adhesion of the latex coatings were substantially enhanced after crosslinking.

To investigate the effects of the ester crosslinks versus ether crosslinks on the coating properties, two series of the model acrylic latex systems were synthesized. The first latex system was carboxyl-functionalized using MAA, and the second latex system was hydroxyl-functionalized using HEMA. The glass transition temperature of the latexes was also systematically varied to investigate any effect on the film properties of the latexes. The resulting model latexes were crosslinked with a cycloaliphatic diepoxide. The crosslink density, water absorption, gel content, hydrolytic stability, Tukon hardness, and pull-off adhesion of both the crosslinked latexes were evaluated in this paper.

2. Experimental

Methyl methacrylate (MMA), butyl acrylate (BA), methacrylic acid (MAA), 2-hydroxyethyl methacrylate (HEMA), ammonium persulfate, *p*-toluene sulphonic acid (*p*-TsOH), phenyl phosphonic acid (PPA), sodium bicarbonate, and ammonia were purchased from Aldrich. Deformer Byk-035 was provided by BYK Chemie Company. Cycloaliphatic diepoxide (UVR-6105) and surfactants (Triton-200 and Tergital-XJ) were supplied by 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 for 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. The recipes for the latexes are shown in Tables 1 and 2. The contents of the functional monomers MAA and HEMA were systematically varied to prepare the latexes with different carboxyl and hydroxyl functionalities. Both the contents of the functional groups of the latexes were equivalent in moles at each level of the addition. The glass transition temperature of the carboxyl and hydroxyl latex copolymers was designed to be 0, 10,



Scheme 2. Crosslinking reaction of the hydroxyl functional latex with cycloaliphatic diepoxide.

and 15°C according to the Fox equations [20]:

$$\frac{1}{T_{\mathrm{g,\ carboxyl\ latex}}} = \frac{\mathrm{Wt.}_{\mathrm{MMA}}\%}{T_{\mathrm{g,\ MMA}}} + \frac{\mathrm{Wt.}_{\mathrm{BA}}\%}{T_{\mathrm{g,\ BA}}} + \frac{\mathrm{Wt.}_{\mathrm{MAA}}\%}{T_{\mathrm{g,\ MAA}}} \quad (1)$$

where $T_{\mathrm{g,\ carboxyl\ latex}}$ was the designed glass transition temperature for the carboxyl latex copolymer; $T_{\mathrm{g,MMA}}$, $T_{\mathrm{g,BA}}$, and $T_{\mathrm{g,MAA}}$ were the glass transition temperatures of MMA, BA, and MAA homopolymers [21], respectively; $\mathrm{Wt}_{\mathrm{MMA}}\%$, $\mathrm{Wt}_{\mathrm{BA}}\%$, and $\mathrm{Wt}_{\mathrm{MAA}}\%$ were the corresponding weight percentages of MMA, BA, and MAA, respectively:

$$\frac{1}{T_{\mathrm{g,\ hydroxyl\ latex}}} = \frac{\mathrm{Wt.}_{\mathrm{MMA}}\%}{T_{\mathrm{g,\ MMA}}} + \frac{\mathrm{Wt.}_{\mathrm{BA}}\%}{T_{\mathrm{g,\ BA}}} + \frac{\mathrm{Wt.}_{\mathrm{HEMA}}\%}{T_{\mathrm{g,\ HEMA}}} \quad (2)$$

where $T_{\mathrm{g,\ hydroxyl\ latex}}$ was the designed glass transition temperature for the hydroxyl latex copolymer; $T_{\mathrm{g,\ HEMA}}$ was the glass transition temperature of HEMA homopolymer [21], and $\mathrm{Wt}_{\mathrm{HEMA}}\%$ were the corresponding weight percentage of HEMA.

Table 1
Recipes for the synthesis of carboxyl latexes[a]

MAA content (wt.%)	MMA	BA	MAA
6.0	71.56	97.64	10.80
9.0	64.50	99.30	16.20
15.0	50.38	102.62	27.00

[a] All the latex synthesis contained 0.81 g ammonium persulfate, 8.04 g Triton 200, and 0.4 g sodium bicarbonate, and the T_g calculated by the Fox equation was 0°C.

The monomers were mixed and then slowly added into another fluted round bottom flask containing a water solution (0.2 g $NaHCO_3$, 7.96 g Triton-200, and 96 g water) being stirred 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 $(NH_4)S_2O_8$, 35.0 g water), 0.2 g $NaHCO_3$, and 0.08 g Triton-200 at 80°C. The contents were 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 a addition pump (ISMATEC REGLO-100), and the initiator was added to the reactor concurrently with the monomer

Table 2
Recipes for the synthesis of hydroxyl latexes[a]

HEMA content (wt.%)	MMA	BA	HEMA
9.1	72.74	90.94	16.33
13.6	66.27	89.24	24.49
22.7	53.34	85.85	40.81

[a] All the latex synthesis contained 0.81 g ammonium persulfate, 8.04 g Triton 200, and 0.4 g sodium bicarbonate, and the T_g calculated by the Fox equation was 0°C.

pre-emulsion feed at a constant rate (0.154 g/min) 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 an additional 2 h at 85°C to digest any residual monomers.

After completion of the synthesis, 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 solids (ASTM D 3926), monomer conversion (ASTM D 4827), acid value (ASTM D 1639), and hydroxyl value (ASTM D 1957) were measured according to the standard methods. The latex particle size was measured using a laser light scattering instrument at Union Carbide Corporation. The typical properties for the carboxyl and hydroxyl functional latexes with a designed glass transition temperature (0°C) are shown in Tables 3 and 4.

The cycloaliphatic diepoxide (UVR-6105) was not soluble or dispersible in water. Thus, it was emulsified into water according to a method reported previously [17–19]. The cycloaliphatic diepoxide (45.0 g) was dispersed in water (55.0 g) containing a defoamer (0.1 g Byk-035) with a mixture of anionic surfactant (Triton-200, 3.21 g) and non-ionic surfactant (Tergital-XJ, 1.35 g) under a high shear rate. After the emulsification, the solids (ASTM D 3926) and consistence (ASTM D 562) were measured. The emulsion particle size was also measured using a laser light scattering instrument at Union Carbide Corporation. The stability against sedimentation was visually evaluated in terms of the phase separation. The properties of the emulsion are shown in Table 5.

