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Properties' improvement of epoxy resin using prepolymers prepared from diisocyanates and 3,9-dihydroxyethyl-3′,9′-dibenzyl-1,5,7,11-tetraoxaspiro(5,5)undecane

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Abstract

The prepolymers were prepared by the reaction of 3,9-dihydroxyethyl-3′,9′-dibenzyltetraoxaspiro(5,5)undecane (**2**) with 4,4′-diphenylenemethane diisocyanate (MDI) or hexamethylene diisocyanate (HDI) for improving the properties of the epoxy resin. The volume changes of the curing system was measured. The effects of the prepolymers on the conversion of epoxy group and thermal stability of the epoxy resin were studied. Glass transition temperature (T_g) of the modified matrix slightly decreased as the content of the prepolymers in the resin system increased. Two peaks appeared on derivative thermal gravimetry (DTG) curves of the modified epoxy resin. The one at the lower temperature was due to the decomposition of the polymeric linkages produced from the prepolymers, the other belonged to the decomposition of epoxy resin. The thermal stability of the modified matrix decreased because of the prepolymers as modifiers. However, the residual carbon of the modified matrix had an increasing tendency with quantity of prepolymer added. The strength of the modified matrix slightly decreased, but the elongation increased. When the mixture of E-51, prepolymers and BF_3-H_2NEt were used as adhesives, the tensile strength and shear strength were improved. The factors influencing the adhesive strength were investigated

1. Introduction

Volume expansion during the cationic double ring-opening polymerization of spiro orthocarbonates and spiro orthoesters is an attractive phenomenon. Many efforts have been made for applications of these compounds in a various fields [1, 2]. For example, 3,9-dimethylene-1,5,7,11-tetraoxaspiro(5,5)undecane was used as one component of the dental material; the adhesive fracture energy was seven times higher than in the case of only poly(methyl methacrylate) being used [3]. During studying the carbon fiber composites by using a mixture of epoxy resin and spiro orthocarbonate **1**, it was found that the work of carbon fiber pulling out of the resin matrix was increased while shear strength did not decrease, and even slightly increased [4]. However, the addition of spiro orthocarbonate or spiro orthoester into epoxy resin often caused the decrease of flexture strength and glass transition temperature (T_g) of the matrix. It was thought that the former may be related to the incomplete polymerization of spiro orthocarbonate; the latter was attributed to low T_g of polycarbonate produced from polymerization of spiro orthocarbonates. In order to improve these properties, the prepolymers prepared from **2** and diphenylenemethane diisocyanate (MDI) or 1,6-hexamethylene diisocyanate (HDI) were used as modifiers instead of only **2**. Then, the thermal and mechanical properties of the matrix modified with prepolymers were investigated. In comparison with spiro orthocarbonate used in modifying epoxy resin, a more

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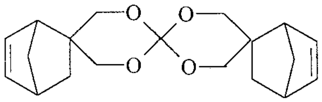
homogeneous three-dimensional structure of the matrix modified with prepolymers was formed.



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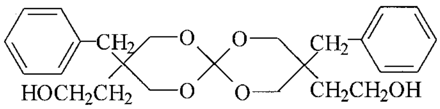

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2. Experimental

2.1. Materials

BF_3-H_2NEt complex and bisphenol-A type epoxy resin were purchased from Aldrich Chemical Co. and Shanghai Resin Co. (trade name E-51), respectively. 3,9-Dihydroxyethyl-3′,9′-dibenzyl-1,5,7,11-tetraoxaspiro(5,5)undecane (2) was synthesized according to the method described in our previous work [5]. Prepolymers were prepared by the reaction of **2** with MDI or HDI [6]. The chemical structures of the epoxy resin and prepolymers are shown in Table 1.

2.2. Preparation of test pieces

E-51 and prepolymer at various weight ratios, 3 wt% of BF_3-H_2NEt (to total weight of E-51 and prepolymer), were homogeneously mixed. Test pieces with dimension of 90×1×2 mm were prepared by putting the mixture in the cage between polished steel plates, then heating at 140°C for 4 h. Before the measurements, the test pieces were annealed at 100°C for 12 h.

The tensile strength, modulus and elongation were performed on Shimadzu DSC-5000 Instron with the displacement rate of 5 mm/min. All the values were the averages of five measurements.

