

Improvement of Surface and Moisture Resistance of Epoxy Resins with Fluorinated Glycidyl Ether

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ABSTRACT: Laurylfluoro glycidyl ether (FGE) was synthesized by laurylfluoro-1-pentanol with epichlorohydrin, and confirmed by FTIR and ^{13}C -NMR. The surface properties, moisture absorption, and mechanical properties of the epoxy resins modified by different content of laurylfluoro glycidyl ether acted as mono functional thinner were investigated by X-ray photoelectron spectroscopy (XPS), universal testing machine (UTM), dynamic mechanical thermal analyzer (DMTA), etc. The fluorine content at the surface of the modified resins were enriched greatly with the increase of the content of laurylfluoro glycidyl ether, and the hydrophobic property of the resins surface increased. When the FGE content was 10%, the fluorine content at the surface of

the modified epoxy resin reached to 66% and the water contact angle was 102° . The equilibrium moisture content of the resin dropped by 30% when the content of FGE was 5%. The mechanical properties of the epoxy resins modified by FGE were improved while the thermal mechanical properties changed little at low content of FGE (less than 3%). Further increase of FGE content in the epoxy resins may result in decreases of the mechanical and thermal mechanical properties of the resins. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 2528–2532, 2009

Key words: laurylfluoro glycidyl ether; surface properties; moisture resistance; epoxy resins

INTRODUCTION

Epoxy resins have been extensively used in many fields as matrices for composite materials, adhesives, constructions, coatings, and insulation materials for electric devices due to their excellent properties. However, some applications were limited to epoxy resins because of their brittleness and high water absorption. Recently, many attempts have been made to overcome the problems,¹ among which the uses of fluorinated monomers and oligomers for modification of epoxy resins were paid much attentions for the unique characteristics such as outstanding chemical resistance, low friction coefficient, low dielectric constant, low water absorption, and broad application temperatures, due to the introduction of fluorine into resins.^{2–7}

Griffith⁸ and Maruno and Nakamura⁹ reported the synthesis of fluorine-containing epoxy resins. The cure and transition behaviors of highly and partially fluorinated epoxy resins were investigated by Twardowski and Geil.¹⁰ Kasemura et al. showed that fluorinated aromatic compounds had been added to tetraglycidyl 4,4'-diaminodiphenylmethane (TGDDM) epoxy resins/4,4'-diaminodiphenyl sulfone (DDS) systems to reduce moisture sensitivity.¹¹ Sasaki and Nakamura¹² reported that perfluorobutenyloxyphthalic anhydride

cured bisphenol-A type epoxy could reduce the water absorption by 75%. Misaki et al. studied the effects of various kinds of aromatic and aliphatic glycidyl compounds as modifiers to improve the fracture properties of 4,4'-diaminodiphenyl methane (DDM) cured epoxy resins.¹³ Recently, some authors reported the synthesis and properties of a new fluorine-containing epoxy resin.¹⁴ However, so far there were few reports related to the synthesis and application of laurylfluoro glycidyl ether in epoxy resins.

In this study, laurylfluoro glycidyl ether was synthesized and characterized by NMR and FTIR. The improvement of the surface property and moisture absorption characteristics of bisphenol-A type epoxy resin were achieved via curing with the laurylfluoro glycidyl ether. The mechanical properties of the bisphenol-A type epoxy resin modified by laurylfluoro glycidyl ether were studied as well.

EXPERIMENTAL

Materials

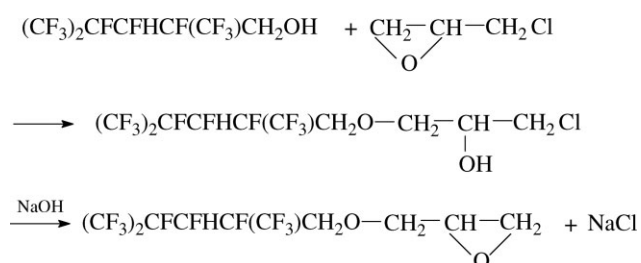
The laurylfluoro-1-pentanol was a colorless and transparent liquid with molecular formula of $(\text{CF}_3)_2\text{CFCFHCFCF}_3\text{CH}_2\text{OH}$ and a density of 1.6 g/mL, and was supplied by XEOGIA Fluorine-Silicon Chemical. Diglycidyl ether of bisphenol A (DGEBA) epoxy resin was produced by Lanxing Company. The epichlorohydrin, boron trifluoride ethyl etherate, and

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4,4'-Diaminodiphenylmethane (DDM) were analytical pure purchased from Beijing Yili Fine Chemical. Co. Ltd. of China.

