

Synthesis of reactive diluents for cationic cycloaliphatic epoxide UV coatings

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Abstract

Reactive diluents for cationic cycloaliphatic epoxide UV coatings were synthesized using caprolactone polyols and tetraethyl orthosilicate (TEOS). The structures of the TEOS functionalized polyols were characterized using IR, ¹H-NMR, ²⁹Si-NMR, and ESI-FTMS spectroscopy. The resulting siloxane functionalized polyols were used to formulate cationic UV coatings with 3, 4-epoxycyclohexylmethyl-3, 4-epoxycyclohexane carboxylate (a cycloaliphatic diepoxide). The crosslinking reactions were monitored using IR and ²⁹Si-NMR spectroscopy. The cured films were evaluated in terms of tensile properties and glass transition temperature. The resultant coatings showed greater tensile modulus, lower elongation, and higher glass transition temperature. In addition, the siloxane functionalized polyols also effectively reduced the viscosity of the coatings formulations. Based on the curing behaviors and spectroscopic data, possible crosslinking reaction(s) were postulated. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Cationic ultraviolet (UV) coatings; Reactive diluent; Tetraethyl orthosilicate

1. Introduction

The implementation of the 1990 Clean Air Act (CAA) has had a major effect on the coatings industry in terms of reducing Volatile Organic Compounds (VOCs). Ultraviolet (UV) curing coatings have emerged as one of the efficient vehicles to challenge the VOC limits in organic coatings [1, 2]. In addition, UV coatings also offer the advantages of fast curing speed, high energy efficiency, and low capital investment and space requirement [3]. These coatings are especially suitable for the wood (furniture) or plastics coating, metal decorating, and paper printing industries. This is a consequence of an ambient temperature cure [4]. There are two principle mechanisms in which the UV coatings polymerize on the substrates, free radical and cationic [5].

In free radical initiated polymerization, free radicals are generated using either unimolecular photoinitiators (benzoylketals) or bimolecular photoinitiators (thioxanthones) [6]. Multi-functional acrylate esters are used with acrylate functionalized oligomers to form highly cross-linked films. The functionality of the monomers can range from one to six functionality. To balance the reactivity and

overall performance, a mixture of mono, di, and tri/higher functional monomers are commonly used [7–9]. Free radical polymerization, however, exhibits oxygen inhibition of propagating radicals. In addition, acrylate monomers also represent odor problems, and more importantly, health hazards [10].

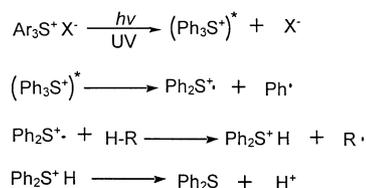
For cationic UV polymerization, typical initiators are triarylsulfonium, diaryliodonium, and aryldiazonium salts [11]. Of the three, aryldiazonium salts are less widely used because of low thermal-stability, and evolution of nitrogen during the photolysis [12]. The initiating species are protons of the super-acids which are generated from the photolysis of the salts under UV irradiation [13–15]. Both homolytic and heterolytic cleavage mechanisms are involved in the formation of the super-acids as shown in Scheme 1 [12–16]. In addition to the formation of the cationic species, free radicals are also generated. The free radicals have sufficient energy to initiate free radical polymerization of acrylate monomers or oligomers [17]. As a result, acrylate monomers can be incorporated into the formulations to form hybrid coating systems.

Typical monomers/oligomers for the cationic coatings are vinyl ethers, propenyl ethers, or epoxide-group-containing compounds [18]. Vinyl ethers readily polymerize and exhibit fast cure speed under cationic conditions. Propenyl ethers are more sterically hindered than vinyl ethers, and

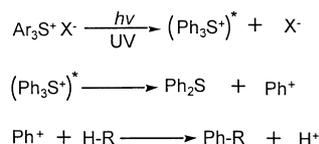
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1) Homolysis Mechanism:

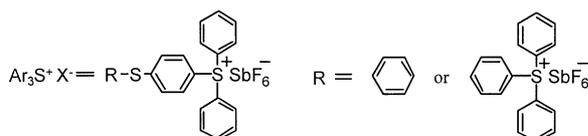


2) Heterolysis Mechanism:



where:

H-R = a proton donor compound



Scheme 1. Photolysis mechanisms of triarylsulfonium salts under UV light.

consequently show a slower cure response than vinyl ethers [19,20]. Epoxides, especially cycloaliphatic epoxides, are one of the major vehicles for cationic UV coatings [16]. In addition to homopolymerization, cycloaliphatic epoxides can also react with a number of active proton-containing compounds such as hydroxyl or carboxyl-group-containing compounds [21,22]. Thus, in comparison with vinyl ethers based coatings, cycloaliphatic epoxide UV coatings offer a wider formulation latitude which allows the formulator wide flexibility in controlling the mechanical properties.

Cycloaliphatic epoxide coatings offer excellent weatherability; and mechanical and electrical insulating properties [23–25]. As a result, cycloaliphatic epoxide coatings have been developed for many applications. Examples of these applications are barrier coatings for polyolefins substrates, protective coatings for can ends, and conformal coatings for the electronics industry [21–26]. Unfortunately, the homopolymerization of cycloaliphatic epoxides typically results in coatings which are brittle and have low-impact resistance [17]. As a consequence, flexible polyols, such as caprolactone polyols, are used to improve the toughness of the overall coatings. Under cationic conditions, the epoxide rings can react with the flexible polyols via copolymerization (chain transfer mechanism) or react with itself via homopolymerization as shown in Scheme 2 [16,17].

To formulate UV coatings suitable for applications, the viscosity of the coatings must be adjusted by using reactive diluents. Reactive diluents have two requirements. One is to function as solvents to reduce the overall viscosity of the coating formulations. The second function is to co-react with monomers or oligomers to form homogeneous films

[27]. As a consequence, reactive diluents usually are low molecular weight compounds containing multiple reactive functionalities. In addition, the ideal reactive diluents also are characterized by low toxicity, low volatility, low odor, and compatible solubility [28].

The goal of this study is to develop new reactive diluents for cationic cycloaliphatic epoxide UV coatings. Caprolactone polyols and tetraethyl orthosilicate were used to synthesize siloxane functionalized reactive diluents. The resulting products were characterized via IR, NMR, and ESI-TFMS. Using these reactive diluents, a series of cationic UV coatings was formulated with a cycloaliphatic diepoxide. The formulations were evaluated in terms of viscosity. The cured films were evaluated in terms of glass transition temperature (T_g) and tensile properties. The cross-linking reactions were also investigated spectroscopically, and the results are also reported herein.

2. Experimental

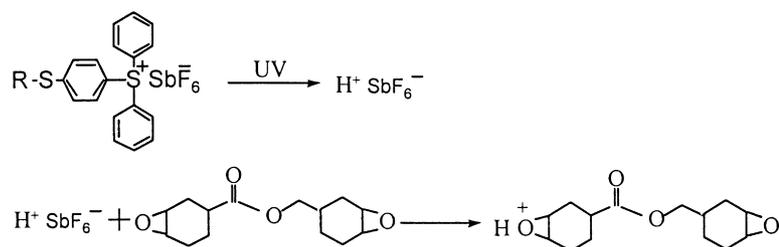
2.1. Materials

Caprolactone polyols (Tone 0201; $\bar{M}_n = 530$, and Tone 0305; $\bar{M}_n = 540$), cycloaliphatic diepoxide (UVR-6105), triarylsulfonium hexafluoroantimonates (UVI-6974) were provided by Union Carbide Corporation. Surface agent (L-7604) was provided by Witco Corporation. Caprolactone polyols were dried and stored with molecular sieves (4 Å). Tetraethyl orthosilicate (TEOS, 98%) and xylene (99%) were purchased from Aldrich. Xylene was purified according to a standard method [29]. Aluminum panels were purchased from Q-Panel Lab Products. All the materials were used as received except where described.

