Synthesis and Characterization of High-Performance Epoxy Resin Based on Disiloxane and 4,4′-Oxybis(benzoic acid) Ester

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ABSTRACT: Epoxy-terminated siloxane-contained resin (BCDS/OBBA-ETS) with high tensile strength and lap shear strength as well as good thermal stability was synthesized and characterized by ^{1}H-NMR and Fourier transform infrared spectroscopy. Carboxy-capped disiloxane-4,4′-oxybis (benzoic acid) ester oligomer (BCDS/OBBA) was firstly prepared from the reaction between 1,3-bis(chloromethyl)-1,1,3,3-tetramethyl-disiloxane and 4,4′-oxybis(benzoic acid) (OBBA) in *N,N*-dimethylformamide in the presence of triethylamine. Then, the BCDS/OBBA oligomer was reacted with epichlorohydrin to obtain the title BCDS/OBBA-ETS resin. Cured with liquid polyamide L-651, or diethylenetriamine, the mechanical and thermal properties as well as the lap shear strength of the BCDS/OBBA-ETS resin were evaluated. The results indicated that the BCDS/OBBA-ETS resin exhibited good thermal stability below 200°C, and the glass transition temperature (T_g) was about 64°C after cured with L-651. The tensile strength of same cured BCDS/OBBA-ETS resin was 27.46 MPa with a stain at break of 42.11%, and the lap shear strength for bonding stainless steel was 18.59 MPa. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 2485–2491, 2012

Key words: adhesion; silicones; mechanical properties; thermal properties

INTRODUCTION

As one of the most important industrial resins, epoxy resin has been widely used for laminating, adhesive, surface coating and semiconductor encapsulation. However, the applications of conventional epoxy resins are quite limited in some fields where more flexibility, better moisture resistance, and higher adhesion are required.[1,2] On the other hand, polysiloxane is well known for its superior properties in flexibility and thermal stability. Hence, to combine the polysiloxane segments into the epoxy resins naturally becomes the focus in the research of developing the new type of epoxy resin.[3,4] Many researches have been carried out, and it is reported the modified epoxy resins exhibited the superior properties in flexibility, thermal stability, dimensional stability, or physical strength as good as to meet the requirements of electronic and information sectors, aerospace components, and composites.[5–10]

Reviewing the literatures, synthesis of silicon-containing epoxides, which are curable by their own or blended with other epoxy resins, may be summarized into two approaches. One method is to introduce the siloxane into the epoxy compounds by using hydrosilylation reaction.[11,12] In this method, the linear or block structure of polymer determines that α,ω-dihydrogen-capped siloxane should be used, in which the two active hydrogen atoms are at the ends of siloxane chain. However, as we known, 1,1,3,3-tetramethyl-disiloxane is the origin of such siloxane.[13] This disiloxane can be prepared by hydrolyzation of dimethylclorosilane, a low-boiling point fraction of silane monomers from Si and chloromethane with a very small percent and is very expensive. Another method to synthesis the silicon-containing epoxides is utilizing the transetherification between alkoxyl silane and glycidol or the condensation of hydroxyl-terminated siloxanes with epoxy resin or epichlorohydrin.[14–16] In this method, it is remarkable that the Si—O—C bond in the products is well known as unstable in moisture. Moreover, the phase separation would take place if the molecular weight of polysiloxane segments was adequately large.

