Effect of Siloxane Functionalized Caprolactone Polyols on Photocurable Epoxy Coatings

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Cationic ultraviolet (UV) coatings were formulated using a cycloaliphatic diepoxide (3,4-epoxycyclohexyl methyl-3′, 4-′epoxycyclohexane carboxylate) with siloxane modified caprolactone polyols. Both di- and tri-TEOS (tetraethyl orthosilicate) functionalized caprolactone polyols were used to modify the UV coatings. The resulting coatings were cured and evaluated in terms of pencil hardness, MEK double rubs, crosshatch/pull-off adhesion, and reverse impact resistance. Addition of the siloxane-functionalized polyols into the caprolactone polyol/cycloaliphatic diepoxide coating formulations improved pencil hardness, MEK double rubs, and enhanced toughness of the coatings. When the addition of siloxane-functionalized polyols was less than 25 wt%, the resulting coatings had significantly increased adhesion. In addition, modification of the coatings with the siloxane-functionalized polyols also reduced surface tension and improved film formation with reduced levels of surface wetting agent. Without the modification, the coatings exhibited a poor balance of hardness and adhesion.

INTRODUCTION

As environmental and public health concerns have become major issues in the coatings industry, the UV curing process has been found to be an effective alternative to solventborne technology in the coatings industry.[1] UV coatings can be formulated with virtually zero VOC (volatile organic compounds) emissions. The high productivity and cost-efficiency of the UV coatings have attracted the coatings industry, and numerous advantages and applications of the UV coatings have been well documented in recent years.[2] In terms of the polymerization mechanisms, the two principal types of UV coatings are the free radical and cationic initiated UV coatings. In comparison with the free radical initiated polymerization mechanisms, the cationic initiated UV curing technology offers the advantages of insensitivity to oxygen and low film shrinkage.[3]

Epoxy resins are widely used polymer binders for high performance protective coatings.[4] In addition to thermally initiated crosslinking, the cationic UV polymerization of epoxy resins, especially the cycloaliphatic epoxides, offers many unique properties for the coatings.[5] The cycloaliphatic epoxides do not have a UV chromophore (no aromatic rings) and are free of chloride in their synthesis (unlike the diglycidyl ether epoxy resins). As a result, the cycloaliphatic epoxide coatings are more durable for outdoor applications and are excellent electrical insulators.[6] In addition, cycloaliphatic epoxide coatings display high gloss and excellent clarity. The first cycloaliphatic epoxide resins appeared in the 1950s. The primary uses were castings, potting compounds, and encapsulants for the electrical and electronic industries.[7] Presently, cycloaliphatic diepoxides are the predominent type of monomer used for formulating cationic UV coatings.

Although cationic polymerization of cycloaliphatic epoxides has been established for a number of applications in the coatings industry,[8] the development of new reactive diluents and prepolymers for high performance coatings are needed for new applications.[9] As previously reported, cycloaliphatic epoxide UV coatings without flexible crosslinkers are brittle and lack toughness.[10] Consequently, flexible crosslinkers containing active protons, particularly polyols, must be incorporated into the coating formulations to modify the toughness of the coatings. Adhesion and hardness of coatings are two primary coatings properties for consideration. Unfortunately, the flexible units decrease the hardness, the abrasion resistance, and the solvent resistance of the coatings.[11] For the cycloaliphatic epoxide/caprolactone polyol UV coatings, the adhesion and hardness are related to

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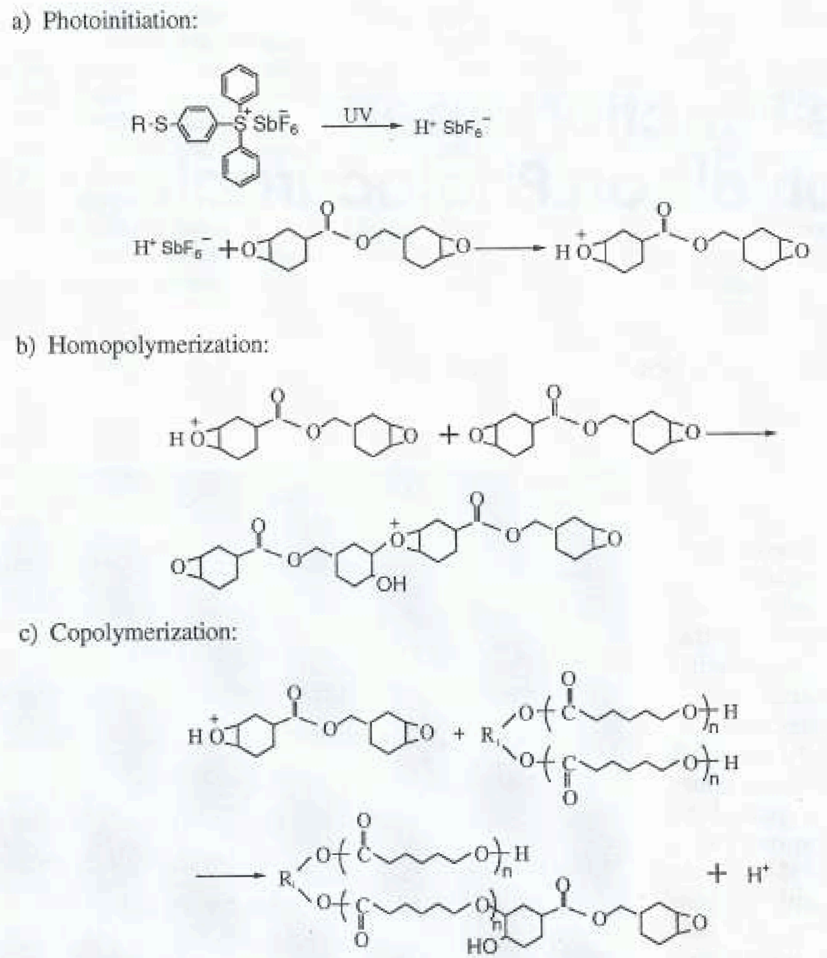


Scheme 1—Photolytically initiated homopolymerization and copolymerization of cycloaliphatic epoxide.

