

# Surface Properties of Cationic Ultraviolet-Curable Coatings Containing a Siloxane Structure

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**ABSTRACT:** A polysiloxane diglycidyl ether was used as a comonomer of epoxy resins to obtain coatings through the ultraviolet curing technique. Notwithstanding its very low concentration (<1 wt %), the siloxane monomer caused a change in the surface properties of the films. Selective surface stratification was evidenced by X-ray photoelectron

spectroscopy analysis, and an interesting surface modification was achieved without changing the bulk properties of the films or the rate of polymerization. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 584–589, 2004

**Key words:** cationic polymerization; polysiloxanes; surfaces

## INTRODUCTION

The past 15 years has witnessed a tremendous resurgence of interest in all types of reactive silicone fluids for ultraviolet (UV)-curable coatings.<sup>1</sup> It is well known that the rapid development of silicone polymers is due to a number of highly desirable properties, including high thermal resistance and resistance to chemicals, ozone, and UV-induced degradation.<sup>2</sup>

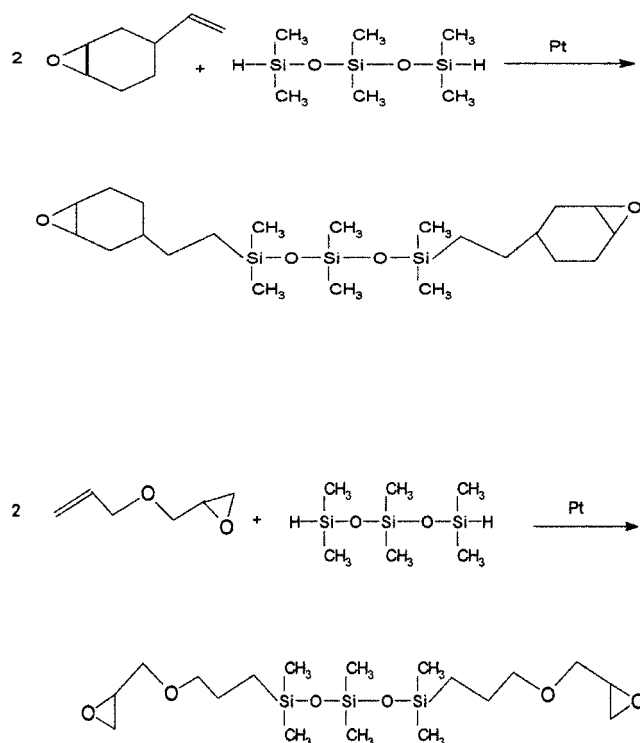
Moreover, the radiation curing technique is advantageous: the formulations are solvent free, the production rates are high, and the energy required is much less than for thermal curing. These advantages have led to the rapid growth of the technique in different fields, mainly in the production of films, inks, and coatings on different substrates but also in the fabrication of a variety of high-tech and electronic applications, such as printed circuit boards.<sup>3</sup> In UV curing, the cationic process, suitable for epoxy resins, vinyl ethers, and oxetanes, presents some advantages over the radical one,<sup>4</sup> in particular the lack of inhibition by oxygen, the low shrinkage of the products, the good mechanical properties of the UV-cured materials, and the good adhesion to various substrates. In addition, the monomers used are generally characterized by low irritation and toxicity properties.<sup>5</sup> Therefore, great effort has been focused on the preparation of epoxy-

functional silicone fluids; both glycidyl siloxanes and cycloaliphatic epoxy silicone derivatives have been prepared and characterized. Dicycloaliphatic polysiloxane oligomers can be readily synthesized by platinum-catalyzed hydrosilation of an epoxy compound bearing a vinyl group, such as 4-vinylcyclohexene oxide, with an appropriate  $\alpha,\omega$ -dihydrogen silane;<sup>6–8</sup> analogous diglycidyl ether polysiloxanes have been obtained by the hydrosilation of allyl glycidyl ether.<sup>9</sup> In Scheme 1, both synthetic routes are reported.