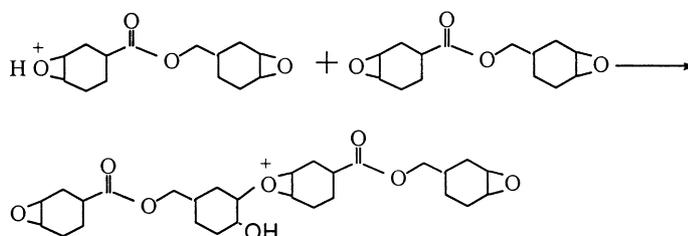
2.2. Instrumentation

A Nicolet Magna-IR 850 Series II spectrometer was used to record IR spectra. The IR spectra were obtained by coating thin liquid samples onto KBr crystals, and then exposing the crystals to UV light. A JEOL GSXFT 270 MHz was used to record $^1\text{H-NMR}$ and $^{29}\text{Si-NMR}$ spectra for all the compounds. $^1\text{H-NMR}$ spectra were obtained in CDCl_3 with chemical shifts (δ) referenced to internal tetramethylsilane. The $^{29}\text{Si-NMR}$ spectra were obtained in CDCl_3 with chemical shifts (δ) referenced to tetramethylsilane. The silicon element analysis was performed by Galbraith Laboratories. The molecular weight of the samples was determined at DuPont's Marshall Research and Development Laboratory. Electron Spray Ionization-Fourier Transform Mass Spectroscopy (ESI-FTMS) with sodium ionization of desorbed species (Na^+IDS) was performed on a Finnigan 4615B quadrupole mass spectrometer. Instron Universal Tester (Model 1000) was used to measure the tensile properties of the cured coatings. Pull-off adhesion tester (Elcometer, Model 106) was used to evaluate the adhesion of the coatings to aluminum substrates. Differential Scanning

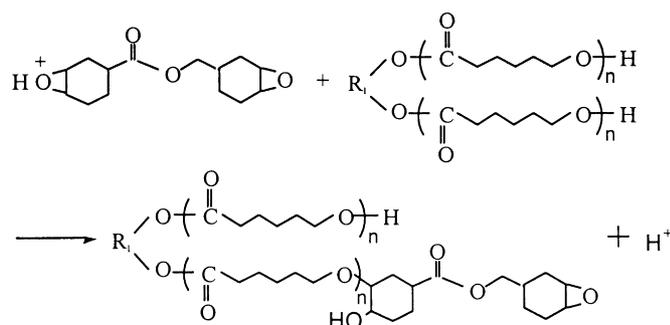
a) Photoinitiation:



b) Homopolymerization:



c) Copolymerization:



Scheme 2. Photolytically initiated homopolymerization & copolymerization of cycloaliphatic epoxide.

Calorimeter (DSC, Perkin Elmer Model 7) was used to obtain the glass transition temperatures of the coatings.

2.3. Preparation of di-TEOS functionalized polyol

The caprolactone diol 0201 (78 g, 73 mL, 0.15 mol) was added into a three neck round bottom flask (500 mL). The flask was equipped with a mechanical stirrer (50 rpm), a reflux condenser connected to a Barrett receiver, and a guard-tube containing calcium sulfate drier. The polyol was purged with dry nitrogen at 60°C for 2 h. Then, the flask was cooled to the room temperature. Tetraethyl orthosilicate (93.6 g, 100 mL, 0.45 mol), xylene (19 g, 20 mL, 0.16 mol), and dibutyltin dilaurate (0.6 g, 0.56 mL, 9.5×10^{-4} mol) were transferred into the flask using syringes. The mixture was allowed to react at the refluxing temperature (133°C–135°C) for 3–4 h. After the reaction was complete, the solvent and excess tetraethyl orthosilicate

were removed in vacuo, and the resultant product was stored in a nitrogen purged bottle: FT-IR (KBr pellet) 2974 (CH₃, asym), 2938 (CH₂, asym), 2885 (CH₂, sym), 1738 (C=O), 1165, 1103, 1078 (Si–O–C, asym), 968 (Si–O), 792 (Si–O–C, sym) cm⁻¹; ¹H-NMR (CDCl₃) δ 1.12–1.18 (CH₃), 3.72–3.81 (CH₂); ²⁹Si-NMR (CDCl₃) δ – 81.65, – 81.68; Element analysis di-TEOS functionalized caprolactone diol Calcd for Si: 6.58 wt.%. Found for Si: 6.02 wt.%; ESI-FTMS 909, 1023, 1137, 1251.

2.4. Preparation of tri-TEOS functionalized polyol

Similar to the caprolactone diol, the caprolactone triol 0305 (78 g, 73 mL, 0.14 mol) was added into a round bottom flask (500 mL) equipped with a mechanical stirrer (50 rpm) and a reflux condenser. The polyol was purged with anhydrous nitrogen at 60°C for 2 h. The flask was then cooled to room temperature. Tetraethyl orthosilicate

Table 1
Formulations of the di or tri-TEOS functionalized polyol/epoxide coatings

Concentration of the di or tri-TEOS polyol, wt. %	0	20	30	40	50
Di or tri-TEOS polyol, g	0.0	2.0	3.0	4.0	5.0
Cycloaliphatic diepoxide, g	10.0	8.0	7.0	6.0	5.0

(117 g, 125 mL, 0.56 mol), xylene (19 g, 20 mL, 0.16 mol), and dibutyltin dilaurate (0.7 g, 0.65 mL, 1.1×10^{-3} mol) were transferred into the flask using syringes. The mixture was allowed to reflux (133°C–135°C) for 3–4 h. After the completion of the reaction, the solvent and excess tetraethyl orthosilicate were removed in vacuo, and the resultant product was characterized without further purification: FT-IR (KBr pellet) 2974 (CH₃, asym), 2938 (CH₂, asym), 2885 (CH₂, sym), 1736 (C=O), 1167, 1099, 1074 (Si–O–C, asym), 966 (Si–O), 794 (Si–O–C, sym) cm⁻¹; ¹H-NMR (CDCl₃) δ 1.04–1.15 (CH₃), 3.65–3.78 (CH₂); ²⁹Si-NMR (CDCl₃) δ – 81.52, – 81.55, – 81.67; Element analysis tri-TEOS functionalized caprolactone triol Calcd for Si: 8.21 wt.%. Found for Si: 7.73 wt.%; ESI-FTMS 1099, 1213, 1327, 1418.