Moreover, many literatures about functional silicon-containing polyester block polymers were reported
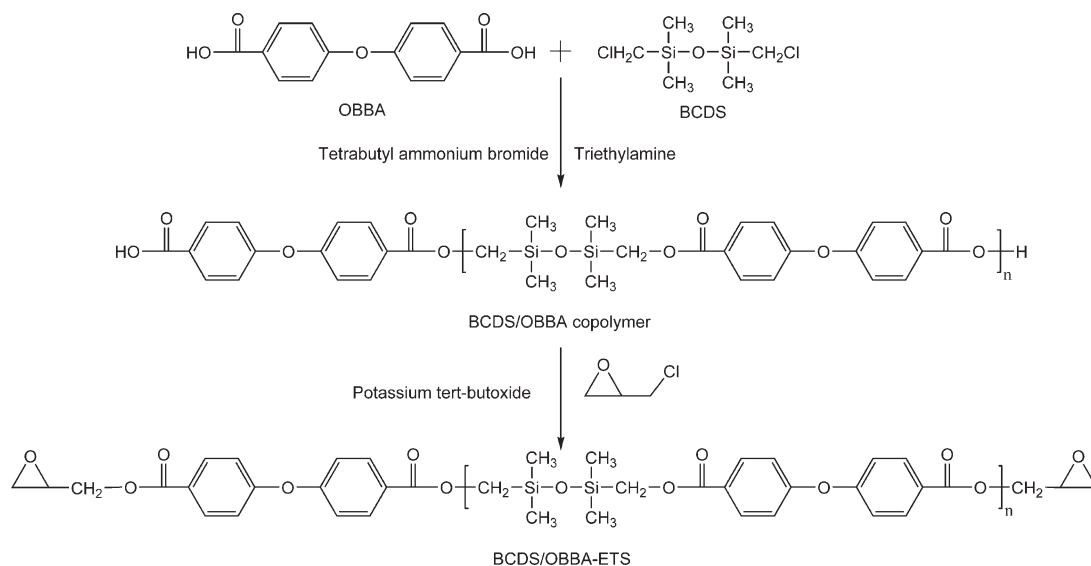
Scheme 1 Synthesis process of the BCDS/OBBA oligomer and BCDS/OBBA-ETS.

during the last decades, which had been reviewed by Kricheldorf,[17] and various synthetic strategies have been postulated, including some undergoing in the melt.[18–20] However, a common feature of these strategies is remarkable, namely that the expensive functional disiloxanes, such as 1,1,3,3-tetramethyl-disiloxane, 1,3-bis(chloropropyl)-disiloxane, 1,3-bis(aminopropyl)-disiloxane, and 1,3-bis(hydroxypropyl)-disiloxane, were commonly selected as the starting materials and played the indispensable roles in preparation of α,ω-difunctional-group-containing silicone copolymer. Therefore, it is urgently imperative to develop a convenient method to synthesize the silicon-containing epoxides with high-performance adhesive ability, thermal stability, and moisture resistance for further application.

In this study, we will address on a new strategy to synthesize a novel epoxy resin containing disiloxane and aromatic diacid ester backbone. As shown in Scheme 1, a commercial available disiloxane, 1,3-bis(chloromethyl)-1,1,3,3-tetramethyl-disiloxane (BCDS), was selected as the starting compound. By synthesizing the intermediate of carboxy-capped disiloxane-4,4′-oxybis(benzoic acid) ester oligomer (BCDS/OBBA), this strategy will allow us to prepare the epoxy-terminated siloxane ester (BCDS/OBBA-ETS) under a relatively mild reaction conditions.

EXPERIMENTAL

Materials

4,4′-Oxybis(benzoic acid) (OBBA; Alfa Aesar, Ward Hill, USA), and epichlorohydrin (Nanjing Chemical Reagent, Nanjing, China) were analytic grade. Low-molecular weight polyamide L-651 (the condensation product of tung oil acid dimer and diethylenetria-mine (DETA), with an amine value of 140 g equiv^{-1}) was industrial grade, whilst Epoxy-618 (bisphenol A type phenolic epoxy resin, with an epoxide equivalent per weight (EEW) value of 196 g equiv^{-1}) was commercial product. Both of them were purchased from Wuxi Resin Factory of Blue Star New Chemical material (Wuxi, China). Solvent and other reagents: potassium tert-butoxide (Alfa Aesar, Ward Hill, USA) and tetrabutyl ammonium bromide (Sinopharm Chemical Reagent, Shanghai, China) were analytic grade, and also DETA, triethylamine, N,N-dimethylformamide (DMF), and 1,1,2,2-tetrachloro-ethane, but purchased from Nanjing Chemical Reagent (Nanjing, China). Chloromethyl-dimethyl-chlorosilane with a purity of 99% was received from Mingtian Chemical (Liyang, China). All reagents were used without further treatment.