Photopolymerizable silicones, by virtue of their unique properties, are well suited for specific applications of the curing technique, such as ophthalmic devices, medical applications, optical fiber coatings, electronic circuits, gas membranes, release applications, and pressure-sensitive adhesives;<sup>10,11</sup> they have the advantages of softness, biological inertness, relatively good thermal stability, excellent dielectric properties, good substrate wettability, and permeability of gases.<sup>12</sup> The main disadvantage is that the dimethyl silicones are nonpolar and nonmiscible with other resins. Moreover, the onium-type photocatalysts, such as the iodonium salts, used in cationic curing are often also immiscible in the silicone media unless sufficient polar organofunctionality is designed into the silicone to render them compatible with the cationic catalyst.<sup>13</sup> Alternatively, a catalyst with low polarity can be used.<sup>14</sup>

Interesting results were obtained when low polarity curable products were used as comonomers in UV formulations: fluorinated epoxy monomers added in a very low amount (<1 wt %) into traditional epoxy systems changed the surface properties of the films,

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Scheme 1

making them hydrophobic and oleophobic. Pursuing this research line, we investigated the use of silicone epoxy monomer as a surface modifier. The behavior of its photopolymerization as a pure resin was also studied.

## EXPERIMENTAL

### Materials

The following monomers were used: 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexyl carboxylate (CE; UVR 6110, Dow-Union Carbide), 1,4-cyclohexanedimethanol diglycidyl ether (DGE; Aldrich, Milan, Italy), polysiloxane diglycidyl ether (SIOG; Coatosil 2810, Crompton Specialties Europe,  $M_n = 605$ ; Geneva, Switzerland). Their structures, as checked by  $^1\text{H-NMR}$ , are reported in Table I. The SIOG monomer presented this proton pattern:

$^1\text{H-NMR}$  (200 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 2.58 (d, 2H), 2.78 (t, 2H), 3.13 (m, 2H), 3.38–3.43 (m, 4H), 1.58 (m, 4H), 0.1 (s, 42H).

The photoinitiator [4(1-methylethyl)phenyl](4-methylphenyl) iodonium tetrakis (pentafluorophenyl) borate (Rhodorsil 2074, Rhodia, Saint-Fons, France) was used at 1 wt % in all of the formulations.

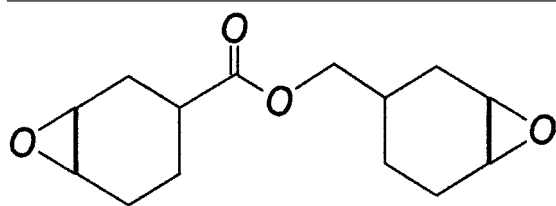
### Film preparation

We obtained the films by coating the photopolymerizable mixtures on a glass substrate. The curing reaction was performed in air with a fusion lamp (D bulb) with a radiation intensity on the surface of the sample of  $280 \text{ mW/cm}^2$  and a belt speed of 6 m/min.

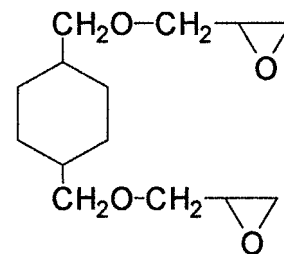
### Analyses and characterization

The kinetics of the photopolymerization were determined by Fourier transform infrared (FTIR) spectroscopy.