the toughness and the modulus of the coatings, respectively.[10,11] While the toughness of the coatings was proportional to the polyol component and content, the tensile modulus was decreased. Furthermore, the viscosity of the coating formulations cannot be effectively reduced by using the caprolactone polyols as reactive diluents since both the di- and tri-polyols have higher viscosity than the cycloaliphatic diepoxide monomer due to the inherent hydrogen bonding (H–O· · ·H–O) between the hydroxyl groups of the polyols.[10]

Previously, we have reported the synthesis of novel siloxane functionalized caproalactone polyols and the investigation of the photoinitiated crosslinking reactions of the siloxane functionalized polyols with a cycloaliphatic diepoxide.[10] The viscosity of the caprolactone polyols was dramatically decreased by functionalizing the hydroxyl groups with siloxane groups. In addition, a reactive siloxane moiety was introduced. The siloxane-functionalized polyols were crosslinked with cycloaliphatic epoxide to form continuous films (*Schemes* 1-3). The cured coatings exhibited improved tensile modulus and high tensile strength while maintaining toughness of the coatings.[10]

In this paper, the siloxane-functionalized caprolactone polyols were evaluated as additives for the cycloaliphatic diepoxide/caprolactone polyol UV coatings. The siloxane functionalized caprolactone polyols were systematically added into the coating formulations to replace the caprolactone polyols. A series of siloxane-functionalized polyols was added to caprolactone polyol/cycloaliphatic epoxide UV coatings and cured with UV radiation. The crosslinked films were evaluated in terms of pencil hardness, MEK double rubs, crosshatch/pull-off adhesion, and the reverse impact resistance.

EXPERIMENTAL

Caprolactone polyols (Tone™ 0201: $\overline{M}n = 530$, and Tone™ 0305: $\overline{M}n = 540$), cycloaliphatic diepoxide (UVR™-6150), triarylsulfonium hexafluoroantimonates (photoinitiator, Cyra Cure™ UVI-6974) were provided by Union Carbide Corporation. Surface wetting additive (Silwet™ L-7604) was provided by Witco Corporation. All the materials were used as received. Tetraethyl orthosilicate (TEOS) functionalized polyols were synthesized as described previously.[10] The chemical structures of the materials used are shown in *Scheme* 4. Aluminum panels were purchased from Q-Panel Lab Products.

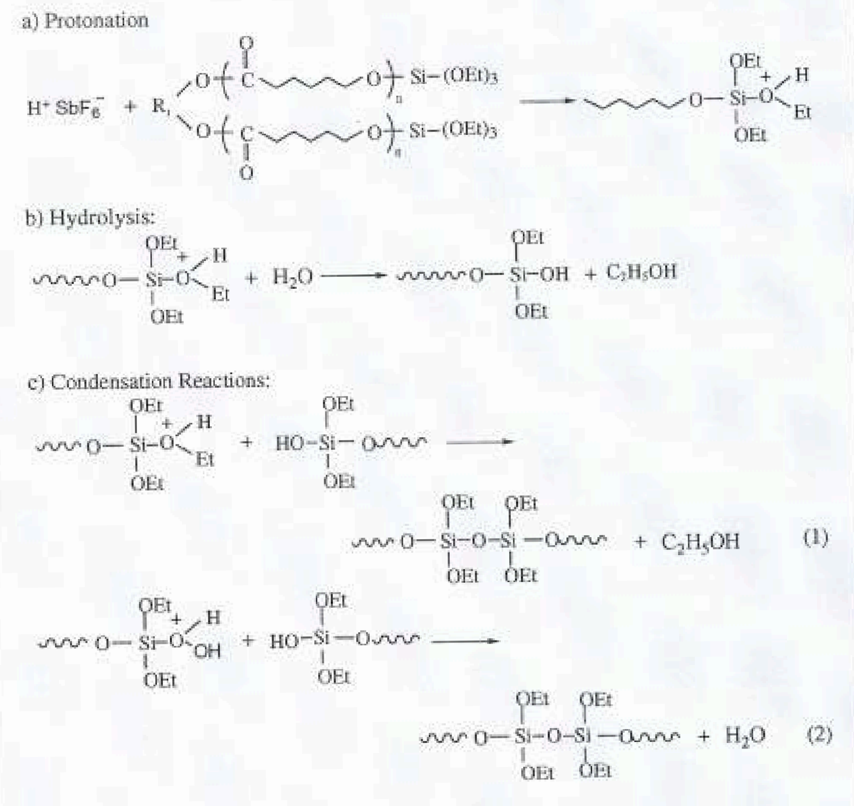
The cycloaliphatic epoxide-caprolactone diol or triol coatings were formulated with UVR-6105 (50-100 wt%), caprolactone diol and triol (50-0 wt%), UVI-6974 (4.0 wt%), and a surface wetting additive Silwet™-L 7604 (0.5 wt%). The relative concentration of the cycloaliphatic epoxide to the caprolactone diol or triol was varied systematically from 50/50 to 100/0. The concentration of the photoinitiator and the surface wetting additive (Silwet L) were kept constant throughout all of the coating formulations. Similarly, the di- or tri-TEOS (tetraethyl orthosilicate) functionalized caprolactone polyol (S-Di or S-Tri) was also used to formulate UV coatings with the cycloaliphatic epoxide, respectively. Both the resultant caprolactone polyol/cycloaliphatic epoxide and siloxane polyol/cycloaliphatic epox-

Table 1—Formulations of the Caprolactone Polyol or TEOS Functionalized Polyol/Epoxide Coatings

Concentration of the polyol or TEOS Functionalized polyol, wt %	20	30	40	50
Caprolactone polyol or TEOS Functionalized polyol, g	2.0	3.0	4.0	5.0
Cycloaliphatic diepoxide, g	8.0	7.0	6.0	5.0

ide coatings were used as control study. The coating formulations are shown in *Table* 1. The di- or tri-TEOS functionalized caprolactone polyol was systematically added into the coatings formulations to partially replace the caprolactone diol or triol. The ratio of the TEOS functionalized diol or triol to the caprolactone diol or triol was varied from 10/90 to 80/20 to elucidate any synergistic effects of the siloxane functionalized polyols while the concentration of the cycloaliphatic epoxide was kept constant (*Tables* 2 and 3).