A stoichiometric amount of the diepoxide emulsion was then added into the latexes, respectively. All the coating formulations were cast using a drawdown bar (5 mils) on glass plates or on aluminum panels 60 min after complete mixing. The coatings cast on the glass substrates were used to provide crosslinked films for the water absorption and gel content measurements. The coating samples were scraped off from the substrates using a razor blade. The coatings cast on the aluminum substrates were used to determine the other coating properties after the crosslinking. To crosslink the carboxyl functional latex coatings with the cycloaliphatic diepoxide, the coatings were baked at 130°C for 105 min. To crosslink the hydroxyl functional latex coatings with the diepoxide, *p*-toluene sulphonic acid (0.6 wt.%) was also added, and the coatings were baked at 170°C for 105 min.

The viscoelasticity (storage modulus, loss modulus, and loss tangent δ) of the latex coatings as a function of temperature was recorded using a dynamic mechanical thermal analysis instrument (Rheometric Scientific DMTA 3E). Dry coating samples were cut into $10 \times 30\ \mathrm{mm}^2$. 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%). The crosslinking density (XLD) of the coatings was calculated based on the storage modulus on the rubbery plateau region according to [22,23]:

$$\mathrm{XLD} = \frac{E'}{3\mathrm{R}T} \tag{3}$$

where XLD is the crosslink density, E' the elastic storage modulus on the rubbery plateau region, R the ideal gas constant, and T the temperature in Kelvin.

The temperature at which the loss tangent δ indicated the glass transition was identified as the glass transition temperature for the sample. In addition, a differential scanning calorimeter (Perkin Elmer DSC 7) was also used to measure the glass transition temperature of the crosslinked latex coatings for comparison. The DSC scanning was performed using 17–20 mg film samples with a 10°C/min heating rate. The water absorption (ASTM D 3419), gel content (ASTM D 2765), pull-off adhesion (ASTM D 4541), Tukon hardness (ASTM D 1474), reverse impact resistance (ASTM G14), and conical mandrel flexibility (ASTM D 522) of the crosslinked coatings were measured 24 h after baking.

3. Results and discussion

Previously, we reported the crosslinking reactions of

Table 3
Properties of the carboxyl functional latexes

MAA (wt.%)	pH	Solids (wt.%)	Conversion (wt.%)	Particle size (nm)	Acid value[a]
6.0	8.4 ± 0.3	44.5 ± 0.7	99.5 ± 0.3	195	40
9.0	8.2 ± 0.3	43.5 ± 1.1	99.3 ± 0.2	196	58
15.0	7.9 ± 0.4	43.7 ± 1.4	98.8 ± 0.4	200	96

[a] KOH mg/g of resin was based on the dry solids.

Table 4
Properties of the hydroxyl functional latexes

HEMA (wt.%)	pH	Solids (%)	% conversion	Particle size (nm)	Hydroxyl value[a]
9.1	8.5 ± 0.2	44.6 ± 0.3	99.7 ± 0.1	223	39
13.6	8.4 ± 0.3	44.8 ± 0.2	99.6 ± 0.1	190	59
22.7	8.5 ± 0.3	44.5 ± 0.4	99.2 ± 0.3	193	98

[a] KOH mg/g of resin was based on the dry solids.

model carboxyl or hydroxyl functional latexes with 3,4-epoxycyclohexyl methyl-3′,4′-epoxycyclohexane carboxylate and the catalyst effects on the crosslinking reactions [17–19]. Carboxyl functional latexes exhibit higher reactivity to the cycloaliphatic diepoxide, and crosslink at a lower temperature than hydroxyl functional latexes. Acid catalysts improve the crosslinking and coating properties for the hydroxyl functional latexes, but deteriorate the coating properties of the carboxyl functional latexes, especially the water and solvent resistance.

As illustrated in Schemes 1 and 2, the crosslinking of the carboxyl and hydroxyl functional acrylic latexes with the cycloaliphatic diepoxide results in formation of two different crosslinks, ester and ether. In general, ether linkages are more stable than ester linkages under acidic or basic conditions [24]. To further investigate the contribution from the ester versus ether crosslinks to the coating properties within a functionality-mixed latex system, two series of carboxyl and hydroxyl functional acrylic latexes were synthesized, and crosslinked with the cycloaliphatic diepoxide as a function of the latex functionalities and glass transition temperatures. The viscoelastic properties and the glass transition temperature of the latexes and the crosslinked films were studied using DMTA and DSC. The crosslink density, water absorption, and gel content were used to evaluate the crosslinking of the latexes.

The model carboxyl or hydroxyl functional acrylic latexes were synthesized using MAA and BA with MAA or HEMA via emulsion polymerization. The carboxyl or hydroxyl functionality of the latexes was changed through addition of the different amounts of MAA or HEMA (Tables 1 and 2). All the latexes were neutralized to basic as indicated by the pH value. The basic condition was adjusted to minimize the hydrolysis of the cycloaliphatic diepoxide crosslinker [17–19]. The solids of all the latexes were consistent with the pre-designed value (45.0 wt.%) suggesting the efficiency of the polymerization. The monomer conversion of the latexes measured by GC also confirmed the efficiency of the polymerization.

The latex particle sizes are typically influenced by the surfactants and the polymerization conditions [25]. The mean particle size of the majority of the latexes, as shown in Tables 3 and 4, varied from 190 to 200 nm. The acid values of the carboxyl functional latexes increased with the addition of MAA, and were consistent with the theoretical acid values. Similarly, the hydroxyl values of the hydroxyl functional latexes increased systematically with increasing HEMA, and were consistent with the theoretical values. The cycloaliphatic diepoxide was not water soluble or dispersible. To use the cycloaliphatic diepoxide as the crosslinker for the latexes, the cycloaliphatic diepoxide was emulsified. As a common phenomenon [20,25,26], the emulsion droplets were much greater than latex particles as shown in Tables 3–5. Despite the large particle sizes, the emulsion was still stable for 7 days without significant separation.