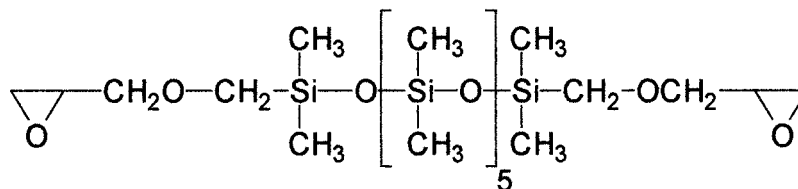
TABLE I  
Structures of the Monomers Used



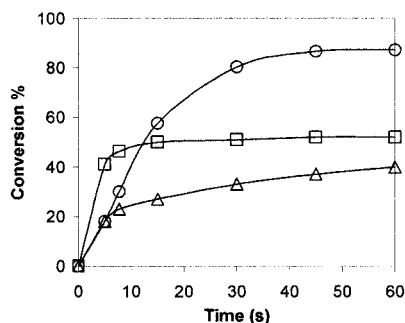
CE



DGE



SIOG



**Figure 1** Conversion curves versus time for (○) pure SIOG, (□) CE, and (△) DGE monomers.

copy. A KBr disk was coated with the photocurable mixture, and the reaction was followed at different irradiation times; in this case, we used a medium-pressure Hg lamp (Italquartz, Milano, Italy) with a light intensity of  $25 \text{ mW/cm}^2$ . The FTIR spectrometer used was a Genesis series ATI Mattson spectrometer (California).

The gel content of the films was determined by measurement of the weight loss after 20 h of extraction at room temperature with different solvents (chloroform and trichlorotrifluoroethane).

We performed a methyl ethyl ketone (MEK) double-rubs resistance test by rubbing an MEK-saturated cotton swab onto the cured film in a back-and-forth motion. The end point was reached when the erosion of the substrate surface was noted (ASTM D 3013). The film hardness was determined according to the ASTM D 3363 standard test.

The adhesion was assessed according to the ASTM D 3359 method (crosscut adhesion test).

Differential scanning calorimetry (DSC) measurements were performed with a Mettler DSC30 (Greifensee, Switzerland) instrument equipped with a low-temperature probe.

Dynamic mechanical thermal analyses (DMTA) were performed with a Rheometric Scientific MKIII (Leek, United Kingdom) instrument at a frequency of 1 Hz in the tensile configuration.

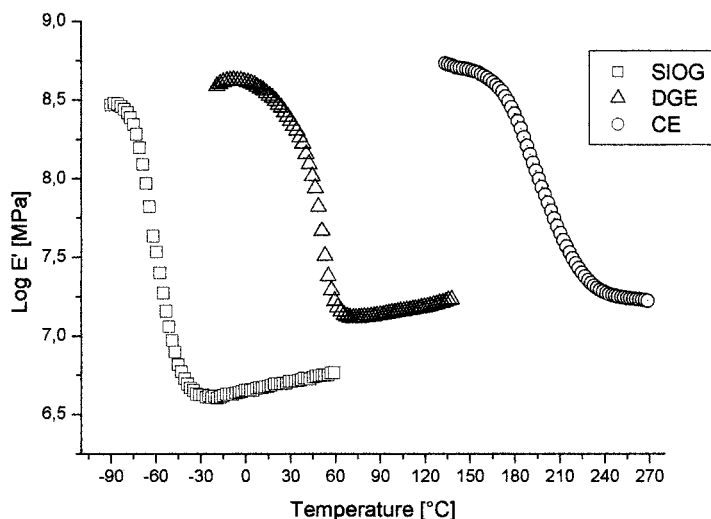
To investigate the surface properties of the films, they were peeled off the glass substrate. The sides were labeled as a glass side and an air side; contact-angle measurements were made on both sides.

Dynamic contact-angle measurements were performed with a Kruss DSA10 instrument equipped with a video camera; analyses were made at room temperature by means of the sessile drop technique. Three to five measurements were performed on every sample, and the values were averaged. The measuring liquid was bidistilled water ( $\gamma = 72.1 \text{ mN/m}$ ).