To evaluate the coating properties of the crosslinked films, the coatings were cast on aluminum panels and glass plates using a wire wound rod (No. 16), and cured in an ultraviolet processor (RPC, 2 × 300 W/in. medium-pressure mercury UV lamps, and 50 fpm). The film properties were measured 24 hr after UV exposure. The pencil hardness (ASTM D 3363), methy ethyl ketone (MEK) double rubs (ASTM D 4752), crosshatch adhesion (ASTM D 3359), pull-off adhesion (ASTM D 4541), reverse impact resistance (ASTM G 14), and flexibility (ASTM D 522) were tested according to the standard methods as indicated, respectively. The surface tension of the siloxane-functionalized polyol modified coatings were recorded on a surface tensiometer (Sensa-Dyne 600, Chem-Dyne Research Corp.) equipped with Sensadyne software (PC-DOS 1.10). The measurement was performed at room temperature using nitrogen as a process gas, and water and heptane were used as the standards for the calibration.



Scheme 2—Proposed possible condensation reactions of the TEOS functionalized polyols under cationic UV conditions.

RESULTS AND DISCUSSION

This study focuses on the coating properties of the siloxane-functionalized caprolactone polyol modified caprolactone polyol/cycloaliphatic diepoxide UV coatings systems. In a previous study, the synthesis of the siloxane-modified polyols and their function as reactive diluents for UV coatings was reported.[10] The possible crosslinking reactions are shown in *Schemes* 1-3. From a preliminary spectroscopic investigation, the reaction depicted in *Scheme* 3c was proposed in addition to the crosslinking reactions in *Scheme* 1. However, a more detailed mechanistic study using model compounds is currently being undertaken.

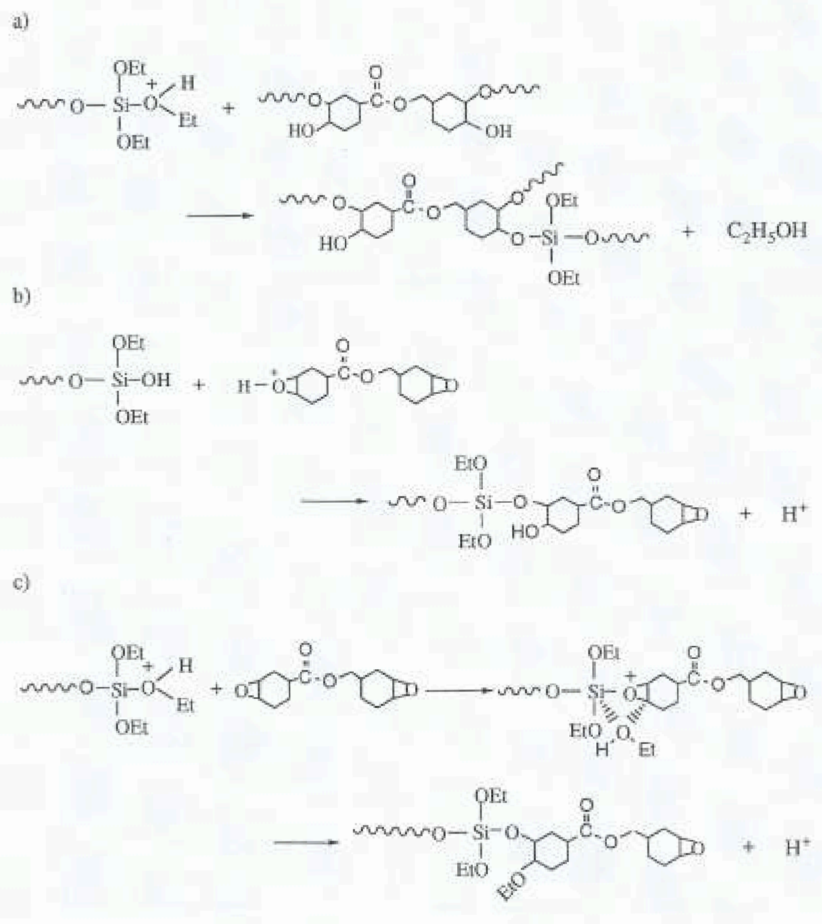
The caprolactone diol/diepoxide and caprolactone triol/diepoxide coatings systems were compared with the di- and tri-TEOS functionalized polyol/epoxide coatings, respectively. The formulations ranged from 5 to 60 wt% unfunctionalized polyol or TEOS functionalized

Table 2—Siloxane Functionalized Polyol Modified UV Coating Formulations Containing 60 wt% Cycloaliphatic Diepoxide

Ratio of the S-Di and S-Tri to diol or triol, wt%/wt%	0/100	10/90	25/75	50/50	60/40	80/20
Cycloaliphatic diepoxide, g	6.0	6.0	6.0	6.0	6.0	6.0
Caprolactone polyol, g	4.0	3.6	3.0	2.0	1.6	0.8
Siloxane functionalized polyol, g	0.0	0.4	1.0	2.0	2.4	3.2

Table 3—Siloxane Functionalized Polyol Modified UV Coating Formulations Containing 70 wt% Cycloaliphatic Diepoxide

Ratio of the S-Di and S-Tri to diol or triol, wt%/wt%	0/100	10/90	25/75	50/50	60/40	80/20
Cycloaliphatic diepoxide, g	7.0	7.0	7.0	7.0	7.0	7.0
Caprolactone polyol, g	3.0	2.7	2.25	1.5	1.2	0.6
Siloxane functionalized polyol, g	0.0	0.3	0.75	1.5	1.8	2.4



Scheme 3—Possible crosslinking reactions of the TEOS functionalized polyols with cycloaliphatic epoxide under cationic UV conditions.

polyol. It was observed that coating formulations with greater than 60 wt% of either the caprolactone polyol or the TEOS functionalized polyols afforded inadequately cured films. It was surmised that the concentration of the cycloaliphatic diepoxide was not sufficient to participate in copolymerization resulting in uncured films.