The water absorption of a polymeric material is especially sensitive to the changes in the polarity and crosslink density. The water absorption of the carboxyl latexes as a function of MAA is shown in Fig. 1. Without crosslinking with the cycloaliphatic diepoxide, the water absorption of the latex films increased with increasing MAA. This is due to increasing incorporation of the polar carboxylic acid groups. After crosslinking with the diepoxide, the water absorption of the coatings was substantially lowered (approximately by 7–40 times), and exhibited an opposite trend as a function of methacrylic acid in comparison with the latexes without the crosslinking. This can be attributable to the decreased polarity and increased crosslink density which reduced the interaction of the latex films with water.

The gel content of the carboxyl functional latexes as a function of the acid monomer and the epoxy crosslinker is dipicted in Fig. 2. The gel content of the latexes without the crosslinker was low (∼10 wt.%), and appeared to decrease with increasing MAA. It can be due to an increasing polarity by MAA. This result is also correlated with the trend of the water absorption of the latexes (Fig. 1). In contrast, the gel content of the latexes with the crosslinker was much higher (>92 wt.%) than the latexes without the crosslinker. The gel content of the latexes also increased when MAA was increased. This increased gel content can be attributed to an enhancement of the crosslink density [22,23].

Table 5
Properties of the cycloaliphatic diepoxide emulsion

PH	Solids (wt.%)	Particle size (μm)	Stability without sedimentation
8.2 ± 0.3	44.8 ± 1.6	0.9–1.1	7 ± 1 days

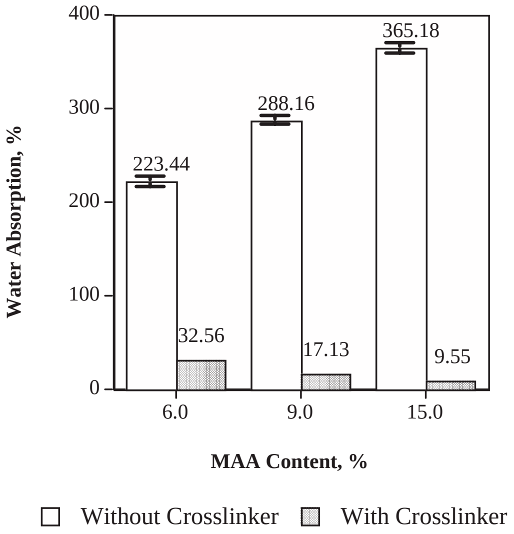


Fig. 1. Water absorption of the carboxyl latexes as a function of the MAA content and crosslinker.

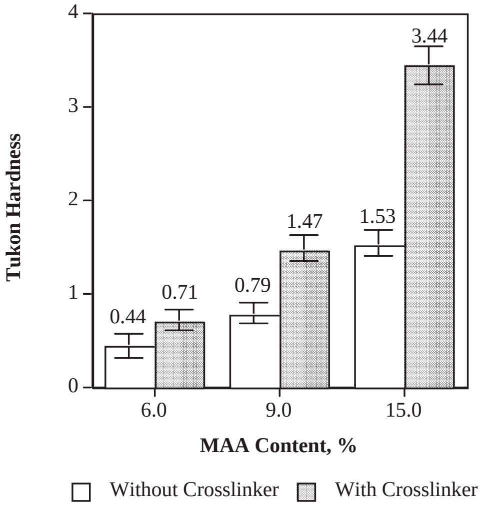


Fig. 3. Tukon hardness of the carboxyl latexes as a function of the MAA content and crosslinker.

The Tukon hardness of the carboxyl latexes is shown in Fig. 3. The Tukon hardness of the latexes with or without the crosslinker systematically increased when MAA was increased. This increase in the hardness with MAA may be due to increasing polarity by MAA. The Tukon hardness of the latexes with the crosslinker was about 2 times higher than the latex without the crosslinker. The improved hardness evidently is due to crosslinking of the latexes with the epoxide.

The crosslinking effect was also reflected in the pull-off adhesion of the latexes. The pull-off adhesion of the latexes as a function of MAA and the crosslinker is shown in Fig. 4. The adhesion of the crosslinked latexes was about 8 times higher than the latexes without the crosslinker, and increased with the MAA content at the low addition. The decrease in the adhesion at the higher addition of MAA may be due to a high crosslink density which made the latex films become brittle.

The water absorption, gel content, Tukon hardness, and pull-off adhesion of the hydroxyl functional latexes were shown in Figs. 5–8, respectively. Similar to the carboxyl functional latexes, the water absorption of the crosslinked hydroxyl latexes was substantially lower. The gel content, Tukon hardness, and the pull-off adhesion of the coatings were considerably higher than un-crosslinked latexes. In addition, the properties of the crosslinked latex films also improved with increasing HEMA; the same trend observed for the crosslinked carboxyl latexes. In comparison with the carboxyl functional latexes, the crosslinked hydroxyl

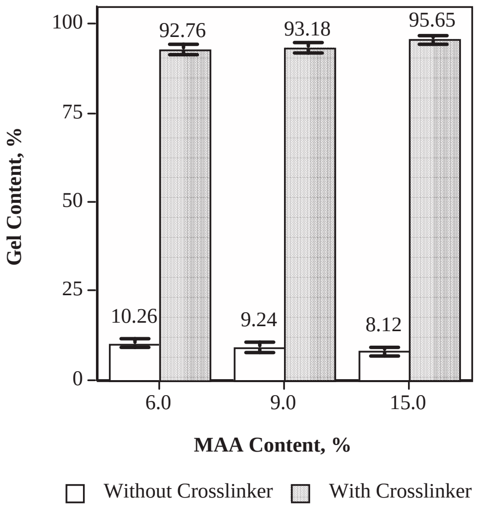


Fig. 2. Gel content of the carboxyl latexes as a function of the MAA content and crosslinker.

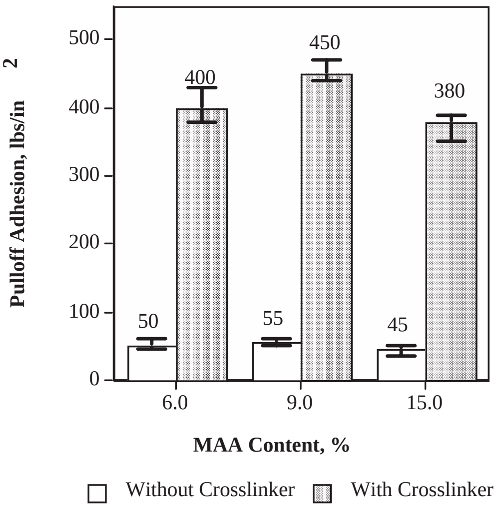


Fig. 4. Pull-off adhesion of the carboxyl latexes as a function of the MAA content and crosslinker.