Synthesis of laurylfluoro glycidyl ether

Laurylfluoro-1-pentanol (0.2 mol) and boron trifluoride ethyl etherate as initiator were added into a three-necked flask with stirring until the product became uniform. The flask was heated to 40–45°C, then epichlorohydrin (0.3 mol) was added dropwise within half an hour. After several hours, the intermediate product was separated by vacuum distillation. Sodium hydroxide saturated aqueous solution was added into the three-necked flask where the product was in. The temperature was controlled at 30–40°C for 3 h. Washed with water, the organic phase was detached and the water was removed by vacuum distillation. The product, namely laurylfluoro glycidyl ether (FGE), was obtained and stored in glass bottle. The reaction formula is as follows:



Sample preparation

Modified epoxy resins were obtained by adding different contents (1%, 3%, 5%, 10%) of fluorinated glycidyl ether (FGE) into bisphenol A type epoxy resin (DGEBA), then the castings were mixed with 27% DDM acting as curing agent. The castings were made by compression molding under a curing procedure of 80°C × 1 h + 150°C × 1 h. The samples for the characterization of moisture absorption or for dynamic mechanical thermal analysis (DMTA) were obtained by the same curing procedure.

Characterization and testing

FTIR spectrums were obtained using the 5DXC ThermoNicoletInstrument. Fourier transfer infrared spectrophotometer at a resolution of 4 cm⁻¹ with 64 co-added scans by casting thin film on KBr plates. ¹³C-NMR spectrum was recorded with a Bruker AV600 spectrometer using acetone as solvent and tetramethylsilane (TMS) as an internal standard.

X-ray photoelectron spectroscopy (XPS) spectra were measured with a Thermo Electron Corporation-ESCALAB 250 X-ray photoelectron spectrometer.

Water contact angle of the cured resins were obtained by contact angle measuring instrument (Dataphysics OCA20).

Moisture absorption

Moisture absorption of the cured resins was measured according to ASTM D570-98 as follows: three specimens, with a size of 60 mm × 6 mm × 2 mm, were dried in an oven until there was no weight change, and their weights were measured as *W_i* (average of three specimens). The accuracy of the electron balance used was ±0.1 mg. Then the specimens were immersed in distilled water bath at a constant temperature of 65°C. After different periods, the three specimens were taken out, wiped, and weighted as *W_t* (average of three specimens). The percent of moisture content (*M_t*) at time *t* was calculated using the following formula:

$$M_t = \frac{W_t - W_i}{W_i} \times 100\%$$

Mechanical properties

According to ASTM D2344-84 and ASTM D-790-00, tension and flexural testing were carried out on an INSTRON-1185 universal testing machine at a cross-head speed of 2 mm/min and 5 mm/min. Each data was the average of five specimens.

Dynamic mechanical thermal analysis

Dynamic mechanical properties of samples were taken on a Rheometri Scientific™ DMTA-V in three-point bend mode. All the specimens, with a dimension of 50 mm × 6 mm × 2 mm, were thermally scanned at a fixed frequency of 1 Hz and a heating rate of 5°C/min from room temperature to 260°C.

RESULTS AND DISCUSSION

Characterization of laurylfluoro glycidyl ether

The FTIR spectra of laurylfluoro glycidyl ether was shown in Figure 1. The strong absorption at 3400 cm⁻¹ due to -OH in laurylfluoro-1-pentanol becomes very small in laurylfluoro glycidyl ether. The appearance of absorptions attributed to epoxy at 800 cm⁻¹ and 970 cm⁻¹ and the absorption due to F-C in the range of 1200–1300 cm⁻¹, which overlap with absorption of epoxy reveals that ring closing reaction occurred. The results show that the product was fluorinated glycidyl ether.