The mixed siloxane functionalized polyol/polyol/epoxide coating formulations depicted in the Experimental Section (*Tables* 2 and 3) are based on the ratio of siloxane functionalized polyols to non-functionalized polyols. Both diol and triol were used, although it is important to note that the di- and tri-polyols were not mixed. Both the diol and triol were used with TEOS functionalized polyol (diol or triol) from a 90/10 ratio to a 20/80 ratio. Two levels of the diepoxide contents (60 and 70 wt%) were used for the comparison of homopolymerization of diepoxide versus copolymerization with either the polyol or the TEOS functionalized polyol. These two diepoxide levels (60 and 70 wt%) were formulations chosen to afford the optimum coatings properties.

The pencil hardness, MEK (methyl ethyl ketone) double rubs, crosshatch adhesion, and the reverse impact resistance for the non-functionalized diol or triol/epoxide coatings are shown in *Tables* 4 and 5, respectively. When the diol content was increased above 20%, the pencil hardness and the MEK double rubs dramatically decreased. The crosshatch adhesion and the reverse impact resistance, however, significantly increased. When the polyol content was below 20 wt%, the pencil hardness and the MEK double rubs of the coatings were significantly higher. However, the crosshatch adhesion and the impact resistance of the coatings decreased substantially. Thus, it was surmised that below 20 wt% polyol, the coatings properties were dominated by the cycloaliphtic diepoxide (homopolymer) component.

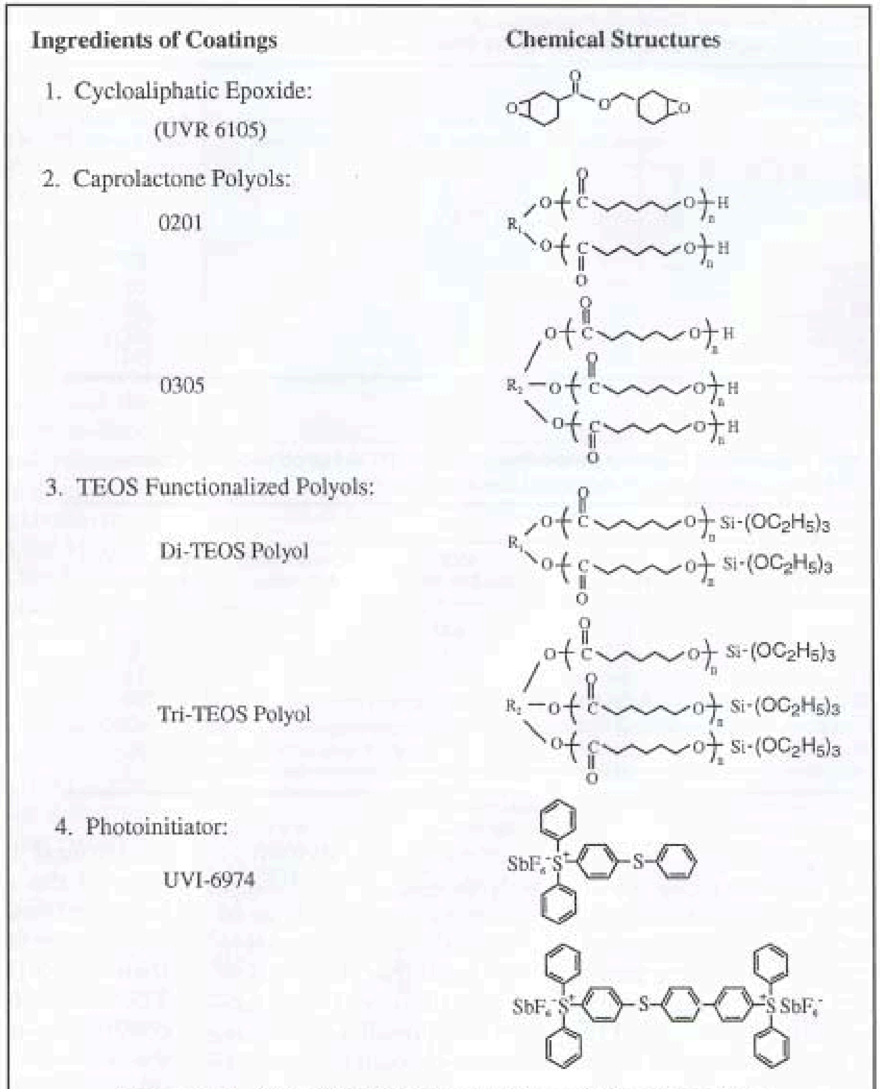
As previously mentioned, the polyols function as flexible crosslinkers. As a result, the MEK rub resistance of the coatings reduced with increasing polyol content. The increased adhesion with the diol may be due to both increased interaction of the coating with the substrate, and increased toughness of the coating against crosscuts. The caprolactone triol/epoxide coatings exhibited similar trends in pencil hardness, MEK double rubs, crosshatch adhesion, and reverse impact resistance. In addition, it appeared that both diol and triol/epoxide coating showed optimized coating properties when the content of the polyol was from 20 to 30 wt%. In addition, the triol/epoxide coatings showed better coating properties perhaps due to higher functionality of the triol.

The coating properties of the di- and tri-TEOS functionalized polyol/epoxide coatings are presented in *Tables* 6 and 7, respectively. Both the TEOS functionalized diol and triol/diepoxide coatings showed decreasing hardness, solvent resistance (MEK double rubs) with increasing the TEOS functionalized polyol content. As the concentration of the TEOS functionalized polyol increased to 30 wt%, both the adhesion and the reverse impact resistance increased to a

Table 4—General Coating Properties of the Caprolactone Diol/Epoxide Coatings as a Function of the Diol

Concentration of the Diol, %	Pencil Hardness	MEK Double Rubs	Crosshatch Adhesion	Rev. Impact Res. (lb/in.)
0	6H	>300	0B	4
5	6H	>300	0B	4
10	5H	>300	0B	16
20	4H	230	0B	36
30	3H	45	4B	>80
40	B	28	5B	>80
50	2B	8	5B	>80
60[a]	~	~	~	~

(a) The cured film did not solidfy under the cure conditions.