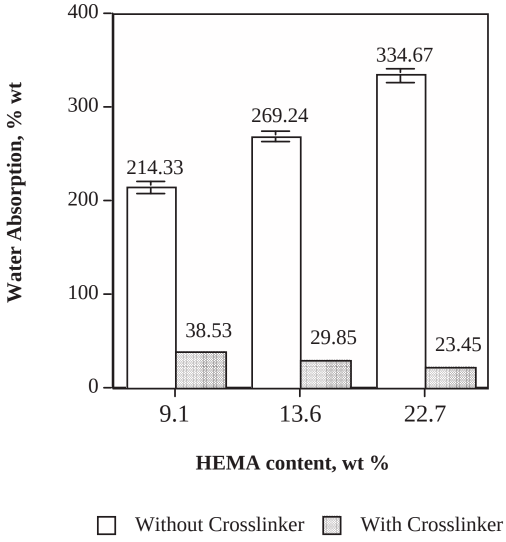


Fig. 5. Water absorption of the hydroxyl latexes as a function of the HEMA content and crosslinker.

latexes, however, showed higher water absorption, lower gel content, lower Tukon hardness, and lower pull-off adhesion. These results may be corroborated with the lower polarity and glass transition temperature of the hydroxyl latexes than the carboxyl latexes.

The DMTA data and the calculated crosslink density for both the crosslinked carboxyl and hydroxyl latexes are shown in Tables 6 and 7, respectively. For clarity, Figs. 9 and 10 illustrate a comparison of the loss tangent (δ) for the carboxyl and hydroxyl latexes as a function of temperature and functionality, respectively. The loss tangent (δ) of both the carboxyl and hydroxyl functional latexes decreased as the content of the functional monomer (MAA or HEMA) was increased. Not surprisingly, the elastic modulus on the rubbery plateau also increased systematically with MAA or HEMA content. The crosslink density, which was calculated from the elastic modulus on the rubbery plateau region, reflected this trend. These results clearly indicate the effectiveness of the cycloaliphatic epoxide crosslinking both the carboxyl and hydroxyl functional latexes.

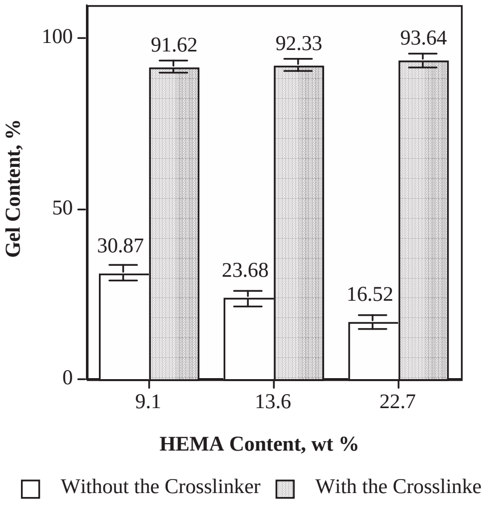


Fig. 6. Gel content of the hydroxyl latexes as a function of the HEMA content and crosslinker.

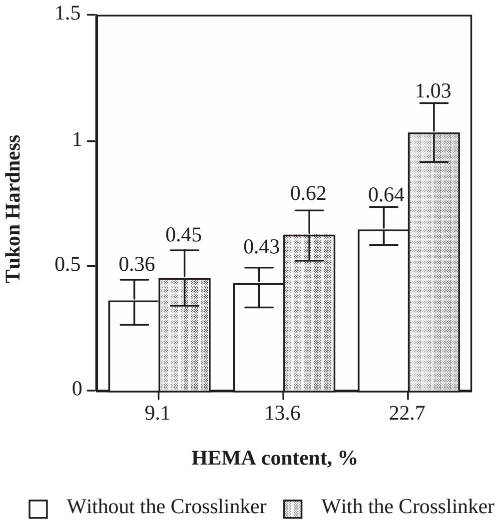


Fig. 7. Tukon hardness of the hydroxyl latexes a function of the HEMA content and crosslinker.

In comparison with the crosslinked carboxyl latex coatings, the loss tangent (δ) data of the crosslinked hydroxyl latexes were higher, indicating higher viscous properties of the latex films. This may be due to the lower polarity and lower rigidity of the ether crosslinks than the ester crosslinks. In addition, the lower reactivity of hydroxyl functional groups toward the cycloaliphatic epoxide may also play a role [17–19]. The lower elastic modulus and lower crosslinked density of the hydroxyl latex coatings were also consistent with the loss tangent δ. The glass transition temperature (T_g), derived from the loss tangent (δ) as a function of temperature, increased systematically with increasing MAA or HEMA due to increased crosslink density. However, the glass transition temperature of the carboxyl latex coatings was much higher than the hydroxyl latex coatings. This again can be attributed to the higher polarity and rigidity of the ester crosslinks than the ether crosslinks [27].

The glass transition temperature of a polymeric material is the temperature at which the micro-Brownian movements of the molecular chain segments become significant [27]. Therefore, any responses of the material to a chemical and physical environment only occurs at or above the glass transition temperature. As a result, the higher the glass transition temperature, the better the chemical and physical resistance. The water absorption, gel content, Tukon hardness, and the pull-off adhesion of both the carboxyl and hydroxyl latexes as a function of the glass transition temperatures measured by DSC are shown in Table 8. As an overall general trend, the water absorption and pull-off adhesion decreased, and the gel content and Tukon hardness increased when the glass transition temperature of the latex

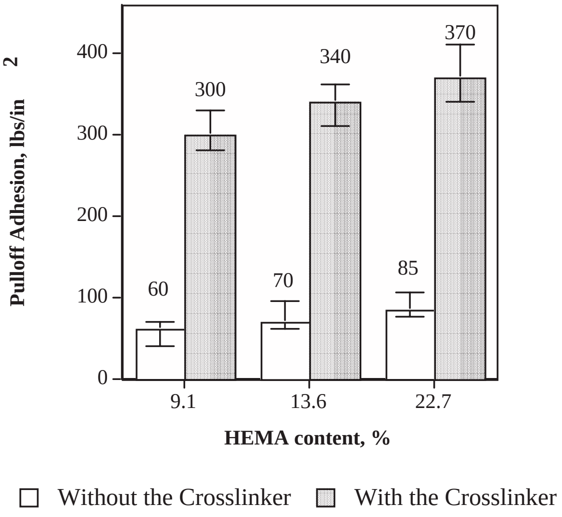


Fig. 8. Pull-off adhesion of the hydroxyl latexes as a function of the HEMA content and crosslinker.

