Synthesis of Novel Reactive Coalescing Agents and Their Application in a Latex Coating

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ABSTRACT: The syntheses and the performance of five glycidyl compounds as novel reactive coalescing agents are presented. The reactive coalescing agents were synthesized with moderate yields, structures were verified using spectroscopic methods, and the properties of glycidyl compounds such as boiling points and evaporation rates were measured. The applicability of five glycidyl compounds as reactive coalescing agents was tested in characterized carboxyl functional latex. Properties like pendulum hardness, gloss, and efficiency of the glycidyl compound to reduce the minimum film-formation temperature (MFFT) of the latex were measured from the cured latex films. The application test results were compared to the commercial nonreactive coalescing agent, Nexcoat™ 795. The films with synthesized reactive coalescing agents with carboxyl functional latex were found to have good pendulum hardness and excellent gloss. Also, the efficiency of three glycidyl compounds in lowering the MFFT of the latex was competitive with the commercial coalescing agent. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 87: 610–615, 2003

INTRODUCTION

Increasing environmental concern and stricter regulations for volatile organic compound (VOC) emissions is also leading to changes in coatings technology and industry, because, by far, the majority of the coatings contain volatile compounds.[1,2] The volatile compounds are organic solvents, which primarily reduce the viscosity of the coating low enough for application. All these organic solvents evaporate during and after application, causing the risk of VOC emissions, which lead to serious health hazards and air-pollution problems by formation of toxic oxidants, especially ozone.[1–3] The coatings industry has responded to this challenge by replacing solvent-based coatings either with water-based or high-solids coatings. However, most coatings, including water-based coatings, still contain at least some VOCs, like coalescing agents, to facilitate the film formation.[1,4]

The coalescing agents have one of the most important roles in the film formation of water-based coatings.[2,4,5] They increase the easiness of latex particles to coalescence by softening the latex particles and lowering the minimum film-formation temperature (MFFT) of the latex. MFFT is the lowest temperature at which the latex film will form, and for success in the film formation, the film must be formed at or above the MFFT. The coalescing agents dissolve in the latex particles, allowing film formation at a lower temperature. Then, after the film has formed, the coalescing agents slowly diffuse to the surface of the film and then evaporate, causing the risk of VOC emissions. Thus, there is still a high demand to develop new nonvolatile coalescing agents to decrease the use of VOCs, even though VOC contents in the latex coatings are well below the current limits.

Reactive functional groups on latex, such as carboxyl groups, are favorable, because they enable the latex to participate in various reactions and thus increase the crosslinking of the latex films. Increase of film crosslinking will improve latex film properties such as chemical resistance, adhesion, flexibility, and durability.[6,7] For example, epoxy silanes have been found to be effective additives as crosslinkers with carboxy and amino functional latexes. Additionally, they reduce the VOC emissions since these silanes may act as reactive diluents to reduce the MFFT of the latex while maintaining performance of the cured film. Also, mono- and diglycidyl ethers have shown promising results as reactive diluents in epoxy curing systems.[8,9]

To increase the solids and crosslinking of a latex film and to reduce VOCs, this article presents a promising approach where the traditional nonreactive coalescing agent is replaced with reactive coalescing agents, which contain one to three epoxide sites. Such additives are low molecular weight materials where the epoxide group enables the reaction with the latex
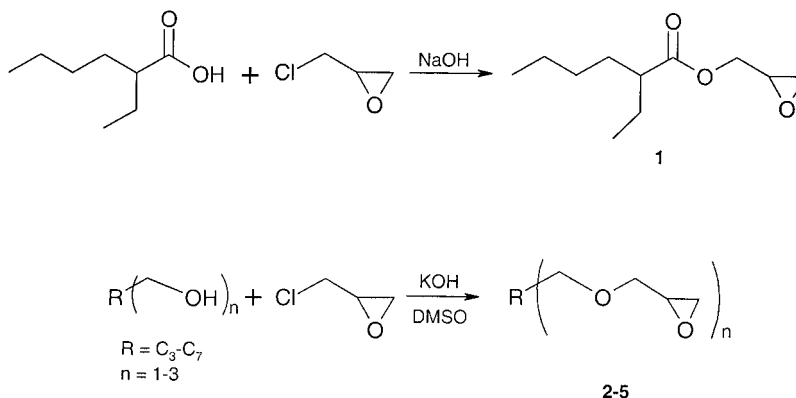
Scheme 1

polymers and thus the reactive coalescing agents become a part of the film, increasing, simultaneously, the solid content of the film. This unique structure allows the reduction of the VOC content in water-borne coatings while still maintaining proper film properties.