Scheme 4—Chemical structures of the major ingredients for the UV coatings.

maximum. Above 30 wt% of the di-TEOS functionalized polyol (*Table* 6), all the coatings properties decreased. Similarly, above 40 wt% of the tri-TEOS functionalized polyol, all the coatings properties decreased for the tri-TEOS polyol based coatings (*Table* 7). The di- and tri-TEOS functionalized polyol/epoxide coatings system showed similar trends in both the pencil hardness and the MEK double rub data as the non-functionalized polyol/epoxide coatings system. The similarity in the siloxane functionalized and non-functionalized polyol/epoxide coatings data suggest that the di- and tri-TEOS functionalized polyols also function as flexible crosslinkers.

In contrast with the non-functionalized polyol/epoxide coatings, the crosshatch adhesion and the reverse impact resistance of both the di- and tri-TEOS polyol/epoxide coatings were lower at low or high content of the siloxane polyols. This may be rationalized in terms of a comparison of the structures. The TEOS functionalized polyols have more reactive groups (four to six more) than the parent polyols, resulting in a higher crosslink density. Above 30 wt% of the TEOS functionalized polyol, the adhesion and impact resistance of the coatings diminished with increasing the TEOS functionalized polyol content. This may be attributed to the siloxane unit of the TEOS functionalized polyol reacting with the cycloaliphatic diepoxide preferentially to self-condensation. As the concentration of available epoxide was reduced, the potential for crosslinking decreased resulting in poor film properties.

In comparison to the unfunctionalized polyol/epoxide coatings, the siloxane functionalized polyol coatings exhibited higher pencil hardness and the MEK double rubs at the same level of addition as the polyols. This result may be attributed to the greater functionality of the siloxane polyols. The parent polyols were limited in terms of their crosslinking potential, thus the flexibility of the soft units dominated the coating properties. As a consequence, the parent polyols experienced a decrease in the pencil hardness and MEK double rubs with increasing polyol content. Unlike the parent polyols, the higher functionality of the siloxane functionalized polyols partially compensated for the flexibility of the soft segments with respect to the hardness and MEK double rubs.

The di- and tri-TEOS functionalized polyols were used to replace part of the caprolactone diol and triol in the polyol/diepoxide coating formulations (*Tables* 2 and 3). The coating formulations contained 60 or 70 wt% cycloaliphatic diepoxide. The concentrations of the cycloaliphatic diepoxide were chosen based on the polyol/diepoxide coating formulations which afforded better overall coating properties (*Tables* 4 and 5). Thus, the TEOS functionalized polyol/unfunctionalized polyol/epoxide coatings were evaluated using both 60 and 70 wt% cycloaliphatic diepoxide loadings. The pencil hard-

Table 5—General Coating Properties of the Caprolactone Triol Epoxide Coatings as a Function of the Triol

Concentration of the Triol, %	Pencil Hardness	MEK Double Rubs	Crosshatch Adhesion	Rev. Impact Res. (lb/in.)
5	6H	>300	0B	4
10	6H	>300	0B	12
20	5H	245	0B	24
30	3H	58	5B	>80
40	HB	25	5B	>80
50	2B	12	5B	>80
60[a]	~	~	~	~

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[a] The cured film did not solidfy under the cure conditions.

Table 6—General Coating Properties of the Di-TEOS Functionalized Polyol/Epoxide Coatings as a Function of the Siloxane Polyol

Concentration of the Siloxane Polyol, %	Pencil Hardness	MEK Double Rubs	Crosshatch Adhesion	Rev. Impact Res. (lb/in.)
0	6H	>300	0B	4
5	6H	>300	0B	4
10	6H	>300	0B	15
20	5H	>300	1B	20
30	4H	210	3B	66
40	3H	53	2B	50
50	3H	15	1B	42
60	HB	8	0B	34

Table 7—General Coating Properties of the Tri-TEOS Functionalized Polyol/Epoxide Coatings as a Function of the Siloxane Polyol

Concentration of the Siloxane Polyol, %	Pencil Hardness	MEK Double Rubs	Crosshatch Adhesion	Rev. Impact Res. (lb/in.)
5	6H	>300	0B	3
10	6H	>300	0B	8
20	6H	>300	0B	14
30	5H	260	3B	34
40	4H	69	2B	42
50	3H	22	0B	40
60[a]	2H	8	0B	30

ness of the di- or tri-TEOS polyol modified UV coatings as a function of the siloxane polyols is shown in *Table* 8. The pencil hardness of all the coatings, especially at 60 wt% epoxide, increased concurrently with increasing replacement of the parent polyol with the TEOS modified polyol. This result may be attributed to the enhanced crosslinking of the TEOS functionalized polyols. In comparison with the 60 wt% epoxide containing coatings, the 70 wt% epoxide containing coatings exhibited significantly greater hardness. This could be due to the greater cycloaliphatic diepoxide content. The homopolymer of the cycloaliphatic diepoxide (*Scheme* 1b) imparts more hardness than either of the TEOS functionalized polyols.

The MEK double rubs of the mixed TEOS functionalized polyol/polyol/epoxide coatings are shown in *Figures* 1 and 2. The double rubs increased with the addition of the di-TEOS functionalized polyol. Similar to the di-TEOS functionalized polyol modified polyol/epoxide formulations, the tri-TEOS functionalized polyol modified coatings exhibited increasing MEK double rubs with increasing the ratio of the tri-TEOS functionalized polyol to parent polyol due to higher functionality of the siloxane functionalized polyol. These results seem to correlate with the pencil hardness data (*Table* 8). In addition, the MEK double rubs of the 70 wt% epoxide coating was significantly higher than the 60 wt% epoxide containing coatings. This is presumably due to the greater content of the cycloaliphatic diepoxide.

