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Cycloaliphatic Diepoxide Crosslinkable Core-Shell Latexes: The Effect of Addition Mode

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Abstract: The two series of the model core-shell acrylic latex systems were synthesized. Both systems had hydroxy-functionalized cores and carboxyl-functionalized shells. The latexes were then crosslinked with cycloaliphatic diepoxide. The mode of addition of crosslinker was studied by adding the cycloaliphatic diepoxide during the polymerization or after the polymerization. The crosslinker was also added after the polymerization via solvent or emulsion. The Tukon hardness, tensile properties, viscoelasticity, and morphology of latex were evaluated as a function of cycloaliphatic epoxide addition mode. The introduction of the epoxide during the polymerization lowered the Tukon hardness, and the solution approach generally provided better mechanical properties than the emulsion approach.

Introduction

Reducing the volatile organic compounds (VOC) has been a major driving force for coatings industry since 1970's. The latexes are considered as one of the effective vehicles to challenge the VOC regulations. This approach has the lower VOC content, in comparison with the high solids or water-reducible coatings. Latexes are colloidal dispersions of particles principally consisting of high molecular weight thermoplastic acrylic or vinyl acetate polymer stabilized in water by either charge repulsion or entropic repulsion. The film formation of latex coatings can be regarded as the three consecutive major steps.[1,2] First, the particles become close contact as the water evaporates. Second, the additional vaporization of water leads to the deformation of particles to form a void-free solid structure. Finally, the chain ends and segments inter-diffuse, and entanglements cross the particle boundaries, resulting in the development of mechanical strength. Due to lack of chemical bonding, their solvent resistance and mechanical properties are generally poorer than thermosetting resins. In recent years, many efforts have been made to develop a new type of latex in which the functionality of carboxyl or hydroxyl group is introduced into the latex during polymerization.[3-12] In addition to retaining properties of high molecular weight acrylate, such as low VOC, their crosslinks with other resins via chemical bonding bring the dramatic improvement in coating properties such as solvent resistance, and hardness. The type and introduction mode of crosslinker play a critical role in the control of crosslinked latex performance.

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A number of crosslinkers have been developed for latex coatings,[3-12] including amino resins, isocyanates, carbodiimides, aziridines, oxazolines, and aromatic epoxides. However these crosslinkers suffer with respect to environmental, public health problems or have unsatisfactory coating properties. For example, amino resins, offer excellent cost performance efficiency and good balance of mechanical properties, but exhibit disadvantages in terms of VOC content and durability.[3] Recently, cycloaliphatic diepoxide has been used as the crosslinker for acrylic latex coatings by Soucek and coworkers.[7-11] The cycloaliphatic diepoxide effectively crosslinked with either carboxyl or hydroxyl functional acrylic latexes. The crosslinking of hydroxyl functional latexes required an acid-catalyst, whereas the crosslinking of carboxyl functional latex did not appear to need a strong acid catalyst. The carboxyl functional acrylic latex coating system provided better overall balanced coatings properties and greater hydrolytic stability than the hydroxyl functional latex coatings system. The water resistance, solvent resistance, pencil hardness, and adhesion of the latex coatings were substantially enhanced via crosslinking.

The "homogeneous" crosslinked polymer matrix has been studied for many years and the effects of crosslink on the dynamic mechanic properties of polymer have been well described.[13] Generally, the formation of homogenous crosslinked network of latex films from dispersed particles is unlikely. The modes of heterogeneous crosslinking network are generally described as intra or inter-particle crosslinking. In the case of intra-particle crosslinking, the crosslinking occurs within the particle, and for inter-particle crosslinking, the crosslinking takes place between the particles.[12] In waterborne epoxide coatings, the crosslinkers generally are introduced after the emulsion polymerization, and as a consequence tend to form inter-particle crosslinks.[4,14-18] Epoxides can also be introduced during the polymerization. However, gelation occurred when a low level of acrylic acid was present in latex particles.[4] In a recent study,[11] a core-shell latex was prepared with hydroxyl functionality in the core and carboxyl functionality in the shell. The latex was prepared via a two step process where the epoxide was added with the hydroxyl functional monomer during preparation of the latex core. The hydrolysis and crosslinking reactions of the epoxide show to be dependent on latex morphology, initiator system, and reaction conditions. The hydrolysis and the pre-mature crosslinking of the epoxide were minimized by basic reaction condition, and lower temperature of the second stage polymerization using a redox initiator.