Characterizations

Fourier transform infrared spectroscopy (FTIR) was performed on a Nexus 870 FTIR (Thermo Nicolet Co., Boston, USA), and KBr plate was used as the support matrix. ^{1}H-NMR was carried out on a Bruker DPX-300 NMR spectrometer (Bruker, Oxford, GB) at 25°C, with CDCl$_3$ or DMSO-d_6 as solvent and TMS as internal standard.

Thermogravimetric analysis (TGA) was conducted in air or nitrogen atmosphere, from 25 to 800°C at a heating rate of 20°C min^{-1} and analyzed with a STA 449 C Jupiter simultaneous thermo analyzer (Netzsch, Germany). To study the thermal curing behavior of the resin, the differential scanning calorimetry (DSC) analysis was employed in nitrogen atmosphere at a heating rate of 20°C min^{-1} and analyzed with the same analyzer.

Dynamic mechanical analysis (DMA) was carried out on a 01dB-Metravib Dynamic Mechanical Analyzer (01dB-Metravib, Limonest, France) with DMA mode between −100°C and 250°C. Heating rate was 3°C min^{-1}, and the frequency was 10 Hz. The shear strength and tensile strength was measured with a drawing speed of 5 mm min^{-1} at 25°C by an omnipotence material testing instrument, Instron 4466 (Instron Co., Grove city, USA).

Synthesis of BCDS

BCDS was prepared by hydrolysis of chloromethyl-dimethyl-chlorosilane in 50 wt % aqueous ethanol solution as described in the literature.[21] Colorless liquid of BCDS was obtained on distillation with a boiling point of 70–72°C at 3 mmHg.

Synthesis of the BCDS/OBBA oligomer

As described in Scheme 1, the BCDS/OBBA was prepared by the direct reaction of BCDS and OBBA in DMF, in the presence of triethylamine.

A 53.84 g (0.21 mol) of OBBA, 27.6 g (0.27 mol) of triethylamine, 3.07 g (0.0095 mol) of tetrabutyl ammonium bromide, and 150 mL of DMF were added into a 500 mL four-necked flask equipped with a mechanical stirrer and a condenser. After heated to 140°C, 23.11 g (0.1 mol) of BCDS was slowly added dropwise, and then standing for 12 h with continuous stirring at 130°C. The organic liquid, the serum of filtration undertaken at ambient temperature, was treated by reduced pressure for removal of DMF. The residue was dissolved in 300 mL of ethyl acetate and washed twice with 200 mL of 5 wt % hydrochloric acid and 500 mL of 10 wt % NaCl solution, respectively. The organic layer was dried by anhydrous Na$_2$SO$_4$. After the solvent was evaporated at reduced pressure, 41.05 g of BCDS/OBBA oligomer was obtained. It was used in next step without further purification. The structure of the obtained product was confirmed by ^{1}H-NMR. The acid value was evaluated by titration of NaOH ethanol solution.