In this article, the synthesis and characterization of five glycidyl esters or ethers **1–5** are presented (Schemes 1 and 2) and application tests of these reactive coalescing agents with the characterized carboxyl functional latex were performed. One way to demonstrate the efficiency of a coalescing agent is to measure its ability to lower the MFFT of the latex, that is, its plasticizing efficiency, which correlates the compatibility of the coalescent agent with the resin.[5,10] The lower the MFFT, the better the film formation. The evaporation rates, MFFTs, and the development of hardness and gloss of the latex films are presented, because they are important criteria in selecting a proper coalescing agent. One traditional and commercial non-reactive coalescing agent, 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate, Nexcoat™ 795, was included in application tests for reference (Nexcoat™ 795 is a registered trademark of Neste Chemicals, Finland).

EXPERIMENTAL

Materials

2-Ethylhexanoic acid (Fluka), 2-ethylhexanol (Aldrich), 1-octanol (Merck), 2,2-dimethyl-1,3-propanediol (Neste Oxo Ab), 1,1,1-trihydroxymethylpropane (Neste Oxo Ab), 1-chloro-2,3-epoxypropane (Fluka), DMSO (Lab Scan), and toluene (Lab Scan) were used without further purification. The commercial latex, which was used in the application tests, was characterized by NMR spectroscopy for monomer composition; the relative composition is 30% 2-ethylhexyl acrylate, 60% styrene, 7% vinyl acetate, and 3% acrylic acid.[11] The solids by weight of the latex is 46%, the MFFT is 15.5°C, and the acid number of the latex is 54 mg KOHg^{-1}.

Measurements and film preparation

The structures of the synthesized coalescing agents were verified using spectroscopic methods. ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker Avance DRX 500 FT NMR spectrometer in CDCl$_3$. Infrared spectra were recorded using a Perkin–Elmer System
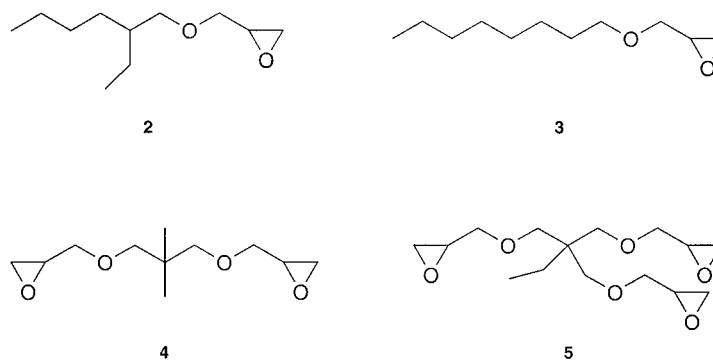
Scheme 2

TABLE I
Properties of the Coalescing Agents

Coalescing agent	Bp (°C)	Evaporation rate[a]
1	242–246	0.002
2	221	0.005
3	255	0.002
4	275	0.0004
5	160/0.04 mmHg[13]	<0.00001
Nexcoat™ 795	254	0.002

[a] Relative to *n*-butyl acetate $\approx$ 1.