The crosshatch adhesion and the reverse impact resistance of the mixed TEOS functionalized polyol/polyol/diepoxide coatings are shown in *Tables* 9 and 10. When the ratio of the TEOS polyol to the parent polyol was below 60/40, the maximum adhesion and the impact resistance of the coatings were maintained. The crosshatch adhesion and the impact resistance decreased after the ratio of the siloxane polyol to the parent polyol was increased to 60 wt%. This trend may be also a result of the greater functionality of the TEOS modified polyol than the parent polyol. As the ratio was increased, more TEOS functionalized polyol was incorporated into the coatings resulting in more brittle films. Consequently, the adhesion and the impact resistance of the coatings decreased with increasing the ratio of the TEOS functionalized polyol to the parent polyol.

Due to the limited sensitivity of the crosshatch adhesion, pull-off adhesion of the coatings was also measured. The pull-off adhesion of the TEOS functionalized polyol/epoxide coatings versus unfunctionalized

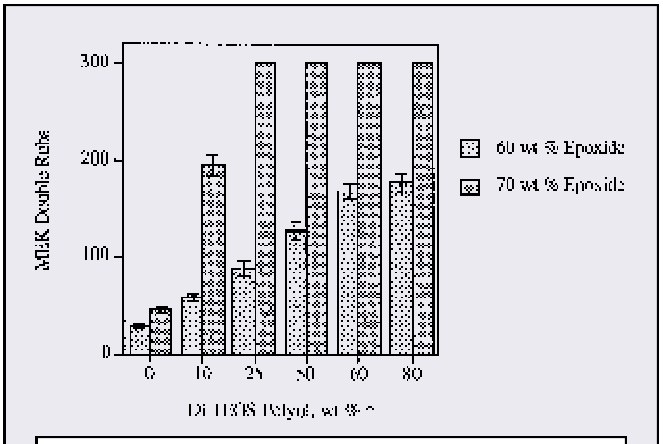

Figure 1—MEK double rubs of the di-TEOS polyol modified tone polyol-epoxide coatings as a function of the di-TEOS functionalized polyol.

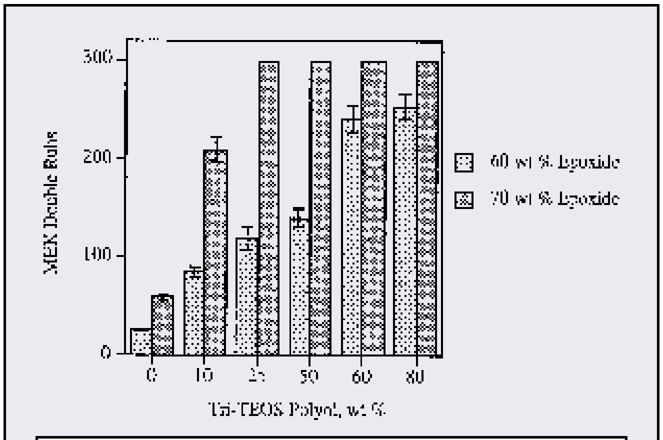

Figure 2—MEK double rubs of the tri-TEOS polyol modified tone polyol-epoxide coatings as a function of the tri-TEOS functionalized polyol.

caprolactone polyol/epoxide coatings is illustrated in *Figures* 3 and 4. The pull-off adhesion of both the di- and tris-TEOS functionalized polyol/epoxide coatings exhibited the same trends as the crosshatch adhesion. However, the pull-off adhesion of the TEOS functionalized polyol/epoxide coatings versus unfunctionalized caprolactone polyol/epoxide coatings did not follow the same trends. The adhesion of the parent polyol/epoxide coatings systematically increased with increasing crosslinkers. This may be due to the fact that the coatings adhere more strongly and uniformly to substrates via anchor mechanism when the coatings become more flexible.[12] The adhesion of the siloxane functionalized polyol/epoxide coatings exhibited the opposite trend, and decreased with the addition of the siloxane functionalized polyols from 30 to 50 wt%. In addition, the adhesions of both the di- and tri-TEOS functionalized polyol/epoxide coatings were lower than the unfunctionalized caprolactone polyol/epoxide coatings when the loading of the crosslinkers was from 30 to 50 wt%. These results were perhaps due to the greater functionality of the siloxane functionalized polyols resulting in the more brittle films. However, when the addition of the crosslinkers was below 30 wt%, the adhesion of both the di- and tri-TEOS functionalized polyol/epoxide coatings appeared to be higher than the unfunctionalized polyol/epoxide coatings. This may be a result of a general siloxane coupling interaction with the substrate which dominated the effect of the crosslinking promoting adhesion.[12]

The pull-off adhesion of the siloxane polyol modified caprolactone polyol/diepoxide coatings shown in *Figures* 5 and 6. The adhesion of the di-TEOS polyol modified coatings increased as the addition of the siloxane polyols were increased initially. A maximum adhesion was reached at a relative concentration of 10 wt% di-TEOS functionalized polyol. Similarly, a maximum adhesion was also obtained for the tri-TEOS polyol modified coatings when the concentration of the tri-TEOS functionalized polyol was increased to 10 wt%. Beyond the concentration, the adhesion of both coatings started to decrease as the siloxane functionalized polyols were increased. However, the adhesion of the modified coatings with 25 wt% di- or tri-TEOS polyols was still higher than the coating without the siloxane polyol modification. Thus, the higher adhesion of the siloxane polyol modified coatings can be due to a result of the siloxane coupling interaction with the substrate. Similarly, the decrease of the adhesion after the 10 wt% addition may be attributed to the more siloxane functionalized polyols which resulted in the more brittle films. Hence, the maximum addition of the di- or tri-TEOS functionalized polyols to the UV coatings seems to be up to 25 wt% to balance the other coatings properties such as pencil hardness and MEK double rubs.