Synthesis of the BCDS/OBBA-ETS

A 37.49 g of BCDS/OBBA oligomer (acid value 2.229 mmol g^{-1}) and 9.10 g (0.08 mol) of potassium tert-butoxide were dissolved in 200 mL of anhydrous dimethyl sulfoxide in a 500 mL four-necked flask and stirred at 30°C for 1 h. Thereafter, 2.07 g (6.4 mmol) of tetrabutyl ammonium bromide and 15.5 g (0.17 mol) of epichlorohydrin were added and reacted for 6 h at 80°C, then cooled down. At room temperature, the reaction mixture was dissolved in 300 mL of ethyl acetate and then washed with water and 10 wt % NaCl solution, respectively. The

TABLE I
The Curing Conditions of the BCDS/OBBA-ETS and Epoxy-618

Sample	Curing agent (wt % of epoxy)	Curing conditions (°C)
BCDS/OBBA-ETS	L-651 (15.0)	110°C/4 h + 150°C/2 h
Epoxy-618	L-651 (36.0)	70°C/4 h + 110°C/4 h
BCDS/OBBA-ETS	DETA (3.0)	110°C/4 h + 150°C/2 h
Epoxy-618	DETA (10.0)	70°C/4 h + 110°C/4 h

organic layer was dried by anhydrous Na$_2$SO$_4$, and the solvent was removed by reduced pressure. Finally, 37.10 g of transparent brown liquid with high viscosity was obtained. The softening point of the product was around 5°C.

Investigating of the EEW of the BCDS/OBBA-ETS

The EEW value refers to the grams of epoxy resin containing an equivalent epoxy group. In this article, it was tested by ^{1}H-NMR, using 1,1,2,2-tetrachloroethane as the internal standard material. Proper amount of 1,1,2,2-tetrachloroethane and the obtained BCDS/OBBA-ETS were added to CDCl$_3$ for ^{1}H-NMR test, and the EEW of BCDS/OBBA-ETS was calculated according to the following equation:

$$EEW = (A \times W_x \times M)/(A_x \times W_y)(g\,equiv^{-1}) \quad (1)$$

where the A_x is the integral area of the protons at 2.91 ppm and 2.74 ppm of —CH$_2$ in the oxirane of BCDS/OBBA-ETS; A_y is the integral area of the protons at 5.97 ppm of 1,1,2,2-tetrachloroethane; W_x is the weight of BCDS/OBBA-ETS; W_y is the weight of 1,1,2,2-tetrachloroethane; M is the molecular weight of 1,1,2,2-tetrachloroethane.

Curing procedure of epoxy resins

L-651 (the condensation product of tung oil acid dimer and DETA with an amine value of 140 g equiv^{-1}) or DETA was served as a curing agent to crosslink the BCDS/OBBA-ETS resin for the mechanical properties test, and Epoxy-618 was also tested for comparison.

Different ratio of the resin to curing agent was tested, and the ratio with maximal lap shear strength was selected for farther test. The curing temperature was determined by DSC tracing of the respective epoxy/(curing agent) compositions. The curing conditions were listed in Table I.

Mechanical properties testing

The resins were cured at the conditions mentioned in Table I to form a flat membrane with a thickness of 0.5 mm. Then the membrane was cut in a
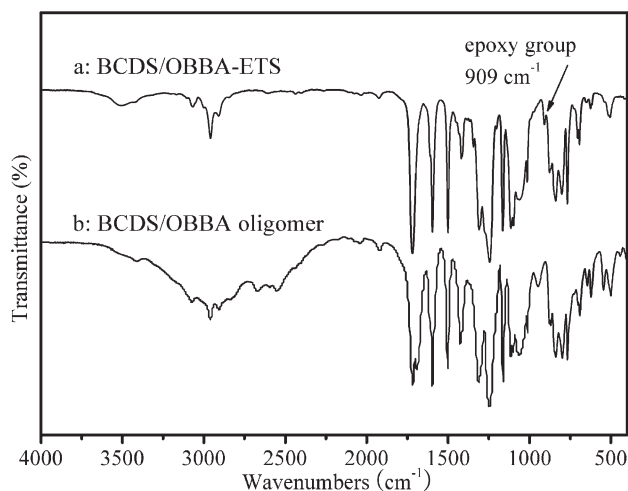
Figure 1 FTIR spectra of BCDS/OBBA-ETS (a) and BCDS/OBBA oligomer (b).

dumbbell-shaped mold to prepare the samples which were used to test the tensile strength, strain at break, and Young's Modulus.