2000 Fourier transform infrared (FTIR) spectrometer (100 scans, 2-cm^{-1} resolution). Electrospray mass spectra were performed on a Micromass LCT mass spectrometer. The evaporation rates were measured with an electronic Precisa 205 A SCS balance, which records the weight loss of the sample as a function of time. Rates determined in this way are called volume-based relative evaporation rates, where the evaporation rate of other solvents are related to the evaporation rate of *n*-butyl acetate, which is defined as 1.[3] The boiling points of the synthesized coalescing agents, except **5**, were measured by a Mettler DSC-30S calorimeter. The pendulum hardness of the films was measured with a BYK Gardner König pendulum hardness tester according to the ASTM D 4366 method from the glass plates, where the film thickness was 150 μm. The time of oscillation from a 6° deviation to 3° is presented in seconds. The MFFT was determined by a Coesfeld gradient plate-thermostair according to the ASTM 2354/86 method and the film thickness was 300 μm. The acid number of the carboxyl-functional latex was determined by the titrimetric method according to the ASTM D 803-82 method. The gloss values at angle 20° and 60° were measured from the coated chess plates 1 week after the application with a BYK Gardner micro-TRI-gloss reflectometer according to

the ASTM E 284 method. Film thickness on the chess plates was 150 μm.

The coated glass and chess plates were stored at a constant temperature of 23 ± 2°C and a relative humidity of 50 ± 5%. The evaporation rates were also measured in these constant conditions.

Synthesis of reactive coalescing agents

The synthesis of **1** was reported recently.[12] All glycidyl ethers **2–5** (Scheme 2) were made with a modified literature synthetic procedure such as the following recipe for the preparation of 1,2-epoxy-3-(2-ethylhexyloxy)propane (**2**) (Scheme 1)[13]:

Powdered KOH (60.24 g, 1.07 mol) was added to a mixture of 2-ethylhexanol (84.8 mL, 0.54 mol) and DMSO (100 mL). The reaction mixture was stirred at 45°C for 1 h. The solution was cooled to room temperature and 1-chloro-2,3-epoxypropane (126.9 mL, 1.62 mol) was added dropwise into the reaction mixture, keeping the temperature under 35°C for 2 h. The reaction mixture was stirred at 25–30°C for 72 h. The formed salt was filtered and washed with CH$_2$Cl$_2$ (600 mL). The filtrate was evaporated and the residual mixture was extracted twice with brine (2 × 100 mL) and ether (2 × 300 mL). The organic layers were combined and then dried with MgSO$_4$ and the solvent was removed under reduced pressure. The product was distilled under reduced pressure to give 50.34 g (50.3%) of **2**.

δ_H (500.13 MHz, CDCl$_3$): 0.84–0.88 (m, 6H), 1.24–1.37 (m, 8H), 1.48–1.50 (m, IH), 2.57 and 2.76 (2×AB-q, 2H), 3.09–3.12 (m, 1H), 3.30–3.39 (m, 2H) 3.35 and 3.66 (2×AB-q, 2H); δ_C (125.76 MHz, CDCl$_3$): 10.97, 13.99, 23.00, 23.77, 29.05, 30.47, 30.48, 39.68, 44.17, 50.89, 71.58, 71.59, 74.45 (**2** has two chiral carbon atoms, and due to that, one CH$_3$R and three CH$_2$R groups are
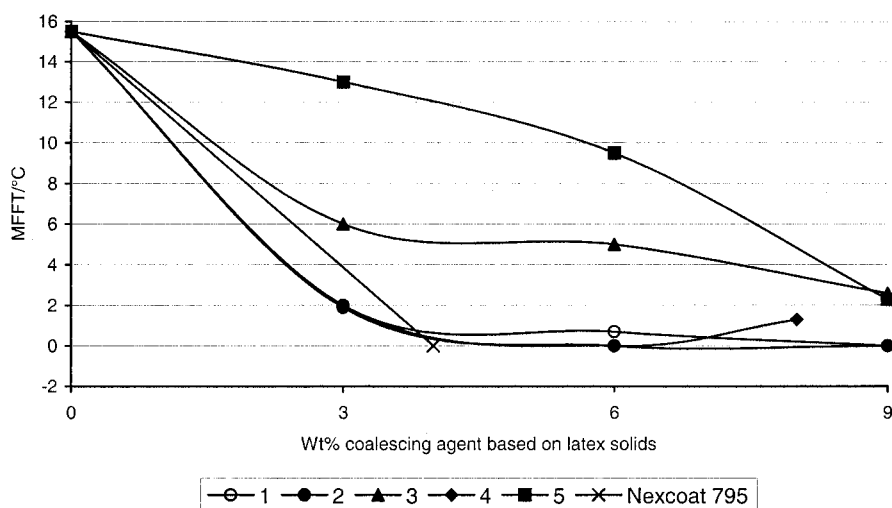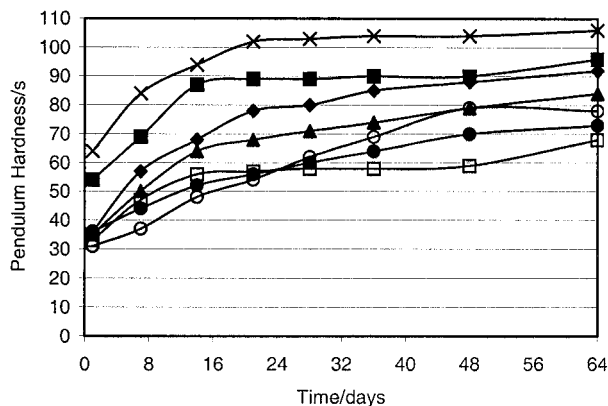