2.5. Coatings formulations and film property tests

The caprolactone diol or triol/cycloaliphatic diepoxide coatings were formulated with UVR-6105 (50–100 phr) with caprolactone diol or triol (0–50 wt. %). The photoinitiator (UVI-6974, phr. %) and surface wetting agent (SILWET L-7604, 0.5 phr) were concurrently added to the coating formulations. In addition, the di or tri-TEOS functionalized caprolactone polyols were also formulated with the photoinitiator (UVI-6974, phr. %) and the surface wetting agent (SILWET L-7604, 0.5 phr). The resultant non-functionalized polyol/epoxide and the TEOS functionalized polyol coatings were used as a control study for the siloxane functionalized base coatings. The di or tri-TEOS functionalized caprolactone polyol was used to formulate UV coatings with cycloaliphatic diepoxide as shown in Table 1. The concentration of the photo-initiator (UVI-6974) and the additive (SILWET L-7604) were kept constant at the same concentrations used in the control study. In addition, the viscosity of the polyols, the TEOS functionalized polyols, and the UV coatings were measured using a Brookfield viscometer (RVT-Wells).

All the coatings were cast on aluminum panels or glass plates using a wire wound rod (No. 16), and cured in a UV Processor (RPC, 2 × 300 W/in medium pressure mercury UV lamps, and 50 fpm). The film properties were measured 24 h after UV irradiation. The tensile properties were measured according to ASTM D2370-82. The free film samples (removed from substrates using a razor blade) were cut 15 mm wide and 100 mm long using a razor blade. The film thickness was measured using a Fowler Thickness Gage (precision 0.01 mm). The jaw separation

was fixed at 40 mm. The tensile testing was performed at a strain rate of 20 mm/min and at an ambient temperature. Five measurements were obtained for each sample and the average values were reported. When the error was less than 10%, it was no longer possible to report the uncertainty graphically. The DSC measurements were performed using 12–15 mg (films), and the samples were heated at 10°C/min from – 50°C to 120°C.

2.6. Spectroscopic investigation of the crosslinking reactions

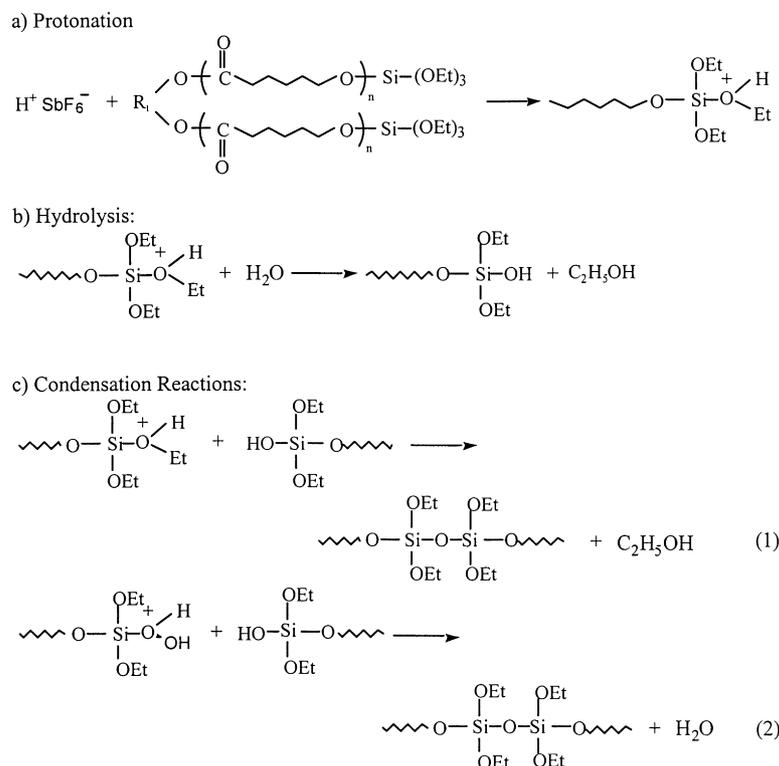
To elucidate the crosslinking reactions of the TEOS functionalized polyols, the di- or tri-TEOS functionalized polyol was formulated with or without the cycloaliphatic diepoxide. The crosslinking reactions of the coatings were monitored using IR and ²⁹Si-NMR. The coating formulation used for the IR spectroscopy consisted of 40 phr di-TEOS functionalized polyol and 60 phr cycloaliphatic diepoxide, and the coating formulation for the ²⁹Si-NMR consisted of 40 phr di- or tri-TEOS functionalized polyol and 60 phr cycloaliphatic diepoxide. The coatings were coated on KBr plates (thin film). After UV exposure, the IR spectra were recorded at a desired time interval. During the interval, the coated KBr plates were stored in a dark dry box. The ²⁹Si-NMR spectra of the coatings were obtained on the coating formulations after UV exposure.

3. Results

Siloxane groups are widely used in coatings as versatile modifiers or as additives to improve interfacial properties such as wetting, spreading, and adhesion [30,31]. Under acidic conditions, siloxane groups can react with water to afford silanol groups which can then condense to form siloxane crosslinks as shown in Scheme 3 [32]. The siloxane addition reaction with epoxy was previously reported in the Epoxy/Silanol/Curing/ Acrylic coating systems known as ESCA coatings [33–35]. The viscosity of a compound is primarily determined by the molecular weight and the interaction of the molecules [36]. The strongest interaction short of a chemical bond is hydrogen bonding (H–X···H–X). For the typical polyol/cycloaliphatic diepoxide UV-coatings formulations, the major component of the viscosity is the hydrogen bonding between hydroxyl groups of the ε-caprolactone polyols. As a result, the viscosity can be dramatically decreased by functionalizing the hydroxyl groups and eliminating the propensity toward hydrogen bonding [36]. By functionalizing the polyols with siloxane moieties, reactive groups are also introduced, resulting in a reactive diluent.

3.1. Preparation and characterization of reactive diluents

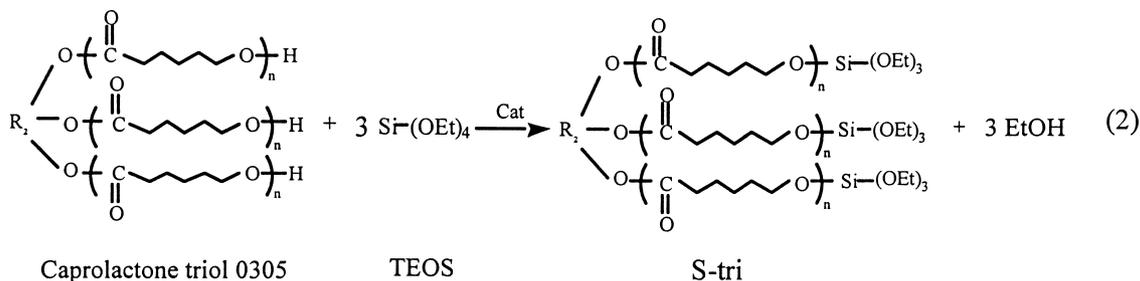
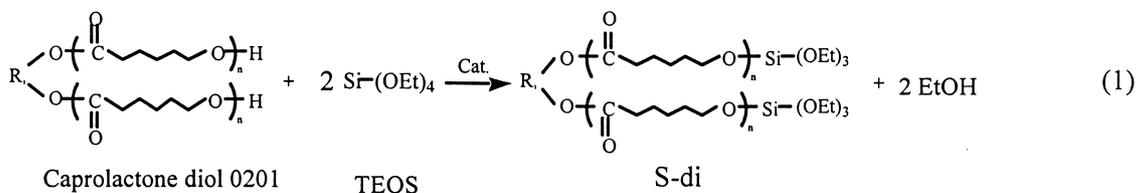
The transesterification reaction of siloxane groups with polyols was acid-catalyzed, and was driven via evolution of



Scheme 3. Proposed condensation reactions of the TEOS functionalized polyols under cationic UV conditions.