At the same time, stainless steel plates were used to test the adhesive properties (lap shear strength). The stainless steel plates (70 mm × 20 mm × 1.5 mm) were burnished and degreased with a commercial detergent. Then they were ultrasonically cleaned with acetone and distilled water and dried in oven at 70°C for 5 h. The mixture of the BCDS/OBBA-ETS resins and curing agent was uniformly applied to the cleaned overlapping surface with an area of 20 mm × 15 mm. The plates were clamped with clips and cured at the same conditions as listed in Table I. The lap shear strength was calculated as the ratio between the maximum force and the bonding area. The tensile strength and the lap shear strength were tested with an omnipotence material testing instrument Instron 4466 at a drawing speed of 5 mm min^{-1} at 25°C.

RESULTS AND DISCUSSION

Characterization of the BCDS

The purity of obtained BCDS was 97% by GC, and the refractive index n_D^{25} was 1.4385. ^{1}H-NMR (CDCl$_3$, δ, ppm): 2.76 (2H, —Si—CH$_2$Cl), 0.24 (6H, Si—CH$_3$).

Characterization of BCDS/OBBA oligomer

In this work, the synthesis of BCDS/OBBA oligomer was referred to Refs. 22–24. Triethylamine was tried as the base in the reaction for preparation of the carboxy-capped BCDS/OBBA oligomer in DMF. To obtain a carboxy-capped ester, the molar amount of OBBA should be larger than that of BCDS.

The structure of the product was confirmed by ^{1}H-NMR and FTIR [see Fig. 1(b)] spectrum.

FTIR (KBr) V_{max} (cm^{-1}) 2960, 1717, 1691, 1596, 1501, 1425, 1312, 1246, 1162, 1064, 947, 839, 799, 692, and 500; ^{1}H-NMR (DMSO-d_6, δ, ppm): 12.94 (0.3H, —COOH), 7.95–8.00 (3.5H, in Ph), 7.11–7.16 (3.5H, in Ph), 3.93 (2H, —Si—CH$_2$—O), and 0.18 (6H, —Si—CH$_3$).

The area of the peaks at 7.15 ppm (in Ph) and 3.93 ppm (—Si—CH$_2$—O) was selected to calculate the average molecular weight of the oligomer. The number-averaged molecular weight, M_n, was 811 g mol^{-1} when the molar ratio of OBBA and BCDS was 0.21 : 0.1, and the average polymerization degree n in Scheme 1 was 1.33.

Additionally, for further confirming the molecular weight of oligomer, the acid value of the BCDS/OBBA product (0.21 : 0.1 for the molar ratio of OBBA to BCDS) was measured by titration with 0.08473 mol L^{-1} of NaOH ethanol standard solution. It was 2.229 mmol g^{-1}, thereby the average molecular weight of the oligomer was 897 g mol^{-1}, consistent with that by ^{1}H-NMR method.

Characterization of the BCDS/OBBA-ETS

The BCDS/OBBA-ETS with epoxy ending groups was synthesized, as shown in Scheme 1, by the reaction of BCDS/OBBA oligomer with excess amount of epichlorohydrin in DMSO. To obtain a resin with low EEW value, BCDS/OBBA oligomer with an acid value of 2.229 mmol g^{-1} was used. Different bases, such as NaOH, K$_2$CO$_3$, and potassium tert-butoxide, were tried in the preparation of BCDS/OBBA-ETS, and the EEW value of the obtained BCDS/OBBA-ETS was evaluated with the ^{1}H-NMR method. The results indicated that, compared with NaOH and K$_2$CO$_3$, which leaded to high EEW value (EEW > 1000 g equiv^{-1}), potassium tert-butoxide was the most suitable one for yielding low EEW value.