As previously mentioned, a surface active agent, Silwet-L™, was added to modify the interfacial surface tension. The addition of the surface tension modifiers, unfortunately, resulted in a reduction of the adhesion. *Figure* 7 indicates the pull-off adhesion of both the polyol and TEOS polyol coatings as a function of the surface active agent concentration. The adhesion of the coatings decreased as the addition of the surface modifier was

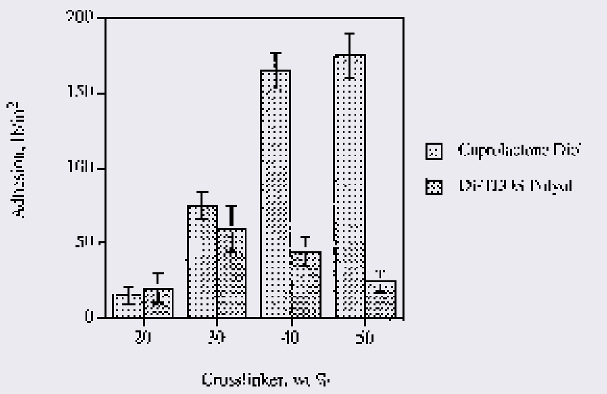

Figure 3—Pull-off adhesion of the caprolactone diol or the di-TEOS functionalized polyol/epoxide coatings as a function of the crosslinker.

Table 8—Pencil Hardness of the TEOS Functionalized Polyol Modified Caprolactone Polyol/Epoxide Coatings as a Function of the Siloxane Polyols

Ratio of the TEOS Polyol to the Parent Polyol[a]	Di-TEOS Polyol Modifed Coatings		Tri-TEOS Polyol Modified Coatings	
	Epoxide 60 wt%	**Epoxide 70 wt%**	**Epoxide 60 wt%**	**Epoxide 70 wt%**
0/100	B	3H	HB	3H
10/90	B	3H	F	3H
25/75	HB	3H	F	3H
50/50	F	4H	H	4H
60/40	2H	5H	3H	5H
80/20	3H	5H	4H	5H

(a) Based on the total amount of the caprolactone polyols and the TEOS functionalized polyols.

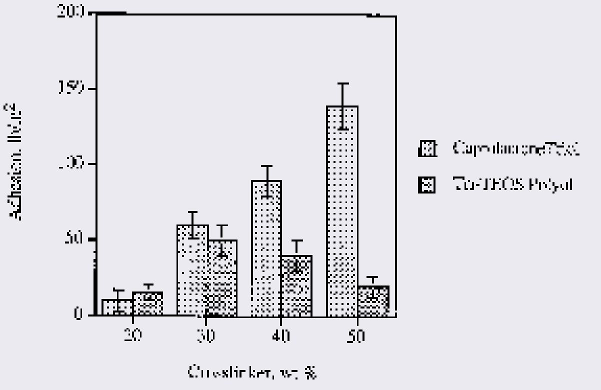

Figure 4—Pull-off adhesion of the caprolactone triol or the tri-TEOS functionalized polyol/epoxide coatings as a function of the crosslinker

Table 9—Crosshatch Adhesion and Reverse Impact Resistance of the Di-TEOS Polyol Modified Tone Polyol Epoxide Coatings as a Function of the Ratio of the TEOS Polyol to the Parent Polyol

Coatings Properties	Epoxide, wt%	10/90	25/75	50/50	60/40	80/20
Crosshatch	60	5B	5B	5B	5B	1B
Adhesion	70	5B	5B	5B	3B	0B
Reverse impact	60	>80	>80	>80	>80	66
Resistance, lb/in.	70	>80	>80	>80	70	28

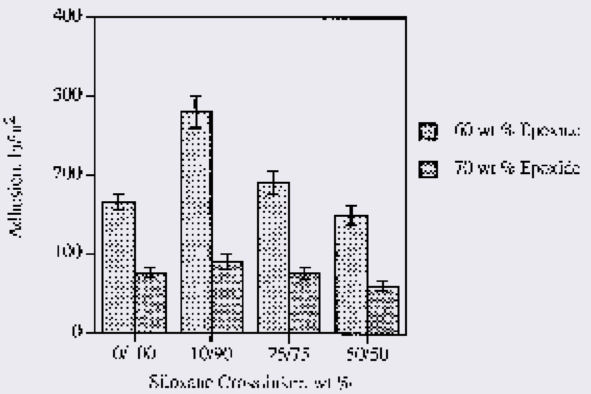

Figure 5—Pull-off adhesion of the di-TEOS polyol modified tone polyol/epoxide coatings as a function of the siloxane polyol.

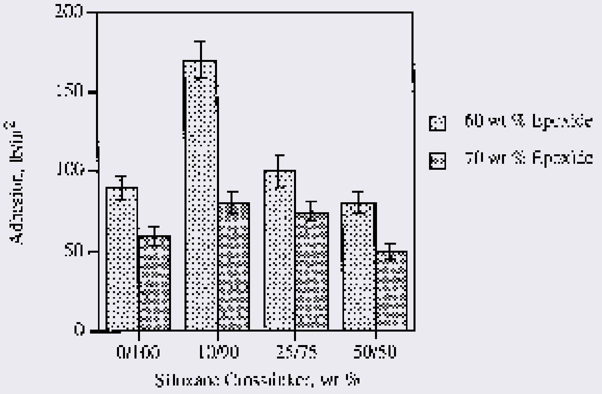

Figure 6—Pull-off adhesion of the tri-TEOS polyol modified caprolactone polyol/epoxide coatings as a function of the siloxane polyol.

Table 10—Crosshatch Adhesion and Reverse Impact Resistance of the Tri-TEOS Polyol Modified Tone Polyol Epoxide Coatings as a Function of the Ratio of the TEOS Polyol to the Parent Polyol

Coatings Properties	Epoxide, wt%	10/90	25/75	50/50	60/40	80/20
Crosshatch	60	5B	5B	5B	1B	1B
Adhesion	70	5B	5B	5B	1B	0B
Reverse impact	60	>80	>80	>80	50	16
Resistance, lb/in.	70	>80	>80	>80	16	8

Table 11—Surface Tension of the Coating Ingredients and the UV Coating Formulations

Ingredients	Surface Tension mN/m	Coating Formulations	Surface Tension mN/m
UVR-6105	34.1 ± 1.4	Caprolactone diol/Epoxide (40/60)	33.6 ± 1.3
Caprolactone diol	28.7 ± 1.4	Caprolactone diol/Epoxide (40/60) with addition of 0.5 wt% Silwet L-7604	27.4 ± 1.1
Di-TEOS functionalized caprolactone diol	23.4 ± 1.9	Di-TEOS polyol modified caprolactone Diol-epoxide (20/20/60)	29.7 ± 1.7
Tri-TEOS functionalized caprolactone diol	25.8 ± 1.8	Di-TEOS polyol modified caprolactone Diol-epoxide (20/20/60) with addition of 0.25 wt % Silwet L-7604	27.8 ± 1.5