In this study, cycloaliphatic diepoxide was used to prepare the thermosetting acrylic latex coatings. The epoxide was introduced into the latexes by three modes. In the first mode, the epoxide was added during the synthesis of latex. In the second mode, the epoxide was dissolved in the solvent, and then formulated into the latex. In the third mode, the epoxide was emulsified, and then formulated into the latex. All the latexes in this study had hydroxyl-functionalized cores and carboxyl-functionalized shells. The crosslink density, Tukon hardness, glass transition temperature, and morphology of latex coatings were evaluated as a function of cycloaliphatic diepoxide addition mode.

Experimental

1. Materials

All the materials were used without further purification. Methyl methacrylate (MMA), butyl acrylate (BA), methacrylic acid (MAA), 2-hydroxyethyl methacrylate (HEMA), ammonium persulfate, sodium bisulfite, and sodium bicarbonate were purchased from Aldrich. Ruthenium tetroxide (RuO_4) was purchased from Polyscience. Copper (II) sulfate was purchased from Mallinckrodt Baker. (Ethylenededinitrilo)-tetraacetic acid tetrasodium salt was purchased from EM Science. Cycloaliphatic diepoxide (UVR-6105) and surfactants (Triton-200 and Tergital-XJ) were supplied by Union Carbide Corporation. 2-sulfoethyl methacrylate (SEM) was provided by Hampshire Chemical Corporation.

2. Synthesis

Two types of latex was prepared as shown in Tables 1 and 2 by using the same procedure as previous study[11] except that the redox initiated polymerization was maintained at the higher temperature (40°C). Redox initiator was prepared with 0.44 g ammonium persulfate, 0.22 g EDTA, 0.22 g sodium bisulfite, and 0.03 g copper (II) sulfate.

3. Latex and Evaluation

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 nonionic surfactant (0.14 g) were dissolved in deionized water (11 g). Then the cycloaliphatic diepoxide (9 g) was slowly emulsified into water solution at 60°C. The epoxide (5 g) was dissolved in isopropanol (5 g). Then water was added dropwise to this stirring solution. The resulting epoxide emulsion or solution was added into the latex over 3 minutes. The

Table 1. Recipes for the synthesis of core latex (Tg=0°C)

Components	Functionality	Weight, g	Equivalent
BA	monomer	44.24	0.35
MMA	monomer	29.39	0.29
HEMA	hydroxyl monomer	16.38	0.12
Cycloaliphatic diepoxide	crosslinker	0 or 15.89	0 or 0.12
$NaHCO_3$	buffer	0.1	-
Triton-200	surfactant	3.2	-
Tergital-XJ	surfactant	0.8	-
Water	solvent	48	-

Table 2. Recipes for the synthesis of shell latex (Tg=0°C)

Components	Functionality	Weight, g	Equivalent
BA	monomer	51.31	0.40
MMA	monomer	27.69	0.28
MAA	carboxyl monomer	10.8	0.12
$NaHCO_3$	buffer	0.1	-
Triton-200	surfactant	3.2	-
Tergital-XJ	surfactant	0.8	-
Water	solvent	48	-
SEM	strong acid monomer catalyst	0.571	0.003

formulations were cast at 6 mils wet thickness on aluminum or glass substrate. After coalescence, the latex coatings were cured at 170 °C for 1h.

The films were prepared over aluminum and glass panels. The films over aluminum panels were tested for Tukon Hardness (ASTM D1474-85). After removing the films over glass panels with a razor blade, the Instron Universal Tester (Model 1000) was used to evaluate tensile properties. A crosshead speed of 2 mm/min was used to determine tensile modulus, tensile strength, and strain at break. Pneumatically actuated 1-inch grips with steel face were used for clamping the specimens. More than five samples were tested for each composition, and average values were reported. The test samples were about 8 cm long and 1.2 cm wide. The viscoelasticity of the latex as a function of temperature was recorded using a Dynamic Mechanical Thermal Analysis (DMTA, Rheometric Scientific). The films were cut into 10 mm x 30 mm. 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 morphology of the latex was determined by transmission electron microscopy (TEM) at CRSS-USDA Electron Spectroscopy Center, Fargo, ND. The core/shell latex was stained with ruthenium tetroxide (RuO_4) and phosphotungstic acid (PTA).