The BCDS/OBBA-ETS prepared by using potassium tert-butoxide was analyzed by FTIR [shown in Fig. 1(a)] and ^{1}H-NMR (shown in Fig. 2).

FTIR (KBr) V_{max} (cm^{-1}) of BCDS/OBBA-ETS: 3507, 2958, 1719, 1595, 1500, 1419, 1309, 1244, 1164, 1062, 909, 839, 767, 692, and 505.

^{1}H-NMR (CDCl$_3$, δ, ppm): 8.01–8.11 (4.1H, in Ph), 7.04–7.07 (4.1H, in Ph), 3.98 (2.0H, —Si—CH$_2$—O), 3.36 (0.6H, —CH in oxirane), 2.91 and 2.74 (1.2H —CH$_2$ in oxirane), and 0.24 (6H, —Si—CH$_3$).

The FTIR spectrum of the obtained BCDS/OBBA-ETS [Fig. 1(a)] was compared with BCDS/OBBA oligomer [Fig. 1(b)] in Figure 1. The disappearance of the peak at 1691.9 cm^{-1}, and the peaks from 3300 cm^{-1} to 2500 cm^{-1} of —COOH group in Figure 1(b) indicated the complete reaction of the carboxy group in BCDS/OBBA oligomer with epichlorohydrin. The
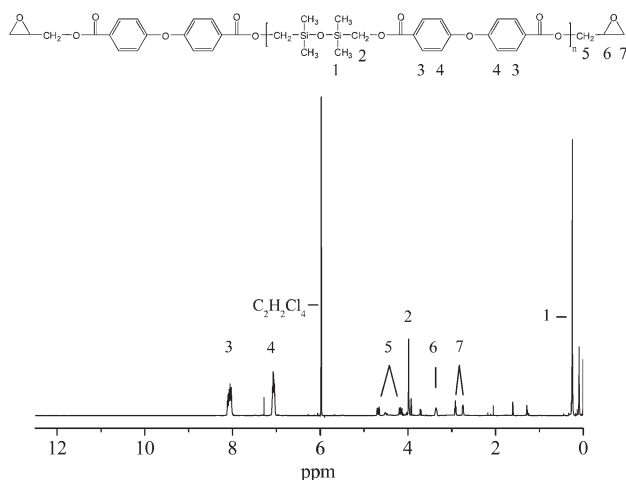
Figure 2 ¹H-NMR spectrum (in CDCl3) of the BCDS/OBBA-ETS.

Figure 4 DMA storage modulus and tan δ curves of the BCDS/OBBA-ETS cured with L-651.

new absorption peak at 909.3 cm^{-1} in Figure 1(a) indicated the formation of epoxy group.

In Figure 2, the peaks at 7.04–7.10 ppm and 8.01–8.11 ppm were attributed to the protons of phenyl group, whilst those at 2.74 ppm, 2.91 ppm, and 3.36 ppm were to the protons of epoxy group. Peaks at about 0.24 ppm were ascribed to the protons of —Si—CH$_3$. The peak at 5.97 ppm (**H**s of 1,1,2,2-tetra-chloroethane) was used to calculate the EEW according to eq. (1). As a result, EEW was 667 g equiv^{-1}. These results indicated that BCDS/OBBA-ETS as expected was successfully prepared.