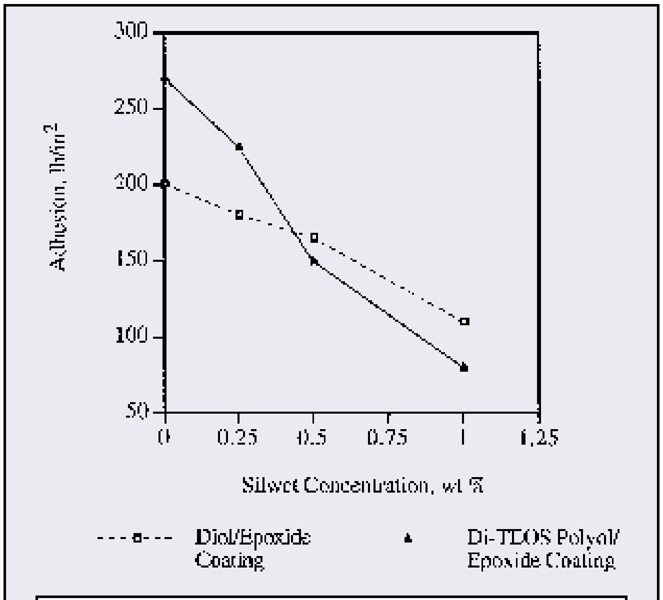

Figure 7—Pull-off adhesion of the UV coatings as a function of Silwet concentration.

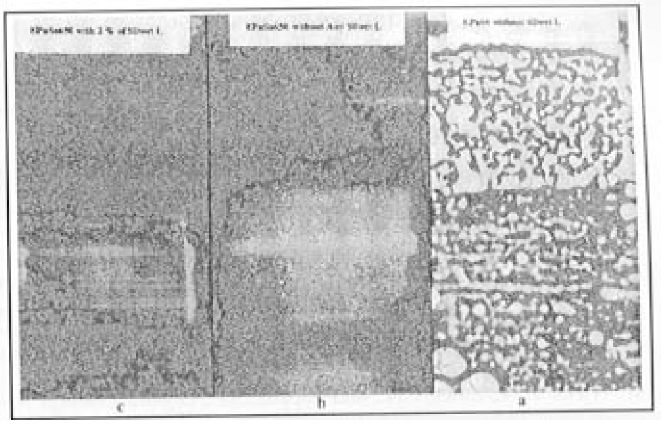

Figure 8—Effects of the di-TEOS functionalized polyol on the film formation: (a) without addition of Silwet™-L 7604 and any siloxane functionalized polyol; (b) with addition of 25 wt% of di-TEOS functionalized polyol; and (c) with addition of 0.25 wt% of Silwet™-L 7604 and 25 wt% di-TEOS functionalized polyol.

increased. Thus, the use of the agent for the coatings was kept to a minimum. Without use of the agent, the caprolactone diol/epoxide coating, however, was unable to wet the substrate as illustrated in *Figure* 8a. The coating modified with the di-TEOS functionalized polyol (25 wt% relative to the caprolactone polyol) only showed a few of the craters created on the surface (*Figure* 8b). After addition of only 0.25 wt% of the agent (half of the amount initially added), the modified coating did not show any craters (*Figure* 8c). Similarly, the ability to improve the wetting and spreading of the coatings was also observed for the tri-TEOS functionalized polyol.

Siloxane containing compounds have been demonstrated to have low surface tension.[13] The ability of the siloxane functionalized polyols to enhance the coating spreading on substrates and to reduce craters on the surface may be attributed to the ability of the siloxane functionalized polyols to reduce coating surface tension and make it more uniform. Hence, the surface tension of the coatings was measured. *Table* 11 shows the surface tension of the siloxane funtionalized polyols and the siloxane polyol modified coating formulations. The surface tension of the siloxane polyol modified caprolactone diol/epoxide coatings was much lower than the coating formulation without modification with the siloxane functionalized polyol. The reduction in the surface tension of the coating formulation may be correlated with the lower surface tension of the siloxane functionalized polyol than the unfunctionalized parent polyols. Thus, the TEOS functionalized polyols reduced the surface tension of the UV coatings formulations, decreased the need for added surface wetting agent, and consequently resulted in an increase in coating adhesion.

The di- and tri-TEOS functionalized caprolactone polyols were different from the parent caprolactone polyols. When the siloxane functionalized polyols were added to modify the caprolactone polyol/diepoxide UV coatings, both the flexibility of the polyols and the characteristics of the siloxane units were incorporated into the coatings system resulting in synergistic effect. The flexible chains of the siloxane functionalized polyols improved the impact resistance, and the siloxane units promoted multiple crosslinks increasing the MEK double rubs. In addition, the siloxane moieties also functioned as an adhesion promoter, viscosity reducer, and surface tension modifier. When the UV coatings were modified with the siloxane functionalized polyols, the resultant coatings had enhanced adhesion, low surface tension, and low viscosity.[10] The UV coatings modified only with caprolactone polyols, however, showed either low pencil hardness and MEK double rubs, or low adhesion and impact resistance. Therefore, modification of the caprolactone polyol/cycloaliphatic epoxide UV coatings with the siloxane functionalized polyols provided the coatings with a good overall balance of the coatings properties.

CONCLUSION

The di- or tri-TEOS functionalized caprolactone polyol has been used to modify caprolactone diol or triol/cycloaliphatic diepoxide UV coatings. The modification of the polyol-cycloaliphatic epoxide coatings with the siloxane functionalized polyols resulted in a significant enhancement of the pencil hardness, MEK double rubs, and adhesion in comparison with the unmodified coatings. In addition, the siloxane functionalized polyols also functioned as flexible crosslinkers increasing the toughness of the overall coatings. Thus, the siloxane functionalized polyol modified UV coating formulations afforded a better balance of the coating properties than unmodified coatings.

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