alcohols [37,38]. The siloxane reactive diluents with different functionalities were synthesized using tetraethyl orthosilicate (TEOS) with caprolactone diol or triol. The reaction of the caprolactone diol or triol with tetraethyl orthosilicate (TEOS) afforded di-TEOS and tri-TEOS functionalized polyols as shown in Equations (1) and (2), respectively.

cm^{-1}), and silicon–oxygen bonds ($\text{Si}-\text{O}$, 968 cm^{-1}). No hydroxyl groups (OH , $3450\text{--}3550 \text{ cm}^{-1}$) were detected. The $^1\text{H-NMR}$ spectrum confirmed the presence of an ethyl group (CH_3 , δ 1.12–1.18; CH_2 , δ 3.72–3.81). The $^{29}\text{Si-NMR}$ spectrum showed silicon resonances at δ –1.65 and δ –81.68 indicating the presence of two slightly different



For the di-TEOS functionalized product (S–di), the IR spectrum indicated the presence of an ethoxyl group ($\text{CH}_3\text{CH}_2\text{O}$, asym 2974 cm^{-1}), silicon–oxygen–carbon bonds ($\text{Si}-\text{O}-\text{C}$, asym 1165, 1103, 1078, and sym 792

silicon atoms. The elemental analysis and the mass spectral data were consistent with the proposed structure. The Na^+ IDS mass spectrum followed the formula $(449 + 114n) \text{ Da}$. The 114 Da fragment was caused by the

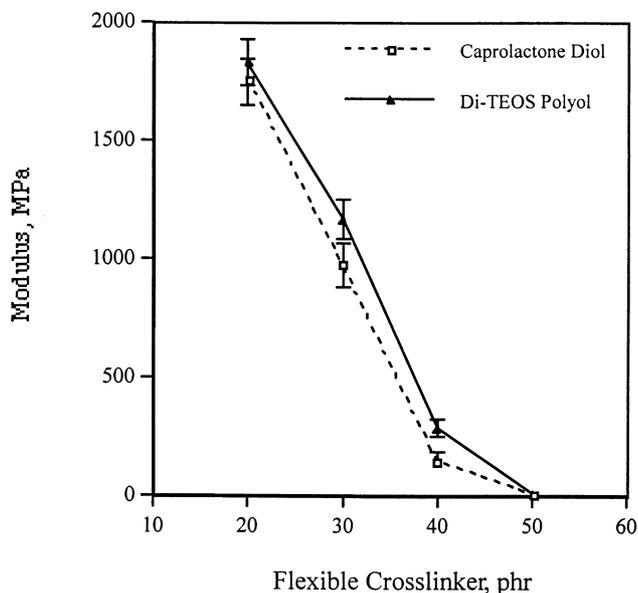


Fig. 1. Tensile modulus of the diol or the di-TEOS functionalized polyol/epoxide coatings as a function of the crosslinker. (□), caprolactone diol; (▲), di-TEOS functionalized polyol.

–(COCH₂CH₂CH₂CH₂ CH₂O)– repeating unit of the caprolactone diol. The 449 Da fragment was the summation of the siloxane group (162 × 2 Da), sodium ion (23 Da), and the caprolactone branching unit (102 Da).

The IR spectrum of the tri-TEOS functionalized product (S–tri) also suggested the presence of ethyl groups (CH₃CH₂, asym 2974 cm⁻¹), silicon–oxygen–carbon bonds (Si–O–C, asym 1167, 1099, 1074, and sym 794 cm⁻¹), and silicon–oxygen bonds (Si–O, 966 cm⁻¹). Again, no hydroxyl groups (OH, 3450–3550 cm⁻¹) were

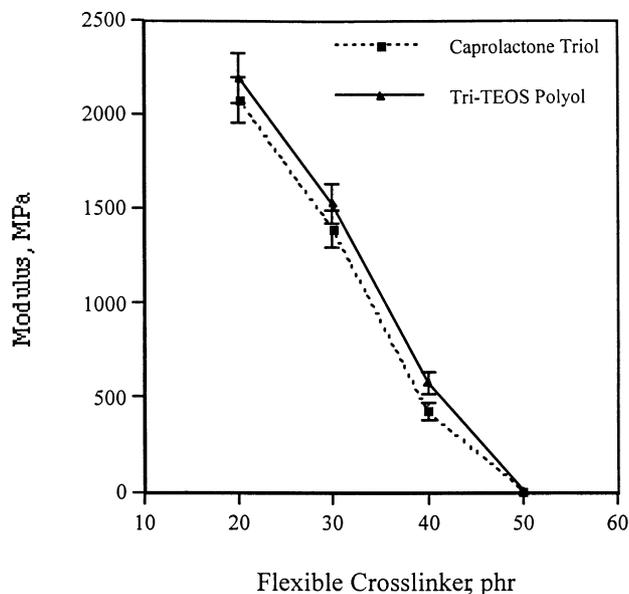


Fig. 2. Tensile modulus of the triol or the tri-TEOS functionalized polyol/epoxide coatings as a function of the crosslinker. (■), caprolactone triol; (▲), tri-TEOS functionalized polyol.

detected, indicating that the hydroxyl groups were completely functionalized. The ¹H-NMR spectrum further confirmed the presence of ethyl group (CH₃, δ 1.04–1.15; CH₂, δ 3.65–3.78). The ²⁹Si-NMR spectrum also resolved different silicon resonances (δ–81.52, δ–81.55, and δ–81.67) corresponding to three different substitutions. Again, the elemental analysis and the mass spectral data were consistent with the proposed structure. The Na⁺ IDS mass spectrum followed the formula (640 + 114*n*) Da for the tri-TEOS functionalized polyol. The 114 Da fragment was caused by the –(COCH₂CH₂CH₂CH₂ CH₂O)– repeating unit of the caprolactone diol, and the 640 Da were the contributions from the siloxane group (162 × 3 Da), sodium ion (23 Da), and the caprolactone branching unit (131 Da).

3.2. Coating formulation and mechanical properties

The siloxane functionalized polyol coatings were formulated with the di- or tri-TEOS functionalized polyol from a 00/100 siloxane polyol/diepoxide up to a 50/50 ratio. The complementary formulations were prepared with non-functionalized caprolactone polyol and cycloaliphatic epoxide for comparison. The viscosity of the coatings containing siloxane polyols were measured, and compared with the unfunctionalized polyol/epoxide formulations. The cured films were evaluated in terms of tensile modulus, tensile strength, and the elongation-at-break. In addition, the glass transition temperatures of the cured coatings were also obtained.

The coatings formulated with the di- or tri-TEOS functionalized polyol without cycloaliphatic epoxide did not appear to exhibit any curing behavior and maintained fluid states several days after UV exposure. Hence, it can be deduced that the TEOS functionalized polyols did not effectively crosslink (see Scheme 3) under the reaction conditions. The coatings formulated with both the TEOS functionalized polyols and the cycloaliphatic epoxide, however, cured instantly into continuous films after UV exposure.