was increased. Again, the carboxyl functional latexes also exhibit better properties than the hydroxyl latexes in the whole range of the glass transition temperatures. This trend is also consistent with the film properties as a function of MAA and HEMA as previously discussed. In comparison, the glass transition temperatures measured by DSC were lower than the glass transition temperatures measured by DMTA. This result can be due to a fact that the glass transition temperature of a polymeric material is a kinetic parameter which is affected by the time scale of the measurements [27,28].

To evaluate the hydrolytic stability of the ester crosslinks versus the ether crosslinks, the gel content of both the crosslinked latex coatings was measured after acid and base hydrolysis. The gel content of the crosslinked carboxyl latex films before and after acid and base hydrolysis as a function of MAA is shown in Figs. 11 and 12. As a result of the hydrolysis, the gel content of the crosslinked carboxyl functional latexes was reduced after the acid or base hydrolysis. However, the gel content of the hydrolyzed films at both the acidic and the basic condition increased systematically with the functionality of the latexes. The increase in the gel content with MAA may suggest the remaining of the crosslink network after the hydrolysis. The stability of the crosslinks against hydrolysis can be attribuable to a stronger steric hindrance of the ester crosslinks near to cyclohexyl ring than the pendant ester groups on the main copolymer chains. Consequently, the reduced gel content after hydrolysis may be due to the loss of the pedant groups (methoxyl and butoxyl) on the copolymer chains. Thus, a hydrolysis mechanism for the crosslinked carboxyl

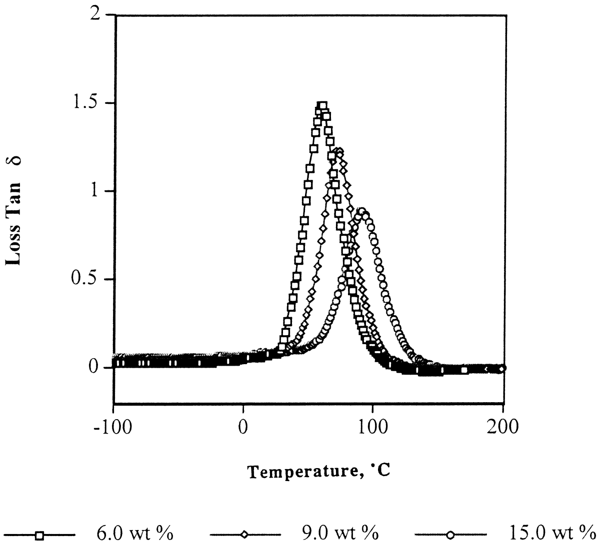


Fig. 9. Loss tan δ (DMTA) of the crosslinked carboxyl functional latexes as a function of MAA.

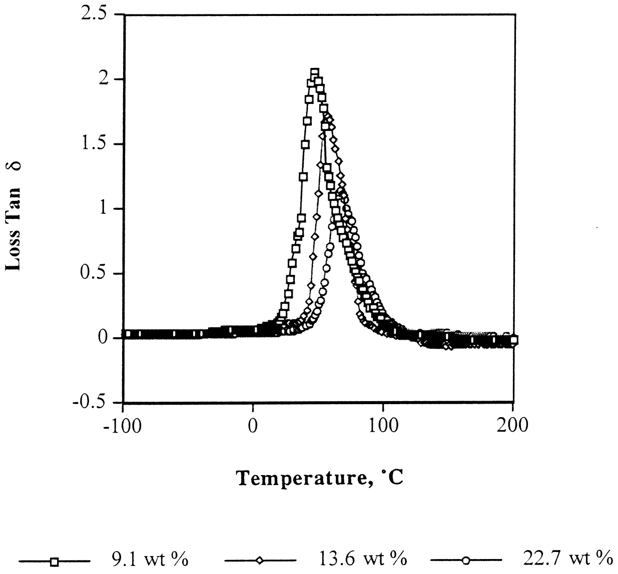


Fig. 10. Loss tan δ (DMTA) of the crosslinked hydroxyl functional latexes as a function of HEMA.

Table 6
The dynamic mechanical thermal analysis data for the carboxyl functional latexes as a function of the MAA content

MAA content	Loss tangent (δ)	Temperature at tan δ	$E'^{a} \times 10^{-6}$ (Pa)	XLD$^{b} \times 10^{4}$ (mol/cm^{3})
6.0	1.49	60	1.303	1.36
9.0	1.22	71	1.874	1.96
15.0	0.88	91	2.434	2.55

[a] The average E' on the rubbery region after the glass transition.
[b] The crosslink density (XLD) was calculated at 383 °K.

Table 7
The dynamic mechanical thermal analysis data for the hydroxyl functional latexes as a function of the HEMA content

HEMA content	Loss tangent (δ)	Temperature at tan δ	$E'^{a} \times 10^{-6}$ (Pa)	XLD$^{b} \times 10^{4}$ (mol/cm^{3})
9.1	1.98	46	1.255	1.31
13.6	1.65	53	1.633	1.71
22.7	1.12	66	2.146	2.25

[a] The average E' on the rubbery region after the glass transition.
[b] The crosslink density (XLD) was calculated at 383 °K.

Table 8
Glass transition temperature and general properties of the crosslinked carboxyl and hydroxyl latexes

Latexes	Calculated T_g (°C)	T_g (DSC) (°C)	Water uptake (%)	Gel content (%)	Adhesion (lbs/in.^{2})	Tukon hardness
COOH[a]	0	16.5	23.45	92.84	450	1.53
COOH	10	24.2	17.13	94.78	400	3.98
COOH	15	31.6	11.97	94.95	380	7.17
OH[b]	0	5.1	25.36	92.11	370	1.03
OH	10	14.6	20.95	94.71	330	1.86
OH	15	21.8	13.06	94.92	260	3.69

[a] Latex films contained 9% MAA and crosslinked with a stoichiometric amount of cycloaliphatic epoxide.
[b] Latex films contained 22.7% HEMA and crosslinked with a stoichiometric amount of cycloaliphatic epoxide.