Thermal behavior and thermal stability of the BCDS/OBBA-ETS

The thermal stability is one of the important properties for the adhesive used at a relative high temperature. Here, the thermal stability of the cured BCDS/OBBA-ETS resin was investigated by TGA at a scan-
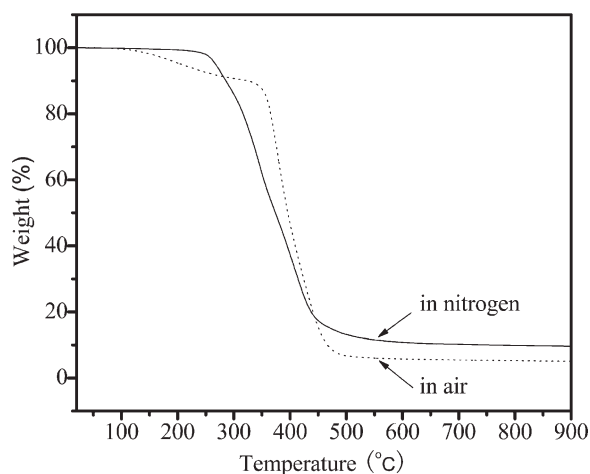

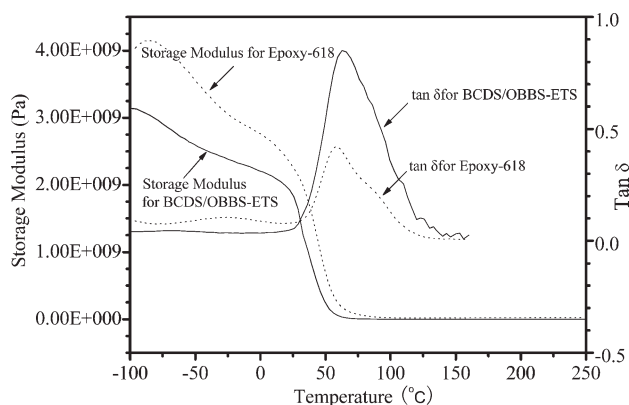Figure 3 TGA analysis curves of the BCDS/OBBA-ETS cured with L-651.

ning rate of 20°C min^{-1} in nitrogen atmosphere and air, respectively. The results are shown in Figure 3.

As shown in Figure 3, after cured with L-651, Td$_5$ (decomposition temperature at 5% weight loss) of cured network of BCDS/OBBA-ETS: Epoxy-618 investigated in nitrogen atmosphere was 264°C, but 239°C in air. It indicated that below 200°C, BCDS/OBBA-ETS exhibited good thermal stability. At the same time, the residue weight retention at 800°C for the BCDS/OBBA-ETS investigated in nitrogen and air was 9.86% and 5.82%, respectively.

The TGA analysis curves of the BCDS/OBBA-ETS cured with DETA (not shown) was almost the same to the resin cured with L-651. The dynamic mechanical analysis (DMA) of the BCDS/OBBA-ETS and Epoxy-618 was carried out to get more details about their thermal properties. The DMA curves of the resins cured with L-651 are shown in Figure 4.

As shown in Figure 4, the storage modulus of these epoxy resins at low temperature (25°C) showed no obvious difference in the range of 1.82–2.27 GPa, and the value of BCDS/OBBA-ETS was a bit lower. The glass transition temperature (T_g, the peak temperature of the loss tangent) of the cured BCDS/OBBA-ETS was 64°C, very closed to that of the cured Epoxy-618, 59°C. The height of tan δ peak indicated the ratio of viscous components to elastic components. It was assumable that the increasing height was associated with the higher segmental mobility and more relaxing species. As shown in Figure 4, the curves of tan δ indicated that the network of Epoxy-618 resin was tighter

TABLE II
The Mechanical Properties of the Epoxy Resins Cured with L-651

Sample	L-651 (wt % of epoxy)	Strain at break (%)	Tensile strength (MPa)	Young's Modulus (MPa)
BCDS/OBBA-ETS	15.0	43.6	27.46	606.91
Epoxy-618	36.0	14.2	37.61	793.92

TABLE III
The Shear Strength of the BCDS/OBBA-ETS and Epoxy-618 Blends Cured with L-651

BCDS/OBBA-ETS : Epoxy-618 (weight/weight)	L-651 (wt % of total resins)	Shear strength (MPa)
100/0	15.0	18.59
75/25	20.4	19.23
50/50	25.4	19.92
25/75	30.6	9.61
0/100	36.0	7.26

than BCDS/OBBA-ETS resin, and the cured Epoxy-618 was more brittle than the cured BCDS/OBBA-ETS resin. It could be attributed to the flexible $-C(O)OCH_2Si(Me)_2OSi(Me)_2CH_2OC(O)-$ segments in the BCDS/OBBA-ETS polymer structure.