X-ray photoelectron spectroscopy (XPS) measurements were carried out on the films containing 0.2–1.0 wt % silicone additives by a VG Instrument electron spectrometer (New Jersey) with a Mg  $K\alpha_{1,2}$  X-ray source (1253.6 eV). The X-ray source in the standard conditions worked at 100 W, 10 kV, and 10 mA. The base pressure of the instrument was  $5 \times 10^{-10}$  Torr, and the operating pressure was  $2 \times 10^{-8}$  Torr typically. Pass energies of 100 and 50 eV were used for wide scans and narrow scans, respectively. We obtained depth profile information by running measurements on electrons taking off from the sample surface with angles of 90, 45, and 25°. According to the equation, sample depth ( $d$ ) is equal to  $3\lambda \sin \theta$ ;  $d$  values are lower when the take-off angle (TOA) is smaller. All data analyses (linear background subtraction and peak integration) were accomplished with VGX900x (Version 6) software. Binding energies were referenced to the C—H level at 285.0 eV.

## RESULTS AND DISCUSSION

Different films were prepared with SIOG homopolymeric systems made of the pure epoxy silicone resin,



**Figure 2**  $E'$  curves for the CE, DGE, and SIOG photocured films

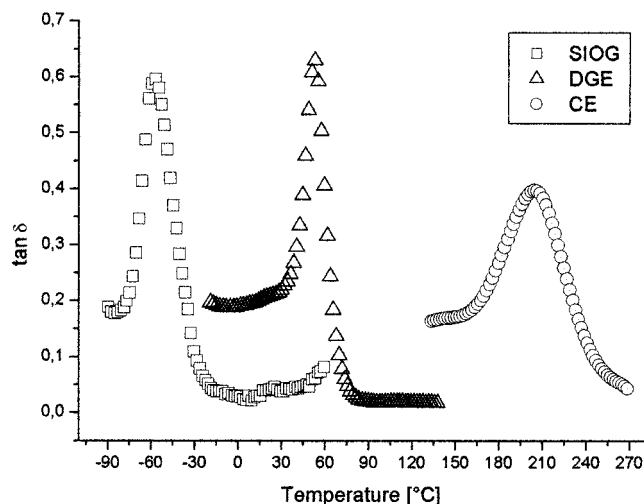


Figure 3 Tan  $\delta$  curves for the CE, DGE, and SIOG photocured films

and copolymer systems with epoxy resins such as CE and DGE were cured together with SIOG. Because of the low solubility of the latter, the silicone comonomer was always less than 1 wt % to obtain homogeneous and transparent films.

### Kinetic investigation

In Figure 1, the conversion curves versus time related to the three different epoxy monomers, CE, DGE, and SIOG, are compared. The curves were obtained by means of FTIR analysis after the decrease of the typical epoxy group peak at different wavelengths ( $760\text{ cm}^{-1}$  for CE,  $850\text{ cm}^{-1}$  for DGE, and  $800\text{ cm}^{-1}$  for SIOG) after different times of irradiation.

The rate of polymerization was determined from the slope of the profile; the plateau indicated the final epoxy-group conversion.

CE was more reactive than DGE both in terms of final conversion and the rate of polymerization because the cycloaliphatic epoxides, according to the literature,<sup>15</sup> are more reactive than the glycidyl ethers. The SIOG monomer had a slower rate of polymerization compared with that of CE but reached, after 60 s of irradiation, a total conversion of 90%, whereas CE stopped at 52% and DGE stopped at 40%.

The limited conversion of the CE and DGE resins has been attributed to the vitrification effect.<sup>16</sup> A rigid network builds up during the polymerization with a reduction in the mobility of the systems so that the epoxy groups cannot react further. In the case of the polymerization of the epoxy silicone, a soft and flexible film is expected, permitting the system to easily complete the reaction.

With the addition of small amounts of SIOG (always <1 wt %) in the epoxy DGE or CE monomers, the kinetics showed no change.