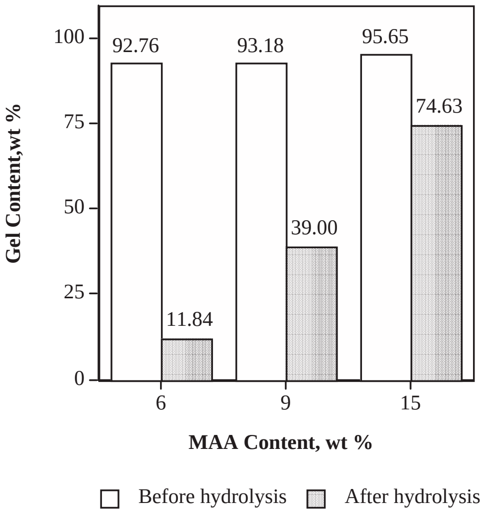


Fig. 11. The gel content of the crosslinked carboxyl functional latexes after acidic hydrolysis (0.5 N HCl) as a function of the MAA content.

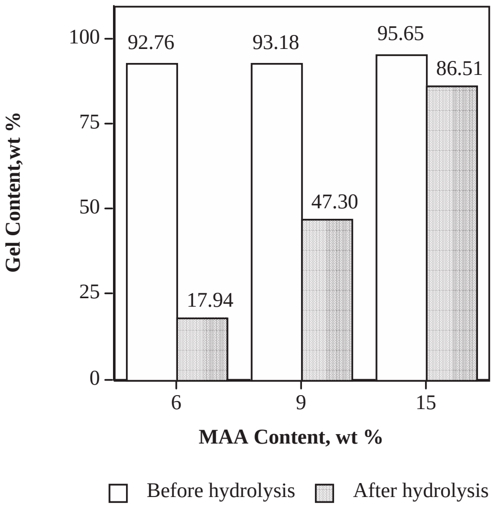
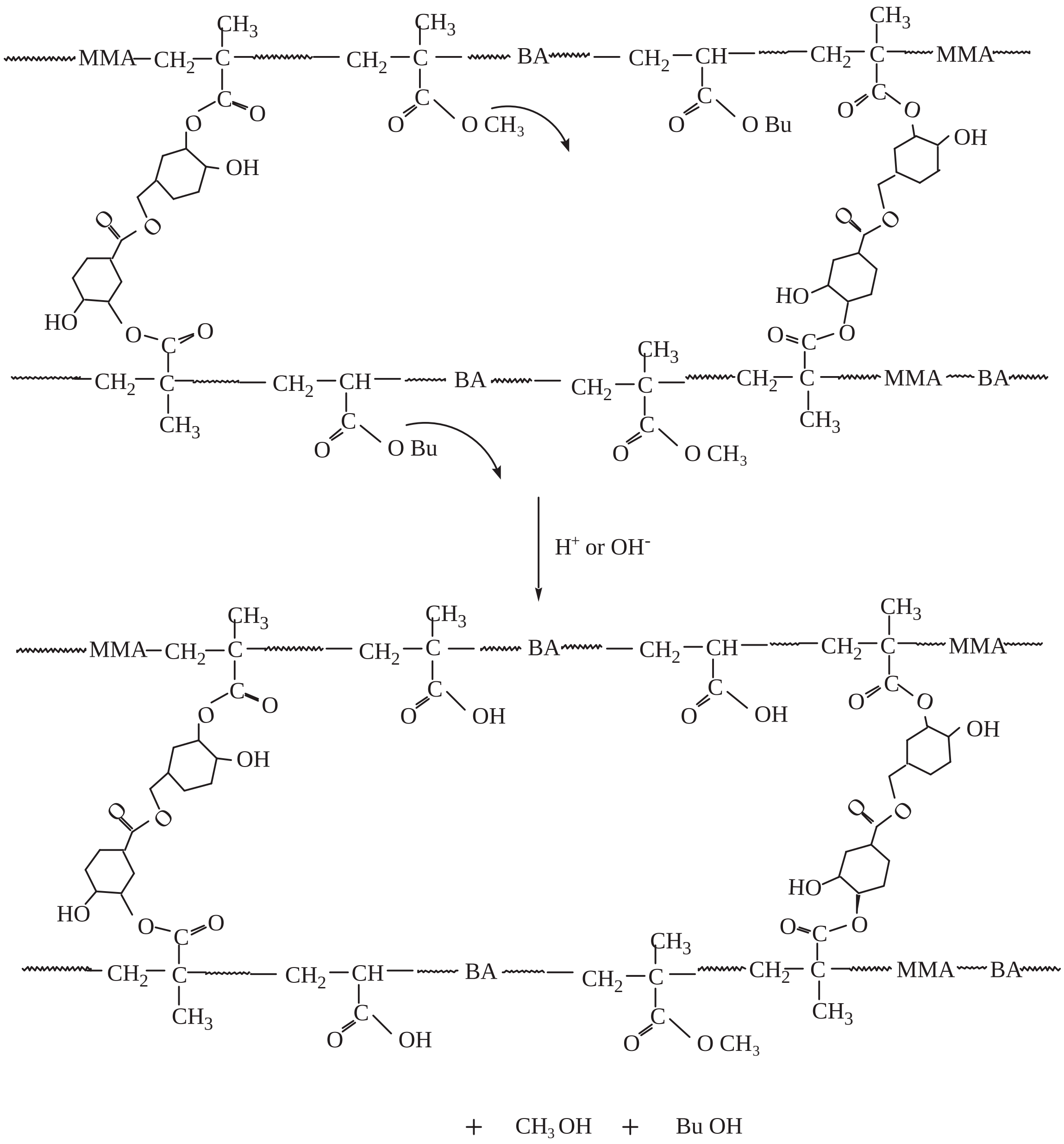


Fig. 12. The gel content of the crosslinked carboxyl functional latexes after basic hydrolysis (0.5 N NaOH) as a function of the MAA content.