¹³C-NMR measurement of the product was also performed. The signals in the range of 118–123 ppm were assigned to CF in laurylfluoro-1-pentanol, and

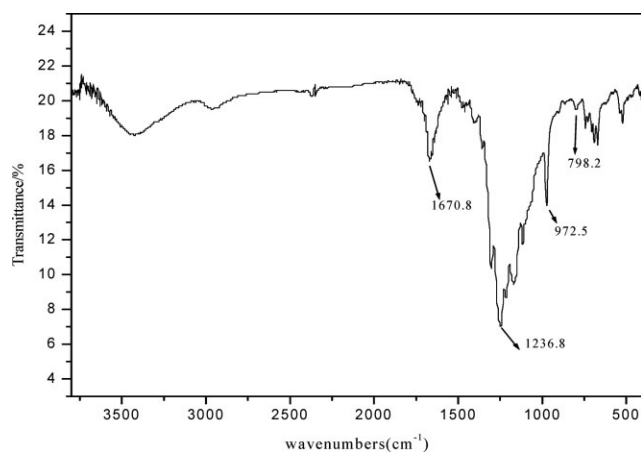


Figure 1 FTIR spectrum of laurylfluoro glycidyl ether.

the new chemical shift signals were at 45.8 ppm(a), 58.8 ppm(b), 68.5 ppm(c), and 118.5 ppm(d), respectively, as shown in Figure 2. In addition, the signal of $-\text{CH}_2-\text{Cl}$ appeared at 84.2 ppm, which revealed that partial organochlorine came into being. The results indicate that the product was glycidyl ether.

Moisture absorption properties of epoxy resin with FGE

The moisture absorption curves of the specimens measured according to ASTM D570-98 were shown in Figure 3. At the initial immersion stage, moisture content increased linearly with $t^{1/2}$ and then tended to an equilibrium state after 120 h. It can be seen from Figure 3 that the equilibrium moisture content and moisture absorption rate decreased with the increase of the usage of FGE. When the FGE are added into epoxy resins, fluorine elements at the surface of the resins were enriched which decrease the hydrophilic property of the resins, so the absorption of the water into the resins was difficult and the moisture content of the resins decreased.

The minimum equilibrium moisture content was obtained when the FGE content was 5% as shown in Figure 3. But with further increase of FGE content to 10%, the value of minimum equilibrium moisture content increased again. This may be caused by poor compatibility between FGE and DGEBA. With the increase of FGE, the microscopic phase separation has been created in resins for the FGE with a poor compatibility with epoxy resin, and the fluorine elements at the surface of the resins were enriched in the

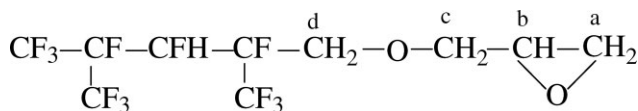


Figure 2 ^{13}C -NMR measurement of laurylfluoro glycidyl ether.

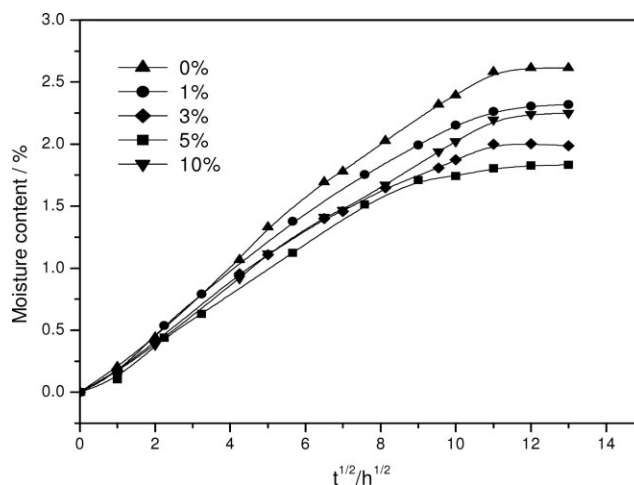


Figure 3 Moisture absorption curve of epoxy resins with different contents of FGE.

domain aggregated by polymers with more fluorinated groups, while the hydrophilic property of the domain with less fluorinated groups may increase, then equilibrium moisture content may increased.