TABLE II  
 $T_g$  Values

Sample	$T_g$ ( $^{\circ}\text{C}$ )	
	DMTA	DSC
DGE	55	30
CE	190	170
SIOG	-60	-70

### Characterization of the UV-cured films

The networks were characterized by means of DMTA and DSC. As expected, the film based on the epoxy resins was glassy, whereas the silicone network was characterized by a strong flexibility and a very low glass-transition temperature ( $T_g$ ). The modulus ( $E'$ ) and the tan  $\delta$  curves are reported in Figures 2 and 3, respectively, for the three different UV-cured resins.

The  $T_g$  values, collected in Table II, explain the different kinetic behaviors previously described; when the network was softer, the epoxy conversion was nearly complete. The networks obtained in the presence of a low amount (0.1–1 wt %) of SIOG were also investigated; in this case, the presence of the additive did not show any effect on the  $T_g$  values. However, the surface properties were deeply affected by the presence of the comonomer. The contact angles of the pure DGE and CE films were around  $70^{\circ}$  both on the air side and the glass side; when the SIOG monomer was added to the curable products and the mixture was coated on a glass substrate, the wettability changed, as shown in Figures 4 and 5.

The data clearly show that the additive was effective only on the air side of the film, making it hydrophobic, whereas the side in contact with the substrate kept the same properties of the pure epoxy resin.

The contact-angle values on the air side depended on the additive concentration with an asymptotic behavior. The hydrophobicity reached by the addition of the silicone monomer was very high and close to that exhibited by the pure photocured SIOG. The contact-

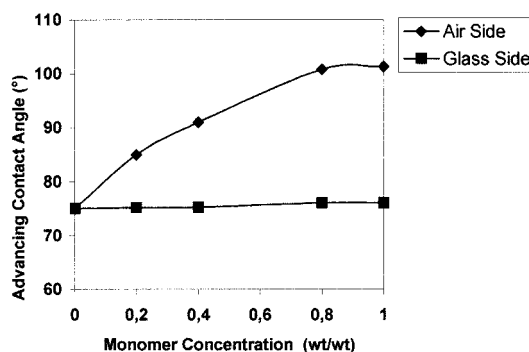


Figure 4 Surface effect of the SIOG monomer on DGE.

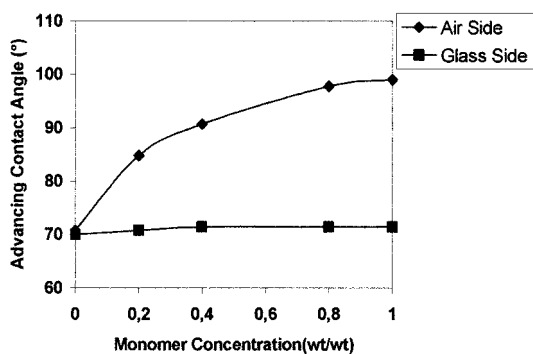


Figure 5 Surface effect of the SIOG monomer on CE.

angle value for this film was  $120^\circ$ , as reported in the literature for silicone materials.<sup>17</sup>

The surface modification of the films, evidenced by the measurement of their wettability, was confirmed by analysis of the surface composition of the systems through XPS. The composition of the film surface exposed to air is reported in the upper part of Table III for several films. In the lower part of Table III, the theoretical calculated values are reported.

The silicone content determined experimentally was one order of magnitude higher than the calculated ones. When the amount of the additive was 1 wt %, the Si/C ratio in the external layers of the films (TOA =  $25^\circ$ ) approached the value of the pure additive. At a different TOA, the Si/C ratio was different and showed the existence of a concentration gradient from the inner surface (higher TOA) to the very external surface of the film. On the substrate side, no silicone was detected.

Because the concentration of silicone in the external layers of the air side of the films was much higher than that in the bulk, one can easily explain the change of hydrophobicity revealed by the contact-angle measurements presented previously: the surface was mainly composed of the silicone comonomer. Therefore, the surface modification, as deeply discussed in the literature for polymer blends,<sup>18,19</sup> copolymers,<sup>20</sup> and polymeric solutions,<sup>21</sup> was a consequence of the surface segregation of the low surface component, in our case, the silicone epoxide.