Figure 1 MFFT of (○) **1**, (●) **2**, (▲) **3**, (◆) **4**, (■) **5**, and (×) Nexcoat™ 795 with the latex.

Figure 2 Pendulum hardness development with 3 wt % of (○) **1**, (●) **2**, (▲) **3**, (◆) **4**, (■) **5** and (□) 4 wt % of Nexcoat™ 795 and (×) pure latex.

diastereotopic and they appear as doublets in the ^{13}C spectrum. This is a typical property for a CH_2R moiety in the vicinity of a chiral center.)[14] The IR spectrum shows the typical absorption, ν_{max} (liquid film/cm^{-1}): 1102 (C—O), and for ESI–MS, $m/z = 209.2$ [M + Na]$^+$, $C_{11}H_{22}O_2$ (186.29).

1,2-Epoxy-3-(octyloxy)propane (**3**): yield 32.3%. The procedure used was as for **2**, using 1-octanol as the starting material.

δ_H (500.13 MHz, CDCl$_3$): 0.87 (t, 3H), 1.26–1.34 (m, 10H), 1.54–1.60 (m, 2H), 2.59 and 2.77 (2×AB-q, 2H), 3.11–3.14 (m, 1H), 3.37 and 3.68 (2×AB-q, 2H), 3.42–3.51 (m, 2H); δ_C (125.76 MHz, CDCl$_3$): 14.01, 22.60, 26.05, 29.20, 29.39, 29.67, 31.78, 44.28, 50.85, 71.42, 71.70. The IR spectrum shows the typical absorption, ν_{max} (liquid film/cm^{-1}): 1111 (C—O), and for ESI–MS, $m/z = 209.2$ [M + Na]$^+$, $C_{11}H_{22}O_2$(186.29).

2,2-Dimethyl-3-(methoxyoxiranyl)propanol (**4**): yield 27.1%. The procedure used was as for **2,** using 2,2-di-methyl-1,3-propanediol as the starting material.

δ_H (500.13 MHz, CDCl$_3$): 0.86 (s, 6H), 2.54 and 2.72 (2×AB-q, 4H), 3.05–3.08 (m, 2H), 3.18–3.24 (m, 4H), 3.33 and 3.65 (2×AB-q, 4H); δ_C (125.76 MHz, CDCl$_3$): 21.93, 36.30, 43.99, 50.80, 71.82, 71.84, 77.17? The IR spectrum shows the typical absorption, ν_{max} (liquid film/cm^{-1}): 1102 (C—O), and for ESI–MS, $m/z = 239.2$ [M + Na]$^+$, $C_{11}H_{20}O_4$ (216.28).

2-Ethyl-2-(methoxymethyloxiranyl)-1,3-bis(meth-oxyoxiranyl)propane (**5**): yield 3.1%. The procedure used was as for **2**, using 1,1,1-trihydroxymethylpro-pane as the starting material.