According to Fick's second diffusion law, the diffusivity of water in epoxy resins can be obtained from the linear portion of $M_t \sim t^{1/2}$ curve. At the initial stage of absorption, following equation is tenable:

$$\frac{M_t - M_i}{M_m - M_i} = 4\sqrt{\frac{Dt}{\pi h^2}} \quad (1)$$

where M_i is initial moisture content, M_m is equilibrium moisture content, M_t is moisture content at discretionary time t , D is diffusivity, and h is the thickness of the specimen.

So, the diffusivity of water in epoxy resin can be calculated using the equation:

$$D = \pi(h/4M_m)^2[(M_2 - M_1)/(\sqrt{t_2} - \sqrt{t_1})]^2 \quad (2)$$

According to eq. (2), the diffusivities (D) of epoxy resins were calculated and listed in Table I, and the equilibrium moisture contents were also listed.

Surface properties of epoxy resin with FGE

Water contact angles of pure and modified epoxy resins were shown in Figure 4. It was revealed that

TABLE I
Moisture Parameters of Epoxy

Composites	Equilibrium moisture content (%)	Diffusivity (mm^2/s)
0% FGE	2.615	3.515×10^{-5}
1% FGE	2.320	3.645×10^{-5}
3% FGE	2.236	3.308×10^{-5}
5% FGE	1.833	4.151×10^{-5}
10% FGE	2.250	3.268×10^{-5}

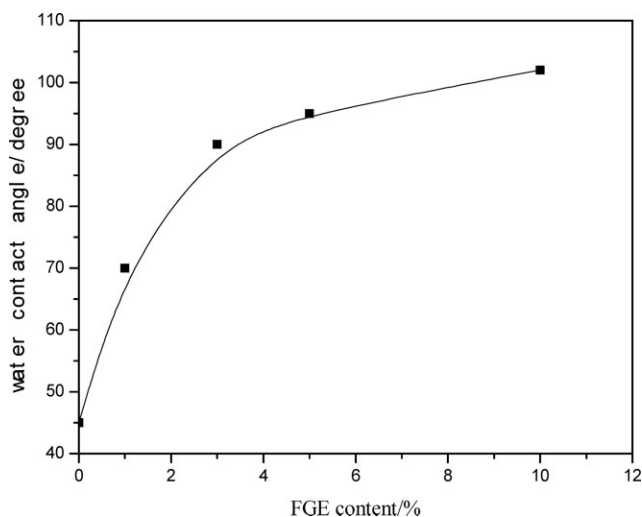


Figure 4 Water contact angles of epoxy resin with different contents of FGE.

the water contact angle increased with the increases of the FGE content, which is due to an increase of the fluorine groups on the modified epoxy resin surface. The water contact angle of pure epoxy resin was 45° and the value was 95° when the FGE content was 5%. Moreover, the water contact angle reached 102° with the FGE increased to 10%.

To understand the changes of moisture absorption property and the water contact angle of the epoxy resins modified by FGE, surface composition of the epoxy resins with or without of FGE were investigated by XPS, and the results were given in Table II. The fluorine content of the blends increased rapidly with the increases of the FGE content. When FGE content was 10%, the fluorine content was 66.16%, which is very close to the fluorine content of FGE, 68.7%. F-C chains in fluorinated glycidyl ether are incompatible with epoxy resin chains and migrate to surface of the resins, so fluorine elements at surface of the resins were enriched and surface energy of the resins were decreased, then water contact angle of the resins were increased obviously. Therefore, the moisture absorption properties of the epoxy resins modified by FGE decreased.

TABLE II
Surface Element Contents of Epoxy Resins with Different Content of FGE

Surface element	0% FGE	1% FGE	3% FGE	5% FGE	10% FGE
C	74	68	55	41.1	19.47
O	13.7	13.1	12.3	11.2	5.14
F	0	7.24	19.82	33.33	66.16
N	8.8	8.56	6.47	5.21	2.29

Mechanical properties of epoxy resin with FGE

Castings were made by epoxy resins with different content of FGE. Tension and flexural properties were investigated and the results are listed in Table III. The tensile strength of pure DGEBA cured with DDM was 58 MPa. When the content of FGE was less than 3%, tensile strength, tensile modulus, and flexural strength of the blends all increased, and at the same time elongation at break increased obviously. However, the mechanical properties of the blends began to decrease when the FGE content was increased to 5%. When the FGE content reached 10%, the tensile strength decreased rapidly to 38 MPa, elongation at break also falls off sharply, but the tensile modulus and flexural strength changed little.