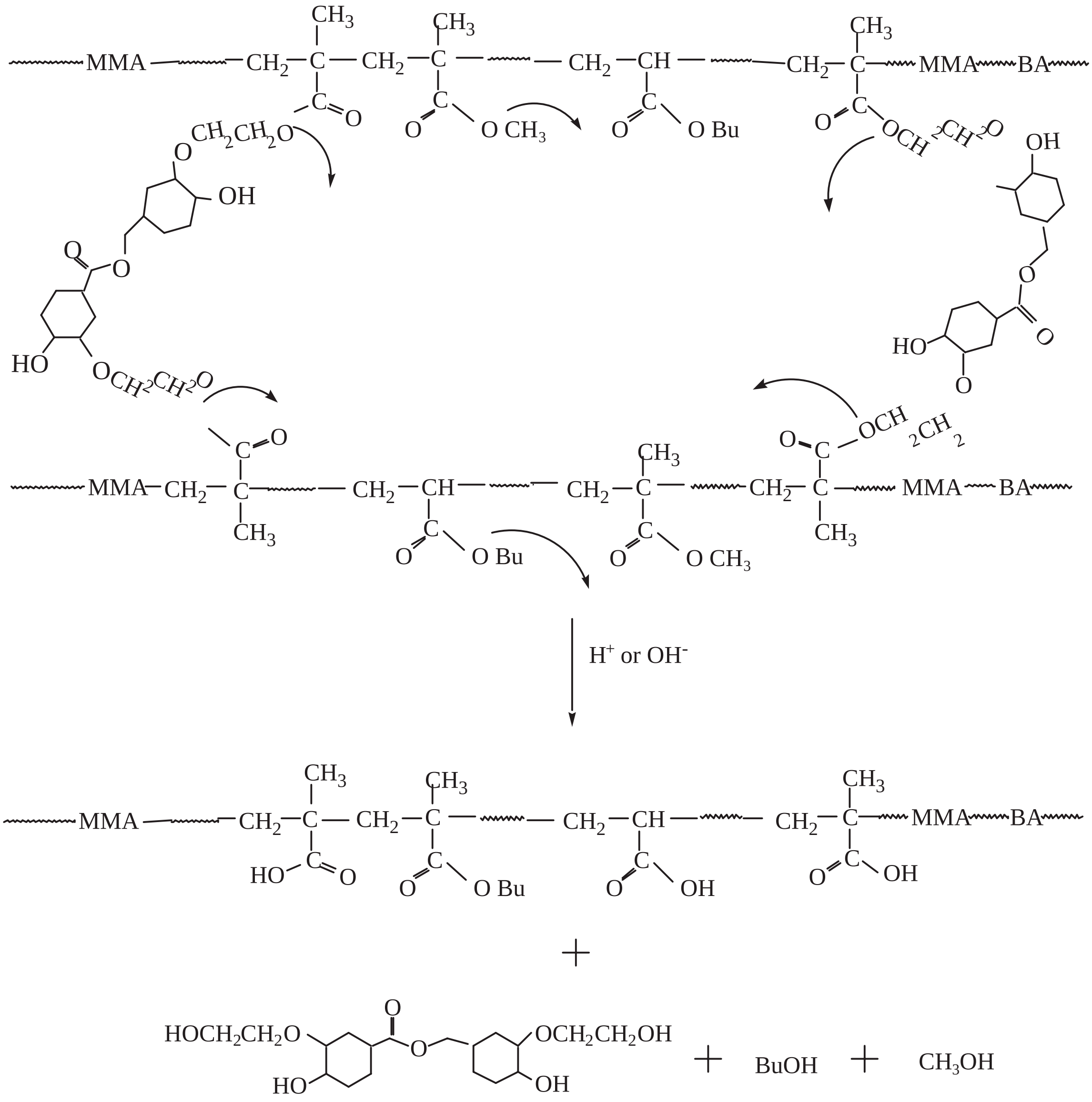


Scheme 3. Proposed hydrolysis mechanism of the crosslinked carboxyl functional latexes under acidic or basic conditions.

latex coatings under acid or basic conditions is proposed in Scheme 3.

The gel content of the crosslinked hydroxyl latex films before and after acid and base hydrolysis as a function of HEMA is shown in Figs. 13 and 14. Similarly, the gel content of the crosslinked hydroxyl latex films was reduced after the acid or base hydrolysis. However, the gel content of the latexes after the hydrolysis decreased with increasing content of HEMA in the latexes. This is in contrast to the trend observed for the carboxyl latexes after the hydrolysis. The decreasing gel content as a function of HEMA for the crosslinked hydroxyl latexes indicates a rupture mechanism of the crosslinked network after the acid or base hydrolysis. The instability of the ether crosslinkages after acid or base hydrolysis can be attributable to the weak ester bond linking the hydroxylethylene unit to the acrylic backbone (HEMA). In addition, the hydrolysis of the pendant ester groups on the copolymer chains may have also contributed to the decrease in the gel content. From the evidence, a hydrolysis mechanism for the crosslinked hydroxyl latexes under acid or basic conditions is also postulated in Scheme 4.

Cycloaliphatic diepoxide crosslinked carboxyl or hydroxyl functional acrylic latexes. The crosslink density of both the carboxyl and hydroxyl latexes increased with the carboxyl and hydroxyl functional monomers (MAA and HEMA). High crosslink density and high glass transition



Scheme 4. Proposed hydrolysis mechanism of the crosslinked hydroxyl functional latexes under acidic or basic conditions.

temperature decreased the water absorption, and increased the gel content and the film hardness. Crosslinking also improved the film adhesion which was attributed to the epoxy ring opening. However, excessive crosslinking resulted in decreased adhesion. The increase in the glass transition temperature monotonously decreased the adhesion of the latexes to the substrate. In addition, the polarity, rigidity, and steric hindrance of the crosslinks also played important functions in the observed coating properties.