Results and Discussion

The objective of this study was to investigate the effect of introduction mode of crosslinker into latex on the structure and properties of the cured latex film. The thermosetting acrylic latexes were synthesized under monomer starved condition by using both thermal and redox initiators. Carboxyl functional groups and strong acid acrylate were located in the shell, and hydroxyl groups in the core. The glass transition temperature of both the core and shell were formulated to be the same (0°C) via the Fox equation.[1)] The epoxide was added into latex by using three introduction modes as has been noted. The preliminary study showed that, when all the epoxide (1:1 stoichiometric amount with the crosslinkable functionality) was added during the polymerization, the latex was unstable. Thus, two alternative approaches were taken. In the first approach, a latex with half of the epoxide incorporated within core during the polymerization was prepared (LAE). The rest of the epoxide was added into the latex by a solution or emulsion approach after the polymerization. In the second approach, no epoxide was introduced during the polymerization of latex (LA), and all the epoxide was introduced into the latex again via solution or emulsion. The films were cured, and the crosslinking was evaluated via hardness, tensile properties, and elastic moduli.

The Tukon hardness of latex coatings is shown in Figure 1. It was found that Tukon hardness of coatings based on LA increased with the introduction of epoxide. However, for LAE based coatings, an increase in Tukon hardness was observed with the introduction of epoxide solution, and not the emulsion approach. Also, the hardness values for latex films based on LAE were generally lower than the LA based latex systems. The maximum hardness value of coatings for both was attained using the solution approach.

The stress-strain behavior of latex coatings was determined and the results are shown in Figures 2, 3 and 4. The tensile modulus followed a similar trend as the Tukon hardness. The incorporation of epoxide improved tensile modulus of the cured films. The solution approach

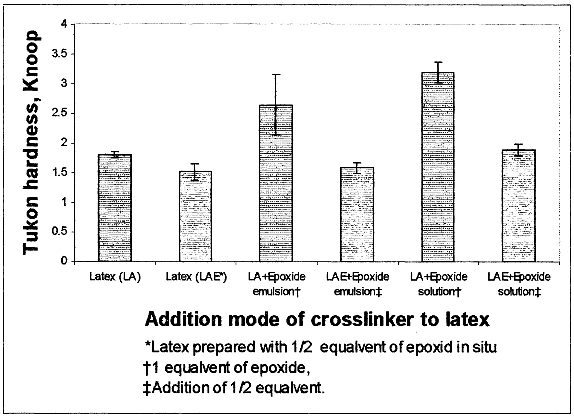

Figure 1. Tukon hardness of latex

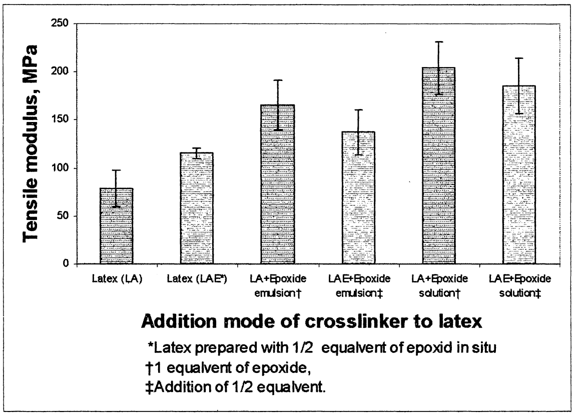

Figure 2. Tensile modulus of latex

appeared to provide a higher value in tensile modulus than emulsion approach. Unlike the tensile modulus, strain-at-break decreased with the introduction of epoxide and the solution approach seems to result in lowest elongation. The tensile strength data of coatings appeared to be independent of mode of crosslinker addition. This not surprising, since the tensile strength is more dependent on film defects than the tensile modulus.[19)]

The dynamic mechanical behavior of latex coatings is shown in Figures 5 and 6. It was found that, a rubbery plateau was observed for all the cured films with crosslinker, and the storage modulus was strongly dependent on the introduction mode of crosslinker into latex. The