FGE acted as a thinner of epoxy resin decreases cross-linking density and brittleness of the resin, so the break elongation of the modified epoxy resins were increases, while the tensile strength were increases at the same time for the cross-linking density decreases little at low content (less than 5%) of FGE. Superfluous fluorinated glycidyl ether has a poor compatibility with epoxy resin and the cross-linking density decreased rapidly which lead to the decrease of tensile strength at high content of fluorinated glycidyl ether.

Dynamic mechanical properties of epoxy resin with FGE

The effect of the FGE on transition temperature (T_g) of epoxy resins were investigated by DMTA. The temperature dependence of $\text{Tan}\delta$ of the resins were shown in Figure 5. T_g value was recorded as the peak value of the $\text{Tan}\delta$ curve. T_g value of epoxy castings were decreased with the increased content of FGE as seen in Figure 5. T_g value changed from 171°C to 165°C when FGE content was within 3%, just a change of 6°C . When FGE content was 5%, T_g value was 150.5°C . In this case, the changes of mechanical properties were little. T_g value dropped to 124°C when the FGE content raised to 10%. Simultaneously, the mechanical properties turned to worse. The reason may be that the fluorinated glycidyl ether was mono functional epoxy and acted as

TABLE III
Mechanical Properties of Epoxy Resin Castings

FGE content	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation (%)	Flexural strength (MPa)
0	58	2440	4.4	123
1%	60	3068	5.2	130
3%	65	3316	5.5	128
5%	55	2891	5.1	123
10%	38	3012	3.2	112

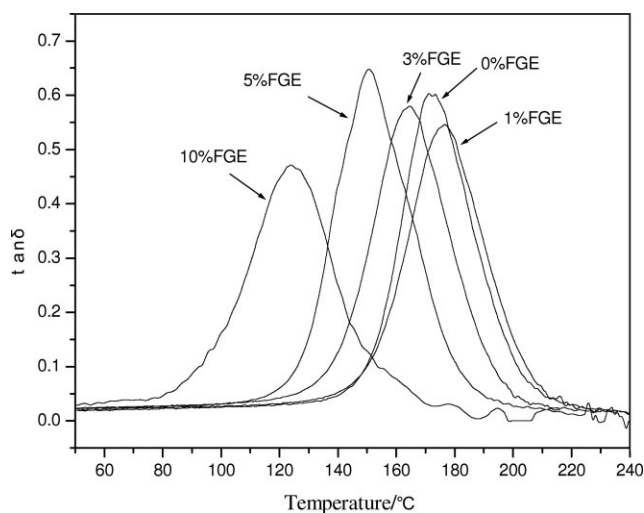


Figure 5 DMTA of epoxy resins with different content of FGE.

thinner for epoxy resins, and the cross-linking density of cured resins were decreased with the increase of FGE content, then the T_g of resins decreased.

CONCLUSIONS

Laurylfluoro glycidyl ether was synthesized by laurylfluoro-1-pentanol with epichlorohydrin, and confirmed by FTIR and NMR. The moisture absorption property and surface property of the epoxy resins were improved by laurylfluoro glycidyl ether. The fluorine content at the surface of the modified resins were enriched greatly with the increase of the content of laurylfluoro glycidyl ether, while the hydrophilic property of the resin surface were decreased rapidly. The equilibrium moisture content of the resin dropped by 30% when the content of laurylfluoro glycidyl ether was 5%. When the laurylfluoro

glycidyl ether ether content was 10%, the fluorine content at the surface of the modified epoxy resin reached 66% and the water contact angle was increased to 102°. The mechanical properties of the epoxy resins modified by laurylfluoro glycidyl ether were improved while the thermal mechanical properties changed little at low content of laurylfluoro glycidyl ether (less than 3%). The above results show that laurylfluoro glycidyl ether is a promising thinner for the formulate novel epoxy resins to balance the mechanical properties, thermal mechanical properties, moisture absorption property, and surface property of the epoxy resins.

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