Mechanical properties of the BCDS/OBBA-ETS

The BCDS/OBBA-ETS could be cured with polyfunctional amine, and the mechanical properties were studied in this work. As for comparison, the mechanical properties of a bisphenol A type epoxy resin Epoxy-618 (EEW = 196 g equiv^{-1}) were also studied. The results are listed in Table II.

In Table II, after cured with L-651, we could find that the tensile strength of the cured BCDS/OBBA-ETS resin was 27.46 MPa, which was about 73% of that of the cured Epoxy-618 resin (37.61 MPa). At meanwhile, the Young's Modulus of the cured BCDS/OBBA-ETS resin was 606.91 MPa, about 76% of the cured Epoxy-618 resin (793.92 MPa). The strain at break of BCDS/OBBA-ETS and Epoxy-618 was 43.6% and 14.2%, respectively. These results imply that the BCDS/OBBA-ETS was more flexible, stemming from the flexible $-C(O)OCH_2Si(Me)_2OSi(Me)_2CH_2OC(O)-$ backbone.

The BCDS/OBBA-ETS resin, or its blend with deferent ratios of Epoxy-618 resin, was cured with proper amount of L-651 (15 parts of L-651 per 100 parts of BCDS/OBBA-ETS and 36 parts of L-651 per 100 parts of Epoxy-618) or DETA (3 parts of DETA per 100 parts of BCDS/OBBA-ETS and 9 parts of

TABLE IV
The Shear Strength of the BCDS/OBBA-ETS and Epoxy-618 Blends Cured with DETA

BCDS/OBBA-ETS : Epoxy-618 (weight/weight)	DETA (wt % of total resins)	Shear strength (MPa)
100/0	3.00	22.15
75/25	4.75	23.55
50/50	6.50	24.32
25/75	8.25	11.80
0/100	10.00	7.93

DETD per 100 parts of Epoxy-618). The results of shear strength for bonding stainless steel plates are listed in Tables III and IV.

As shown in Table III, after cured with L-651, it could be found that the maximal shear strength of the pure BCDS/OBBA-ETS was 18.59 MPa, whereas for the blends with BCDS/OBBA-ETS : Epoxy-618 ratios of 75/25, and 50/50, they were 19.23 MPa, 19.92 MPa, respectively. Obviously, these data were much larger than 7.26 MPa and 9.61 MPa, corresponding to the pure Epoxy-618, and the blend of 25/75 BCDS/OBBA-ETS and Epoxy-618. When cured with DETA, the shear strength results listed in Table IV could also show the similar tendency to Table III. According to the above results, we think the overall mechanical properties of BCDS/OBBA-ETS resin are good enough for adhesive application.

CONCLUSIONS

A novel BCDS/OBBA-ETS containing disiloxane and OBBA ester backbone was developed in this work, and the structure was confirmed by ^{1}H-NMR and FTIR. The thermal stability of the cured BCDS/OBBA-ETS was tested, and the results of which showed that the BCDS/OBBA-ETS had good thermal stability below 200°C. The mechanical property test showed that the BCDS/OBBA-ETS had high tensile strength, excellent flexibility, and adhesive property, and it was suitable for adhesive application.

1,3-Bis(chloromethyl)-tetramethyl-disiloxane is easier available and much cheaper than the gamma difunctional disiloxane, such as 1,3-bis(chloropropyl)-tetramethyl-disiloxane. This work significantly enriches the ideas for synthesis of new silicone epoxy resin with good adhesive ability and flexibility.

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