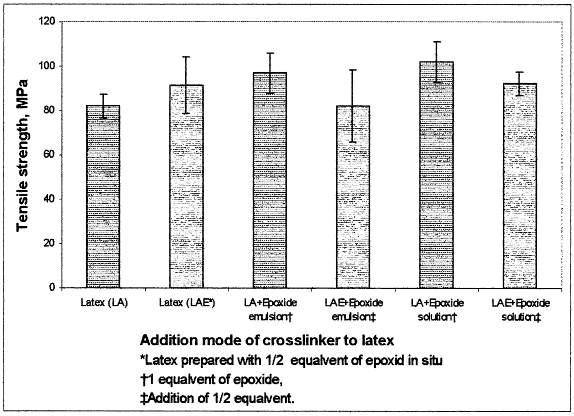

Figure 3. Strain-at-break of latex

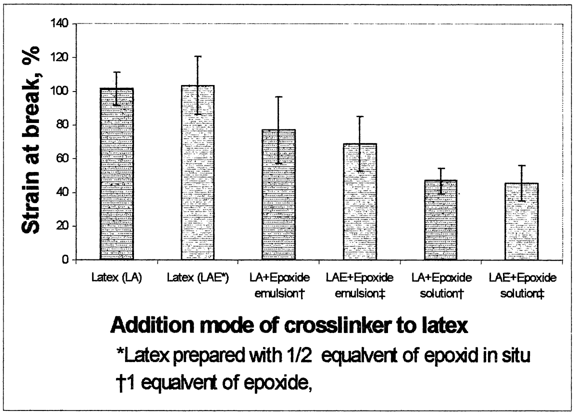

Figure 4. Tensile strength of latex

crosslinked plateau increased with the introduction of epoxide, and the solution approach provided a slightly higher crosslinked plateau than the emulsion approach for the same type of latex. When the solution approach was utilized to introduce the epoxide, the coatings based on LA exhibited higher elastic modulus (rubbery plateau) than the LAE based. The emulsion approach however did not provide a significant improvement for these two types of latex. In comparison, the elastic moduli appeared to be independent of mode of addition.

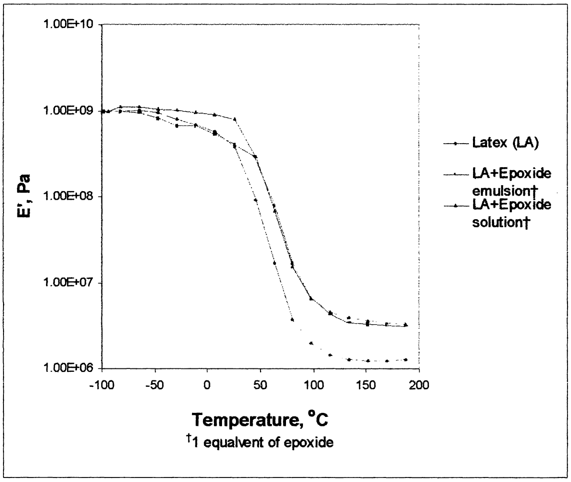

Figure 5. Storage modulus of coatings based on LA as a function of introduction mode of epoxide into latex

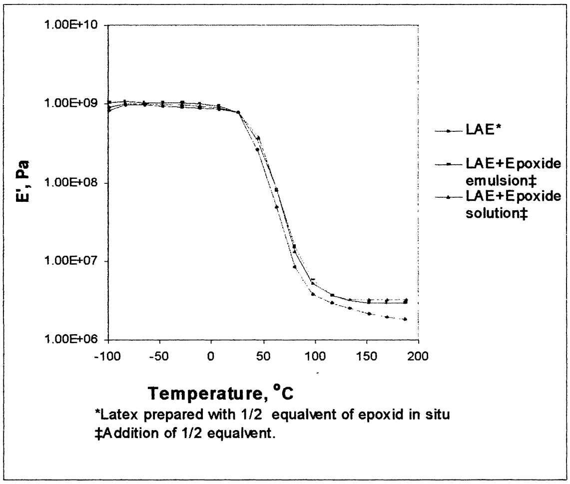

Figure 6. Storage modulus of coatings based on LAE as a function of introduction mode of epoxide into latex

Transition electron microscopy (TEM) was further utilized to study the effect of addition mode of crosslinker into latex on latex coating morphology. Figures 7 and 8 displays the TEM, latex with epoxide emulsion, and epoxide solution, respectively. It was found that the latex prepared by using the core-shell mode featured perfectly spherical structure. The large

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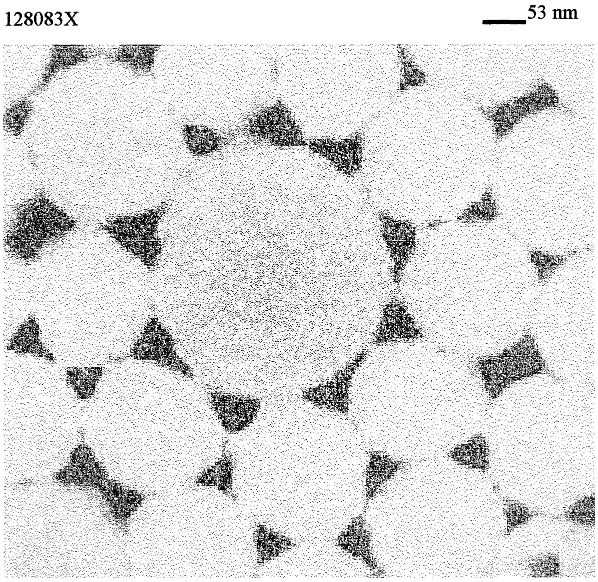