The modification was permanent; the wettability was checked many weeks after the film preparation, and the contact-angle values were unchanged. This was due to the fact that the additive was covalently linked to the network as they took part in polymerization process.

To check the linking of the silicone additive to the epoxy network, we subjected the UV-cured films containing the SIOG monomer to an extraction with trichlorotrifluoroethane, which is a good solvent for the silicone derivative.  $^1\text{H-NMR}$  analysis was performed on the solution. No signals due to SIOG were present;

therefore, the presence of free monomer in the network was excluded.

The adhesion, hardness, and chemical resistance of the films were also investigated. The data are reported in Table IV.

The epoxy resin showed good adhesion to the substrate, and the silicone-based film was weakly adhesive, as well known from the literature.<sup>22</sup> Also, the hardness of the silicone network was poor compared to the pure epoxy resin, which was maintained in the presence of the additive. The MEK resistance was clearly better for the photocured silicone-based film.

When small amounts of SIOG were copolymerized with the epoxy resins, the films showed the same adhesion and the same hardness as the epoxy resins.

For adhesion onto glass, the results were in agreement with the data on the surface wettability (contact angle, XPS) and surface composition. In fact, the side of the film in contact with the glass substrate was always unchanged in the presence of SIOG; its wettability was equal to that of the pure CE or DGE resins, and no silicone was present in its chemical composition.

An increase in the MEK resistance was observed in the presence of the silicone additive, indicating a chemical resistance improvement induced by the presence of the epoxy silicone monomer.

TABLE III  
XPS Experimental and Calculated Data

Sample and TOA	Atomic ratio	
	Si/C	O/C
Experimental		
Pure CE		
25	0	0.41
45	0	0.44
90	0	0.39
Pure SIOG		
25	0.41	0.42
45	0.44	0.43
90	0.39	0.41
CE + 0.2 wt % SIOG		
25	0.17	0.31
45	0.13	0.31
90	0.094	0.30
CE + 0.4 wt % SIOG		
25	0.20	0.34
45	0.11	0.34
90	0.086	0.34
CE + 0.8 wt% SIOG		
25	0.28	0.38
45	0.18	0.36
90	0.13	0.34
CE + 1.0 wt % SIOG		
25	0.29	0.37
45	0.23	0.38
90	0.17	0.35
Calculated		
Pure CE	0	0.28
Pure SIOG	0.32	0.45
CE + 1.0 wt % SIOG	$3.2 \times 10^{-3}$	0.54



TABLE IV  
Properties of UV-Cured Films

Test	Pure CE	Pure SIOG	CE + 0.2 wt % SIOG	CE + 0.4 wt % SIOG	CE + 0.8 wt % SIOG
Crosscut test (%)	100	25	100	100	100
Pencil hardness	7H	B	7H	7H	7H
MEK resistance	200	>500	250	250	250

### CONCLUSIONS

A polysiloxane diglycidyl ether was polymerized by means of the UV curing technique and was also copolymerized in a low amount with the traditional epoxy resins CE and DGE.

SIOG was less reactive than the cycloaliphatic epoxide but gave an almost complete conversion of the epoxy group because of the high flexibility of the network.

Although CE and DGE formed glassy polymers characterized by high  $T_g$  values (190°C for CE and 55°C for DGE), SIOG gave a very soft network with a low  $T_g$  (-60°C).

When the SIOG was copolymerized with CE and DGE in very small amounts, no modification on the rate of polymerization or the bulk properties was achieved, although a deep modification of the surface properties of the UV-cured films was obtained. The SIOG monomer, having a low polarity, selectively migrated to the film surface exposed to air; the external layer of the films was, therefore, made highly hydrophobic, whereas the opposite side, in contact with the glass substrate, retained the same properties of the reference resins.

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