Fig. 1 shows the tensile modulus of the diol and the di-TEOS polyol/epoxide coatings as a function of the crosslinkers (the caprolactone diol and the di-TEOS polyol), respectively. The tensile modulus of the coatings decreased as the concentration of the crosslinkers was increased. The tensile modulus of the triol and the tri-TEOS polyol/epoxide coatings as a function of the crosslinkers is depicted in Fig. 2. Similarly, the tensile modulus of the triol and the tri-TEOS polyol/epoxide coatings was reduced as the content of the crosslinker was increased. The polyols and the corresponding TEOS functionalized polyols both functioned as flexible modifiers, decreasing the hardness of the coatings. In addition, it appeared that the tensile modulus of the TEOS polyol/epoxide coatings was 10%–80% higher than the unfunctionalized polyol epoxide coatings. This result may be attributed to greater functionalities of the TEOS

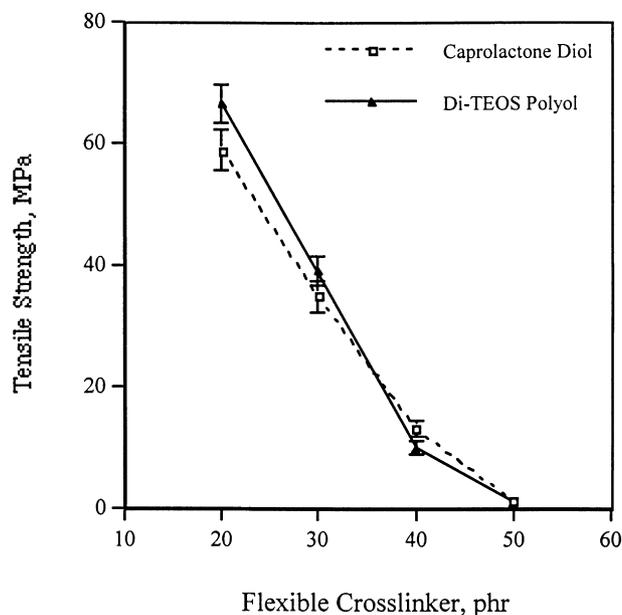


Fig. 3. Tensile strength of the diol or the di-TEOS functionalized polyol/epoxide coatings as a function of the crosslinker. (□), caprolactone diol; (▲), di-TEOS functionalized polyol.

functionalized polyols which gave rise to a higher crosslinking density for the coatings.

The tensile strength of the di- and tri-TEOS polyol/epoxide coatings as a function of the TEOS functionalized polyol is shown in Figs. 3 and 4, respectively. The tensile strength of all the coatings decreased systematically as the content of the crosslinkers was increased. When the concentration of the di-TEOS polyol was low (20–30 wt.%), the tensile

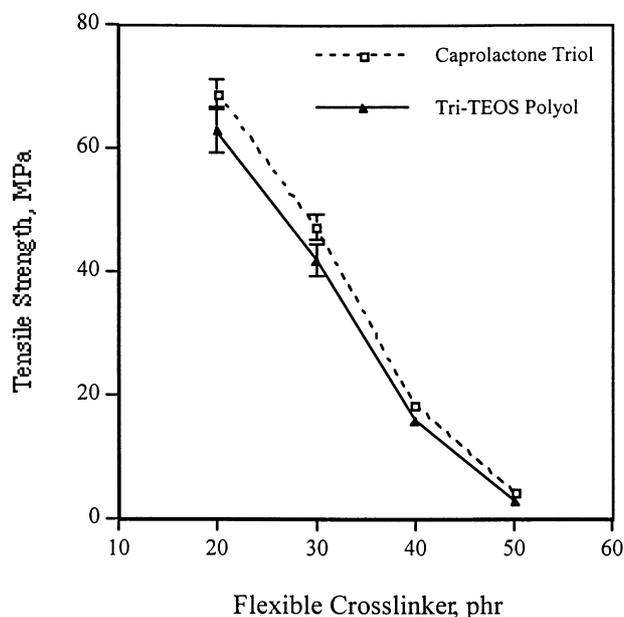


Fig. 4. Tensile strength of the triol or the tri-TEOS functionalized polyol/epoxide coatings as a function of the crosslinker. (□), caprolactone triol; (▲), tri-TEOS functionalized polyol.

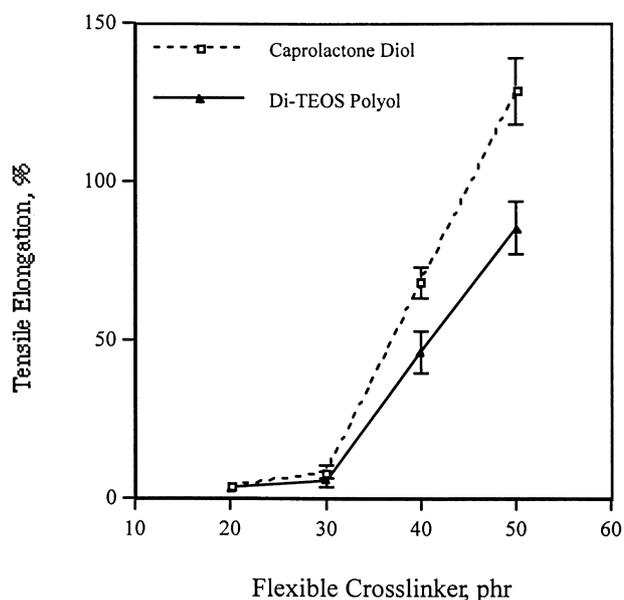


Fig. 5. Tensile elongation of the diol or the di-TEOS functionalized polyol/epoxide coatings as a function of the crosslinker. (□), caprolactone diol; (▲), di-TEOS functionalized polyol.

strength of the di-TEOS polyol/epoxide coating appeared to be higher than the parent diol/epoxide coating. This result may correlate with the greater functionality of the TEOS polyol in comparison with its parent polyol. However, when the di-TEOS polyol content was increased to 40 wt.%, the tensile strength of the coatings was lower than the parent diol/epoxide coating. A similar result was also shown for the tri-TEOS polyol epoxide coating (Fig. 4). However, the tensile strength of the tri-TEOS polyol epoxide coating was lower than the corresponding parent triol/epoxide coating at all crosslinker contents studied.

The tensile elongation-at-break of the polyol and the TEOS functionalized polyol epoxide coatings as a function of the crosslinkers is depicted in Figs. 5 and 6, respectively. The elongation of the coatings increased with the contents of the polyols and the TEOS functionalized polyols because of the flexibility of the polyol crosslinkers. This trend is opposite to the tensile modulus of the coatings with respect to the crosslinkers. The elongations of both the TEOS functionalized polyol/epoxide coatings were lower than the parent polyol coatings, especially at the high addition of the crosslinkers (40–50 wt.%). As a consequence of the greater functionalities of the TEOS polyols, the coatings became less flexible than the unfunctionalized polyol/epoxide coatings especially when the addition was high (40–50 wt.%). This relationship is consistent with the tensile strength of the coatings as previously described.