Figure 7. Uncured latex with epoxide emulsion

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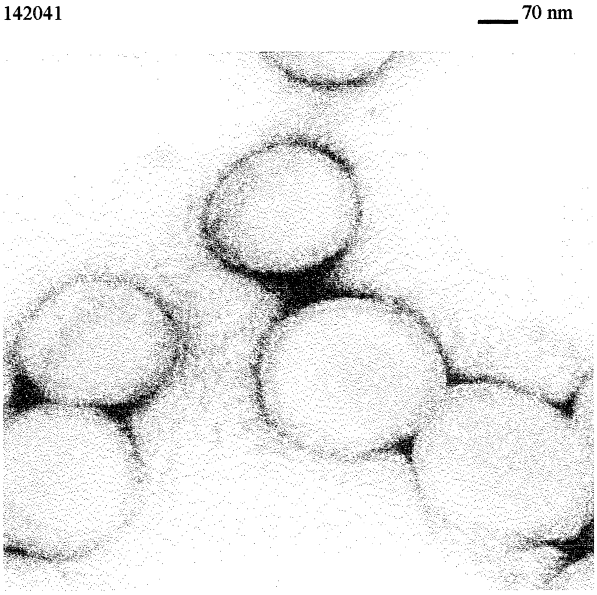

Figure 8. Uncured latex with epoxide solution

spherical particle for latex with epoxide emulsion is presumed to be the emulsified epoxide. The size of emulsified epoxide is in agreement with light scattering data. In contrast, the latex added with epoxide solution exhibited different surfacial morphology. It was postulated that the solvent and epoxide were adsorbed on the surface of latex particles, resulting in expanded shell (darker area).

This study demonstrated the dependence of mechanical properties of latex coatings on the introduction mode of cycloaliphatic diepoxide into latex (emulsion or solution approach). There were some differences in hardness, tensile properties, and dynamic properties between the two introduction modes of epoxide into latex. The hardness, and tensile modulus for the solution approach were generally higher than emulsion approach. Not surprisingly, the later yielded a higher elongation-at-break. These variations can be attributed to the influence of introduction mode on film formation process. The film formation is a competitive process of inter-diffusion and crosslinking. A very specific situation is expected for film prepared from latex coatings with high concentration of hydrophilic group (COOH). It forms a separate phase as membrane phase to inhibit or retard latex inter-diffusion, depending on acid concentration, and structure of latex.20-22) Moreover, the crosslinking of epoxide and functionality during the curing process can act as a barrier to limit the extent of polymer inter-diffusion and the crosslinking reaction. Inter-diffusion prior to crosslink is expected to provide a film with a uniform crosslink network, and consequently higher mechanical strength. If crosslinking occurs before inter-diffusion, the film has weaker mechanical strength.23) From TEM data, it was observed that, just before coalescence, emulsified epoxide was still isolated from latex particle. Whereas dissolved epoxide was adsorbed on the surface of latex particle. Accordingly, the distribution of dissolved epoxide in latex emulsion is presumed to be more random than epoxide emulsion, and therefore the film will form with a more uniform crosslink network. This is manifested by the hardness and tensile data.

Coatings based on LA and LAE had differences in Tukon hardness, and the tensile data. The tensile properties, and dynamic thermal mechanical properties rely on the bulk properties of film, and Tukon hardness is surface dominated. When the crosslinker was added during the core latex polymerization, the intra-particle crosslink is presumed to be dominant, thus the process results in a harder core, suppressing the film surface hardness. In addition, the intra-particle crosslink is prone to yield short dangling ends.12) When such ends cross the intra-particle boundaries, substantial entanglement cannot form. However, both intra-particle crosslink and inter-particle crosslink contribute to the overall crosslink density as shown in the elastic moduli data. The presence of inter-diffusion suppresses the difference between the crosslink mode especially for latexes with low glass transition temperatures as used in this study. Consequently, when the same amount of epoxide was included in both types of latex, the similar bulk properties (tensile properties and crosslink plateau height) were observed.

Conclusion

Core-shell carboxyl and hydroxyl functional acrylic latexes were crosslinked with a cycloaliphatic diepoxide. The introduction mode of the epoxide played an important role in the coatings performance. The epoxide can be introduced into the latex by either solution or emulsion approach. Generally, the former provides coatings with high hardness, and tensile modulus. This was attributed to a more homogenous crosslink network, resulting in more entanglement. When the epoxide was added during synthesis of the latex, a significant increase in Tukon hardness was observed.

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