Preliminary results from this study suggest that a safe waterborne thermosetting coating system using a cycloaliphatic diepoxide as the crosslinker has potential. It was shown that the carboxylic–cycloaliphatic epoxide crosslinkage is stable under acidic or basic conditions [17–19]. In addition, the crosslinker, cycloaliphatic diepoxide, is not sensitive to ultraviolet light due to absence of aromatic rings [29]. Consequently, an acid etching problem as occurring in the melamine–formaldehyde crosslinked coating system can be reduced or eliminated [7]. Thus, it is predictable that the coating system will display excellent weatherability. Because of the crosslinking nature, the coating system will also exhibit excellent chemical and mechanical resistance. Moreover, the crosslinker is a nontoxic compound. Besides the function as the crosslinker for the latex binder(s), the epoxy crosslinker also plasticized the latex particles, decreasing the latex coalescing temperature. As a consequence, the crosslinker can further function as a coalescing aid-agent in the latex film formation, eliminating the addition of an organic volatile coalescing compound(s). Finally, the coating system did not involve use of any other environmental or public health related hazard compounds. Therefore, an environmentally friendly high performance coating system with low or zero VOC can be anticipated.

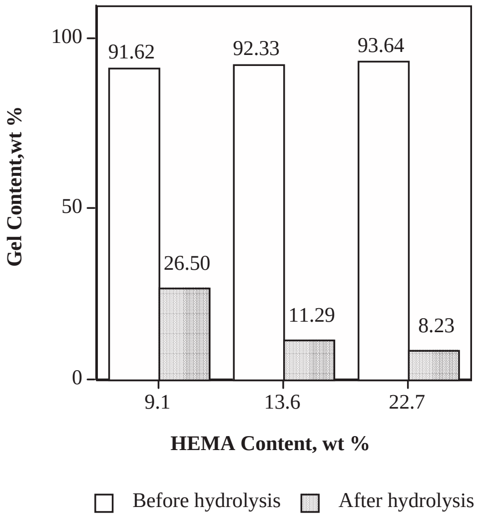


Fig. 13. The gel content of the crosslinked hydroxyl functional latexes after acidic hydrolysis (0.5 N HCl) as a function of the HEMA content.

4. Conclusion

The model carboxyl and hydroxyl functional acrylic latexes have been synthesized, and crosslinked with a cycloaliphatic diepoxide. The functionality and the glass transition temperature of the acrylic latex polymers influenced the chemical and physical properties of the crosslinked latex films. An increase in the functionality of the latexes resulted in cured films with improved water resistance, solvent resistance, and film hardness of the coatings. In addition, a high glass transition temperature (10°C) of the waterborne polymers enhanced these physical properties. The epoxide crosslinking also significantly improved the adhesion, however an excessively high crosslink density led to a decrease in the adhesion. Carboxyl functional acrylic latexes provided better overall balanced film properties and greater hydrolytic stability than the hydroxyl functional latexes.

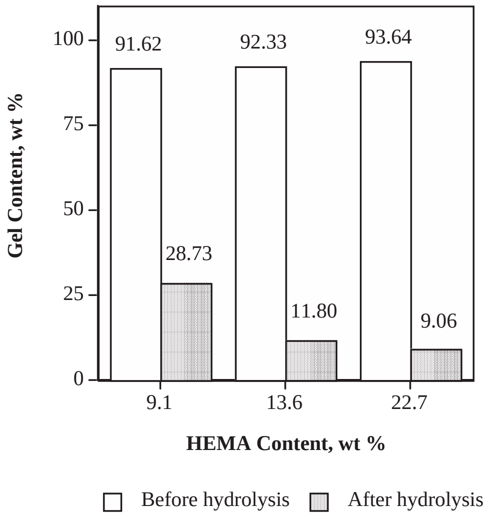


Fig. 14. The gel content of the crosslinked hydroxyl functional latexes after basic hydrolysis (0.5 N NaOH) as a function of the HEMA content.

Acknowledgements

The authors would like to thank the NSF-Coatings Research Center for the funding of this project and the Summer Undergraduate Research Program of the Polymers and Coatings Department at North Dakota State University.

References

[1] Ryntz RA. Paint Coat. Industry 1997;3:36.
[2] Ferrell PE, Gummeson JJ, Hill LW. J Coat Tech 1995;67(851):63.
[3] Wicks ZW, Jones F, Pappas SP. Organic coatings science and technology. New York: Wiley, 1992 Chapter 6.
[4] Nakane Y, Ishidoya M. Prog Org Coat 1997;31:113.
[5] Santer JO. Prog Org Coat 1984;12:309.
[6] Bauer DR. Prog Org Coat 1986;14:193.
[7] Essenfeld A, Wu K-J. Polym Mater Sci Engng 1997;77:385.
[8] Brown W. Surf Coat Int 1995;6:238.
[9] Williams A. Chem Rev 1981;81:589.
[10] Moles P. Polym Paint Color J 1991;181(267):4279.
[11] Pollano G. Polym Mater Sci Engng 1997;77:383.
[12] Moor G, Zhu D-W, Clark G. Surf Coat Int 1995;9:376.
[13] Nippon Shokubai Products Information Bulletin: Novel waterborne crosslinkers.
[14] Wu S, Soucek MD. Polymer 1998;39(23):5747.
[15] Wu S, Soucek MD. Polym Commun 1998;39(15):3583.
[16] Wu S, Soucek MD. J Coat Tech 1997;68(869):43.
[17] Wu S, Soucek MD. Polymer 1999; in press.
[18] Wu S, Soucek MD. Polym Prep 1998;39(1):654.
[19] Wu S, Soucek MD. Polym Mat Sci Eng Prepr 1997;37(1):64.
[20] Wicks ZW, Jones FN, Pappas SP. Organic coatings science and technology. New York: Wiley, 1992 Chapter 5.
[21] Brandrup J, Immergat EH. Polymer handbook. 3. New York: Wiley, 1989 Chapter 8.
[22] Hill LW. J Coat Tech 1992;64(808):29.
[23] Hill LW. J Coat Tech 1987;59(751):63.
[24] Wicks ZW, Jones FN, Pappas SP. Organic coatings science and technology. New York: Wiley, 1992 Chapter 25.
[25] Odian G. Principles of polymerization. 3. New York: Wiley, 1991 Chapter 4.
[26] Wicks ZW, Jones FN, Pappas SP. Organic coatings science and technology. New York: Wiley, 1992 Chapter 29.
[27] Sperling LH. Introduction to physical polymer science. New York: Wiley, 1992 Chapters 8–10.
[28] Hill LW. Mechanical properties of coatings. Federation of Coatings Societies for Coatings Technology, Monograph, 1987.
[29] Buchwalter SL, Kosbar LL. J Polym Sci Part A Polym Chem 1996;34:249.