δ_H (500.13 MHz, CDCl$_3$): 0.72–0.76 (m, 3H), 1.23–1.32 (m, 2H), 2.45–2.50 (m, 3H) 2.63–2.67 (m, 3H), 2.97–3.03 (m, 3H), 3.20–3.65 (m, 12H); δ_C (125.76 MHz, CDCl$_3$): 7.24, 7.31, 22.56, 43.10, 43.14, 43.68, 43.73, 43.80, 50.50, 71.22, 71.65, 71.67, 71.69. The IR spectrum shows the typical absorption, ν_{max} (liquid film/cm^{-1}): 1099 (C–O), and for ESI–MS, $m/z = 325.2$ [M + Na]$^+$, $C_{15}H_{26}O_6$(302.36).

RESULTS AND DISCUSSION

The syntheses of glycidyl compounds **1–5** proceeded smoothly with reasonable yields, except **5,** where the poor yield probably is due to steric hindrance. The structures of **1–5** were verified by the spectroscopic measurements. The carboxyl functional latex, which was used in the application tests, is commonly used in water-based coatings with the addition of coalescing agents.

Evaporation rate and boiling point

The evaporation rate of the pure coalescing agent correlates with the rate at which the coating dries.[5] It is important that the evaporation rate of the coalescing agent is slower than with water. After the evaporation of water, the coalescing agent softens the latex parti-cles, enabling them to fuse into a continuous film. The evaporation rates of **1–5** and boiling points of **1–4** were measured and the values of Nexcoat™ 795 were obtained from the supplier (Table I). The evaporation rates of **1–5** are relatively slow, and in the case of **4** and **5**, they evaporate slower than does Nexcoat™ 795. It is important for **1–5** that they are retained in the latex film and start to react with the latex polymers.

The boiling points of **1–5** are comparatively high or equivalent to the currently used coalescing agents in high solids and latex paints.[15–17] The boiling points of **3–5** are over 250°C, which is one of the criteria for non-VOC compounds.[18]

Minimum film-formation temperature

The ability of the coalescent agent to lower the MFFT generally leads to better film properties, that is, film integrity, strength, and smoothness of the film.[19] The lower the MFFT at a specific coalescent level, the more effective or more efficient the coalescent is in plasti-cizing that particular latex.[5,10]
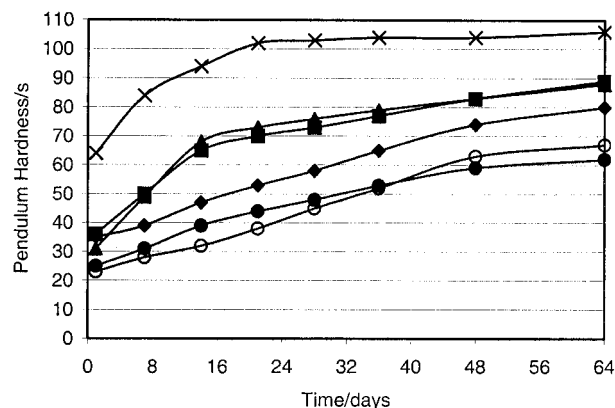
Figure 3 Pendulum hardness development with 6 wt % of (○) **1**, (●) **2**, (▲) **3**, (◆) **4**, (■) **5** and (□) 4 wt % of Nexcoat™ 795 and (×) pure latex.

The effectiveness of **1–5** to lower the MFFT of the latex was measured and the results were compared to the results with Nexcoat[TM] 795. The MFFT curves of **1–5** and Nexcoat[TM] 795 with the latex can be seen in Figure 1. The ability of **1, 2,** or **4** to lower the MFFT of the latex is better than with Nexcoat[TM] 795, when 3 wt % of the coalescent is used. The MFFT value of the latex is under 1°C when the level of **1, 2, 4,** or Nexcoat[TM] 795 is about 4 wt %, while the level of **3** or **5** has to be over 9 wt % to reach this value. So, the effectiveness of **1, 2,** or **4** to lower the MFFT of the latex is better than that of **3** or **5**.

Pendulum hardness development

Pendulum hardness correlates with an intender performing a reciprocating rolling motion on a horizontal coating.[20] The film hardness development correlates directly with the evaporation rate of water and coalescing agents,[5] with the reactivity of coalescing agents with the carboxyl functional latex and with crosslinking of the latex film. The results of the hardness development rates give an excellent view of how **1–5** affect drying.