The glass transition temperatures of the cured polyol or the TEOS functionalized polyol/epoxide coating formulations are shown in Table 2. The glass transition temperature of a polymeric material is mainly influenced by flexibility of the molecular chains. The more flexible the molecular

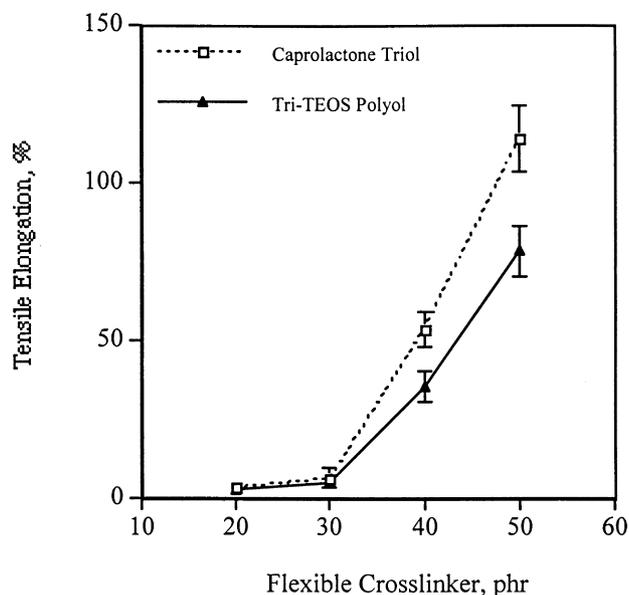


Fig. 6. Tensile elongation of the triol or the tri-TEOS functionalized polyol/epoxide coatings as a function of the crosslinker. (□), caprolactone triol; (▲), tri-TEOS functionalized polyol.

chains, the lower the glass transition temperature. Both the polyols and the TEOS functionalized polyols functioned as flexible crosslinkers with respect to the tensile data (Figs. 1–5). As the concentration of the polyols or the TEOS functionalized polyols was increased, the glass transition temperatures of the crosslinked coatings decreased. The glass transition temperatures of the di- or tri-TEOS polyol/epoxide coatings were 3°C–22°C higher than the polyol/epoxide coatings. This again could be because of the greater functionality of the TEOS functionalized polyols. In comparison with di-TEOS functionalized polyol/epoxide coatings, the glass transition temperatures of the tri-TEOS polyol/epoxide coatings were 5°C–13°C higher as a result of the higher functionality of the tri-TEOS functionalized polyol.

3.3. Spectroscopic characterization of crosslinking reactions

The crosslinking reactions of the TEOS functionalized polyol/cycloaliphatic epoxide coatings were evaluated using IR and ^{29}Si -NMR spectra. The loss of the epoxide

Table 2
Glass transition temperature (T_g) of the UV coatings (DSC)

Concentration of caprolactone polyols or TEOS polyols, wt. %	30	40	50
Diol/epoxide coatings	40.5	12.3	-13.7
Di-TEOS polyol/epoxide coatings	43.3	23.6	9.7
Triol/epoxide coatings	47.4	30.8	8.5
Tri-TEOS polyol/epoxide coatings	48.7	36.8	11.5

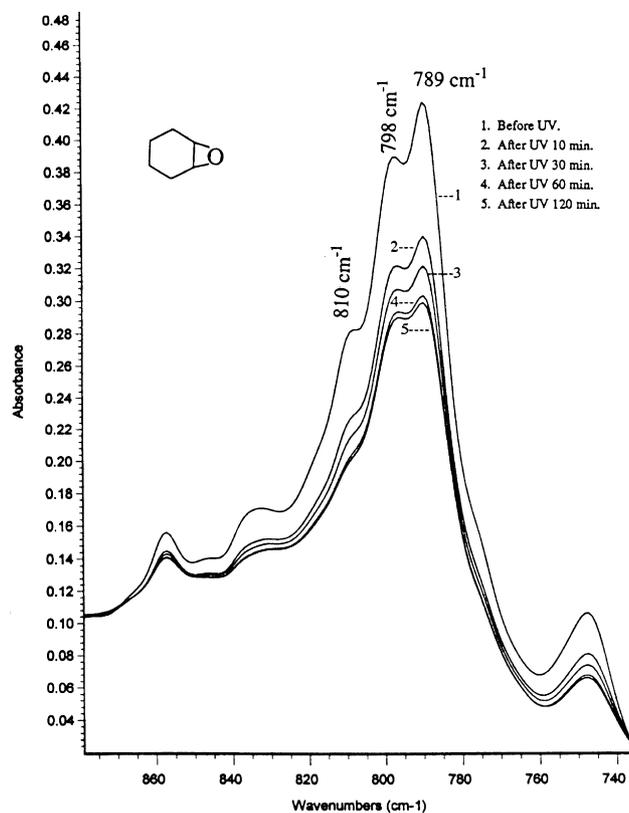


Fig. 7. IR spectra of the cycloaliphatic epoxide ring of the di-TEOS functionalized polyol/epoxide coating as a function of the dark cure time.

was monitored via IR bands at 810, 798, and 789 cm^{-1} [39]. The formation of new C–O–C and Si–O–C bonds was also monitored using IR (1100–1070 cm^{-1}) [39]. Unfortunately, the C–O–C and Si–O–C bands overlap, and as a consequence, ^{29}Si -NMR was used to confirm the formation of the new Si–O–C bonds. The IR spectra monitoring the consumption of the cycloaliphatic epoxide ring as a function of dark cure is shown in Fig. 7. After UV irradiation, the consumption of the cycloaliphatic epoxide is apparent in the decreasing intensity of the epoxide bands. The consumption of the epoxide bands continued for 2 h after exposure, indicating the dark cure or the living nature of the cationic polymerization [40,41].

Spectroscopically, the formation of new Si–O–C bond was monitored via IR and ^{29}Si -NMR. The Si–O–C bond has characteristic double absorption peaks at 1102, 1086 cm^{-1} because of asymmetrical stretching. As previously stated, the C–O–C (ether) and Si–O–C (or Si–O–Si) bonds exhibit similar absorptions in the same range from 1100 to 1070 cm^{-1} , as a consequence the two bands overlap. Fig. 8 depicts the absorbance at 1102 and 1086 cm^{-1} as a function of the dark cure time. The absorption of the two peaks (1086 cm^{-1} and 1102 cm^{-1}) increased with the dark cure time. In addition, the relative intensity of the peak at 1086 cm^{-1} to the peak at 1102 cm^{-1} was increased with time. These results suggest formation of new C–O–C or Si–O–C bonds. Both the formation of

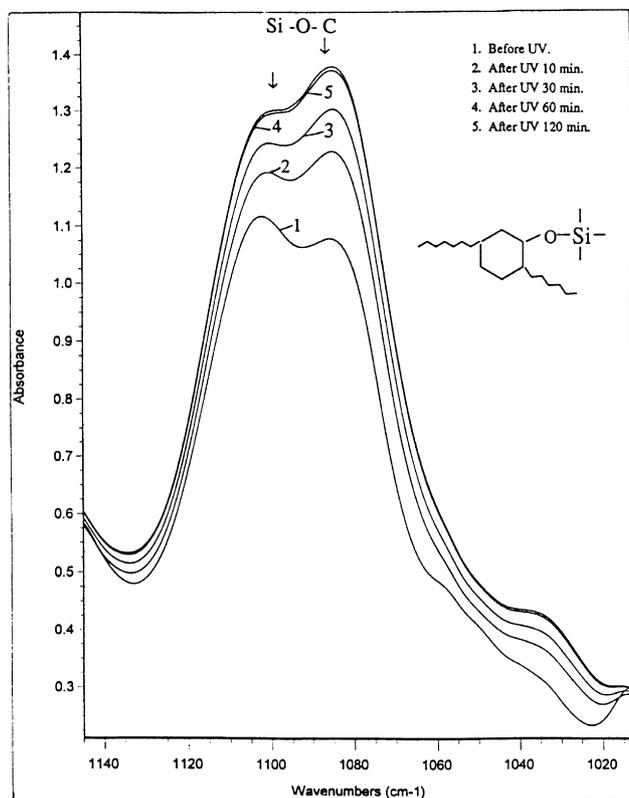


Fig. 8. IR spectra of the Si–O–C bond of the di-TEOS functionalized polyol/epoxide coating as a function of the dark cure time.

ether bonds via copolymerization and homopolymerization of cycloaliphatic epoxide may also contribute to the enhanced C–O–C absorption at 1086 cm^{-1} . The change in the relative intensity of the two peaks could be because of formation of new Si–O–C bonds. The ^{29}Si -NMR spectra of the TEOS polyol/epoxide coatings indicated appearance of multiple peaks after UV irradiation. The chemical shifts of these peaks are shown in Fig. 9. The chemical shift values of the peaks are consistent with the reported values [32].

3.4. Silicon analysis

The silicon analysis results of the crosslinked siloxane functionalized caprolactone polyol/epoxide coatings are shown in Table 3. As expected, the silicon content of the crosslinked coatings increased with increasing siloxane functionalized polyol content. The silicon content of the crosslinked coatings were generally higher than the theoretical values. This may be because of the loss of hydrocarbon compounds during the curing reaction(s). The presence of elemental silicon in the crosslinked films strongly suggests that siloxane functionalized caprolactone polyols had been successfully incorporated into the crosslinked films.

3.5. Viscosity and film formations

The viscosity of the polyols, the TEOS functionalized polyols, and the formulated coatings are shown in Table 4. The viscosity of the TEOS functionalized polyols were significantly lower than the parental polyols and the

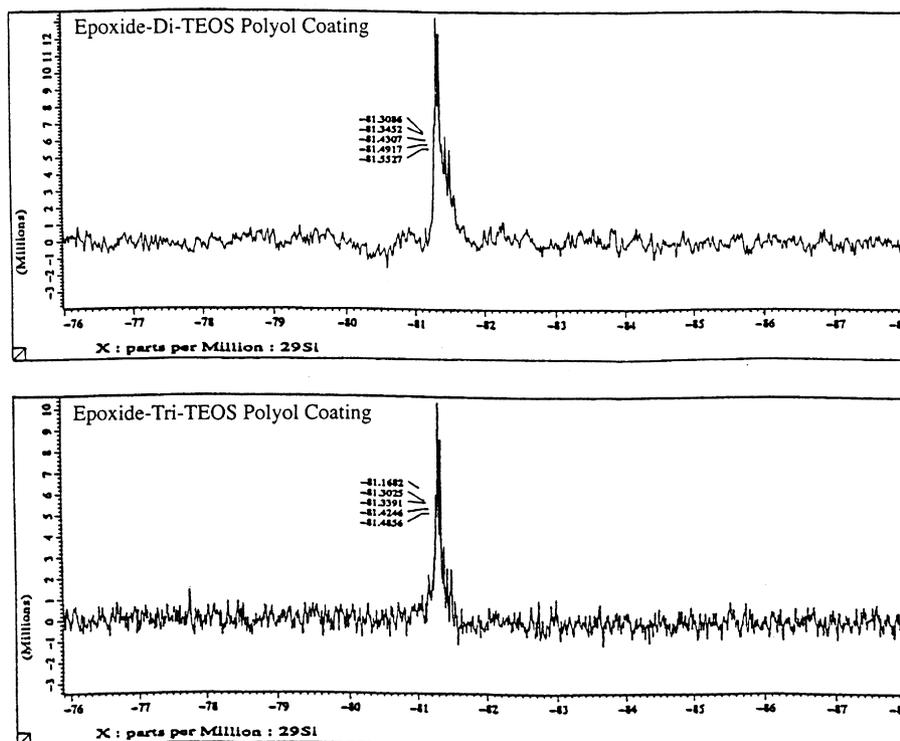


Fig. 9. ^{29}Si -NMR spectra of the di/tri-TEOS functionalized polyol/epoxide coatings 60 min after UV irradiation.

Table 3
Silicon analysis of the crosslinked siloxane functionalized caprolactone polyol/cycloaliphatic epoxide coatings

Epoxide Content	0 ^a		60		80	
	Calcd.	Found	Calcd.	Found	Calcd.	Found
Di-TEOS polyol/epoxide coating	6.58	6.12	2.52	3.02	1.26	1.87
Tri-TEOS polyol/epoxide coating	8.21	7.63	3.14	3.47	1.57	2.15

^a The silicon results at the column were for the di- and tri-TEOS functionalized caprolactone polyols, respectively.

cycloaliphatic epoxide. In comparison with the parent polyols, the viscosities of the TEOS functionalized polyols were 10–30 times lower. The viscosities of the siloxane functionalized polyols were also 5–8 times lower than the cycloaliphatic diepoxide. In addition, the coatings formulated with the siloxane functionalized polyols also exhibited lower viscosity than the coatings formulated with caprolactone polyols because of the lower viscosity of the siloxane polyols.

4. Discussion

The coatings formulated with 100 wt % TEOS functionalized polyols did not result in cured films after UV exposure. Hence, the TEOS functionalized polyols did not undergo condensation reactions under the cationic conditions (see Scheme 3). Normally, the self-condensation of siloxane groups contributes to the formation of the Si–O–Si bonds or silicon clusters via water or alcohol evolution. It appeared that our result contradicted the normal reactivity of the siloxane groups. Nevertheless, the reaction conditions may have been responsible for the unusually low reactivity of the siloxane groups under the UV-initiated cationic curing conditions. Further study will be conducted to address this question.

Surprisingly, the coatings formulated with the TEOS functionalized polyols with cycloaliphatic diepoxide cured instantly with photo-generated super-acid. This type of coating system has not been previously reported. As the TEOS functionalized polyols were shown to be essentially non-reactive toward self-condensation under UV conditions, it is surmised that the TEOS functionalized polyols were incorporated into the cycloaliphatic diepoxide network as previously stated. The crosslinked films exhibited greater tensile modulus, lower elongation, and higher glass transition temperatures than the coatings which were formulated with unfunctionalized caprolactone polyols with cycloaliphatic diepoxide. The enhancement of the coatings properties also suggests that a curing mechanism occurs between

Table 4
Viscosity of the caprolactone polyols, siloxane functionalized caprolactone polyols and the UV coatings before UV exposure at 25°C and 2 s⁻¹ ^a

Epoxide content, wt. %	0 ^b	60	70	100
Diol/epoxide coating	0.283	0.184	0.172	0.225
Di-TEOS polyol/epoxide coating	0.0268	0.0922	0.0614	0.225
Triol/epoxide coating	1.297	0.344	0.233	0.225
Tri-TEOS polyol/epoxide coating	0.0407	0.135	0.0737	0.225

^a The viscosity unit is Pa s.