The hardness development of the latex film was measured as a function of the drying time during 1–64 days with and without coalescing agents. The studied coated films contained 3–9% by weight, relative to the latex solids, of **1–5** or Nexcoat[TM] 795 as a reference. The latex film is quite hard without coalescing agents, because of the high portion of styrene and vinyl acetate monomers in the latex, which are classified as hard monomers.[21] The presence of coalescing agents during the film formation leads to plasticization of the coated films, in all cases. However, the change in the final hardness value is not dramatic. The hardness development curves with coalescing agents are shown in Figures 2–4.
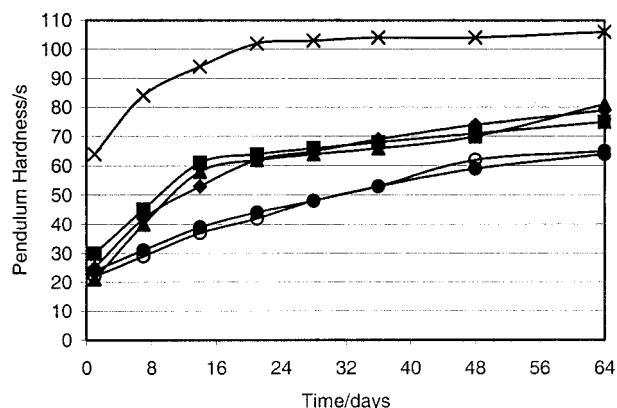

Figure 4 Pendulum hardness development with 9 wt % of (○) **1**, (●) **2**, (▲) **3**, (◆) **4**, (■) **5** and (□) 4 wt % of Nexcoat[TM] 795 and (×) pure latex.

TABLE II
Gloss 20° and 60° Values of the Films with the Latex

Sample	Gloss 20°	Gloss 60°
3 wt % of **1**	82.4	98.2
6 wt % of **1**	83.9	98.0
9 wt % of **1**	85.8	97.8
3 wt % of **2**	86.0	97.5
6 wt % of **2**	86.4	98.0
9 wt % of **2**	84.2	97.4
3 wt % of **3**	82.4	98.6
6 wt % of **3**	83.4	98.1
9 wt % of **3**	85.6	97.8
3 wt % of **4**	81.0	97.7
6 wt % of **4**	85.3	96.8
3 wt % of **5**	84.4	97.9
6 wt % of **5**	85.5	97.9
9 wt % of **5**	87.2	96.4
Pure latex	78.7	94.2
4 wt % of Nexcoat[TM] 795	—	98.6

The films with 3 wt % of **1–5** are harder than with 4 wt % of Nexcoat[TM] 795. The hardest films with 3–9 wt % of coalescing agents are formed with **3, 4,** or **5, 1** and **2** plastize the latex film more effectively than do the other studied reactive coalescing agents, which is due to their better ability to lower the MFFT of the latex, as also mentioned previously.

Gloss values

The gloss values at 20° and 60° were measured 1 week after the application of the mixture of the latex and coalescing agent to the chess plates. The studied coated chess plates contained 3–9% by weight, relative to the latex solids, of reactive coalescing agents. As a reference material, 4 wt % of Nexcoat[TM] 795 was used. The gloss values of the films are summarized in Table II. All coated films formed very high gloss and transparent films and the gloss values improved with different amounts of **1–5**, compared to the values of the latex without coalescing agents.

CONCLUSIONS

The glycidyl compounds **1–5** are readily synthesized in reasonable yields and the structures were verified by spectroscopic methods. The film properties of the studied latex with **1–5** are comparable to the coatings formulated with the commercial nonreactive coalescing agent, Nexcoat[TM] 795. The efficiency in lowering the MFFT of the latex, especially with **1,2,** and **4,** are competitive with the commonly used coalescing agent, Nexcoat[TM] 795. Thus, the unique structure and

suitability of **1–5** to act as a coalescing agent with the carboxyl functional latex indicates that they are excellent alternatives to be used as reactive coalescing agents in the water-based coatings.

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