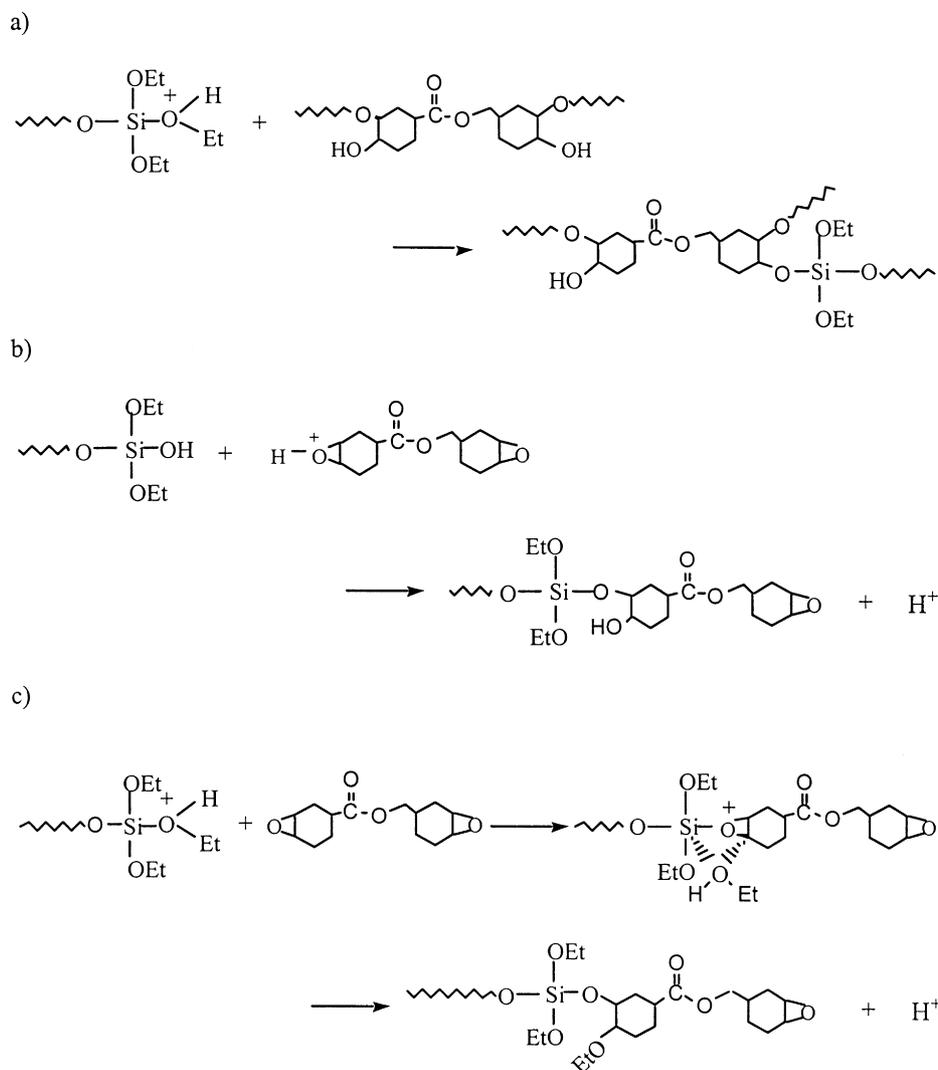
^b The viscosity at the column actually were for the caprolactone polyols and the TEOS functionalized polyols, respectively.

the siloxane functionalized polyol and the cycloaliphatic epoxide.

The possible reaction pathways for the siloxane functionalized polyol to participate in the film curing are shown in Scheme 4. Scheme 4a depicts the protonated silyl species attacked by the hydroxyl group from the homopolymerization of the diepoxide (Scheme 2). This pathway is unlikely as it has been previously shown that the secondary hydroxyl group is not a strong nucleophile, presumably because of the steric hindrance [42]. The second pathway (Scheme 4b) is the attack of a silanol upon the oxirane ring. This pathway has been previously proposed by Isozaki and co-workers [33–35]. The lack of siloxane condensation reactions under UV conditions seems to preclude this mode of crosslinking as the major pathway. The third pathway involves the attack of the oxirane ring on the protonated silyl species. It is proposed that an ethoxide group is transferred onto a cyclohexyl ring either stepwise or in a concerted fashion as shown in Scheme 4c. A model compound study is presently underway to elucidate the crosslinking mechanism.

Although IR spectroscopy was not able to differentiate Si–O–Si bond from Si–O–C bond, ²⁹Si-NMR was an effective tool to study the structures of Si containing groups. No Si resonances were observed for Si–O–Si or Si–OH bonds (Fig. 9) for the siloxane functionalized polyol/epoxide coating systems. Therefore, the siloxane hydrolysis, and the subsequent self-condensation reactions were not favored in the coatings system as shown in Scheme 3b and 3c, respectively. Thus, the copolymerization of the cycloaliphatic diepoxide with a silanol group, as shown in Scheme 4b, may not be favored also because of the limited hydrolysis of the siloxane (Scheme 3b).

The IR spectroscopic data of the coatings indicated the reduction of the epoxy rings and the concurrent formation of new C–O–C or Si–O–C bond. The ²⁹Si-NMR further confirmed the formation of new Si–O–C bonds. It is known from previous work that both the homopolymerization of the cycloaliphatic diepoxide and the copolymerization of the diepoxide with polyols occur simultaneously under photo-generated super-acid conditions (Scheme 2b and 2c) [16, 17]. Thus, in an analogous fashion, it is presumed that both the copolymerization and



Scheme 4. Possible crosslinking reactions of the TEOS functionalized polyols with cycloaliphatic epoxide under cationic UV conditions.

homopolymerization reactions occur in the siloxane functionalized caprolactone polyol/cycloaliphatic diepoxide system. The homopolymerization of the diepoxide under cationic condition, as shown in Scheme 2, contributed to the disappearance of the epoxy ring and the formation of C–O–C bonds for the coatings system. The formation of the new Si–O–C bonds suggested that the TEOS functionalized polyols reacted with cycloaliphatic diepoxide via a copolymerization mechanism as shown in Scheme 4c. Thus, it is proposed that both the homopolymerization and copolymerization of the cycloaliphatic diepoxide with siloxane functionalized polyols contribute to the film formation.

As an overall trend, the tensile modulus and tensile strength of the siloxane functionalized polyol/epoxide coatings increased, and the elongation-at-break decreased with increasing cycloaliphatic diepoxide content. Conversely, the coatings were toughened with increasing siloxane functionalized polyol content, indicating that the TEOS

functionalized polyols contributed to the overall flexibility of the coatings. The trends in the tensile properties closely followed the non-functionalized polyol/epoxide coating system. This could also be shown as an indirect evidence for the incorporation of the siloxane units into the epoxide homopolymer network.

After the siloxane functionalization, the hydroxyl groups of the caprolactone polyols were replaced with siloxane groups effectively eliminating the hydrogen bonding. Although the molecular weights of the polyols were increased by functionalization with TEOS, the viscosity of the functionalized polyols was substantially decreased. Moreover, the coatings formulated with the TEOS polyols showed much lower viscosity than the coatings without the siloxane functionalized polyols (Table 3). In view of the UV curing reactivity and the reduced viscosity of the TEOS functionalized polyols as previously discussed, the TEOS modified ϵ -caprolactone polyols successfully functioned as reactive diluents for UV-coatings formulations.

5. Conclusion

Siloxane functionalized polyols were synthesized using caprolactone polyols with tetraethyl orthosilicate. The resulting siloxane functionalized polyols did not undergo self-condensation under cationic UV conditions. However, the siloxane functionalized polyols were cationically cured in the presence of cycloaliphatic diepoxides to form cross-linked films. The siloxane functionalized polyols were effective reactive diluents reducing the viscosity of the overall coating formulations. In addition, the siloxane polyols also functioned as interfacial surface tension modifier minimizing film defects and increasing the coatings adhesion to the substrates. The coatings formulated with the siloxane functionalized polyols exhibited greater tensile modulus and higher glass transition temperature than the corresponding unfunctionalized caprolactone polyol coatings.

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