2.3. The measurement of adhesive tensile strength and shear strength

The surfaces of the steel adherends were polished, then washed with acetone. For the measurements of adhesive tensile strength, the adherends were cylinders with a diameter of Φ25 mm and a holder. For measurements of shear strength, the adherends were rectangular steel plates with dimensions 100×20×2 mm. The adhesives prepared from E-51, prepolymers and BF_3-H_2NEt were homogeneously coated on the full surface of one steel cylinder, or the surface of 15×20 mm at the end of one rectangular steel plate, then another one was put on it. The tightly fixed adherends were put into the oven, which was preheated to 140°C. After 4 h, they were gradually cooled down to room temperature. Tensile strength and shear strength were measured on a ZDM-9000/91 Instron with the displacement rate of 6 mm/min. All the values were the averages of five measurements.

2.4. The measurement of thermal properties

The samples for measuring T_g and thermal stability were prepared in the same way as that for measuring mechanical properties. T_g was measured on a Perkin-Elmer DSC-2 at a heating rate of 10°C/min. The thermal decomposition temperatures of the matrix were measured on a Perkin-Elmer Thermal Gravimetry (TG)-2 type instrument at a heating rate of 10°C/min in helium atmosphere.

2.5. Conversion measurement of epoxy group

BF_3-H_2NEt (3 wt% of prepolymer and E-51) was added into the mixture of E-51 and prepolymer at various weight ratios. After being homogeneously mixed, the viscous liquid was put between two KBr plates. The curing reaction was carried out at 140°C for 2 h. IR measurement was performed on a Shimadzu IR-440 Instrument. Based on the decrease of peak height at $\upsilon 913\ \mathrm{cm}^{-1}$ corresponding to epoxy group, and the peak of benzene ring at $\upsilon 1610\ \mathrm{cm}^{-1}$ used as standard, the conversion of epoxy group can be calculated according to Eq. (1) [7,8].

$$\alpha = \frac{(A913/A1610)_0 - (A913/A1610)_t}{(A913/A1610)_0} \times 100\% \qquad (1)$$

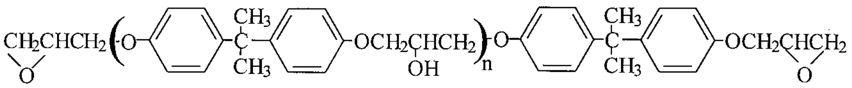
where subscripts 0 and t mean start time and reaction time at t, respectively.

2.6. The measurement of volume changes during curing process

The volume changes of the modified epoxy resin during the curing process were measured according to the procedure described in Ref. [9]. Brief description is as follows: a mixture of E-51, prepolymer and cure agent was filled into the emulsoid rubber tube under vacuum, then the rubber tube was closed with a fine metal wire, and it was put into a dilatometer. The change of the height of silicone oil in the capillary was read using the cathetometer, indicating the volume change of the resin mixture during the curing process.

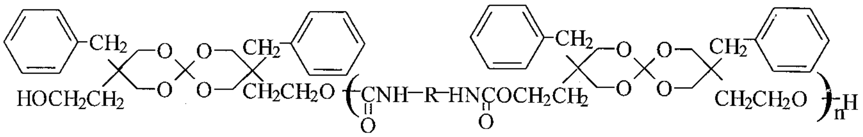
Table 1
Chemical structures of epoxy resin and prepolymers

Epoxy resin

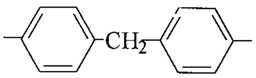


(Shanghai Resin Co.,
Trade name: E-51
Epoxy value: 0.48-0.54 mole of epoxy group/100 g resin)

Prepolymers



3 R=



a. Mn = 1030 (n = 1)
b. Mn = 1630 (n = 2)
c. Mn = 2390 (n = 3)

4 R = $\left(CH_2\right)_6$

a. Mn = 1010 (n = 1)
b. Mn = 1540 (n = 2)
c. Mn = 2180 (n = 3)

The ratio of volume change (β) can be calculated according to Eq. (2).

$$\beta = \frac{\pi r^2 h}{w/d} \tag{2}$$

In Eq. (2), r was the radius of the capillary tube; h was the height change of oil surface; w and d were the weight and density of the resin mixture.

3. Result and discussion

The curing behavior of the epoxy resin modified with prepolymers was investigated in another paper [6]. In fact, complete conversion of the epoxy group was impossible because the isolation effect of the crosslinked network caused the unreacted epoxy group difficulty in encountering each other. In order to clarify the effect of the prepolymer on T_g of the matrix, the mixture of epoxy resin, the prepolymer and boron fluoride-ethyl amine complex was cured at 140°C for 2 h; the result is shown in Fig. 1. The conversion of the epoxy group increased as the content of the prepolymer increased (see Fig. 1). Possibly, the unreacted prepolymer molecules remained highly mobile, and were easier to attach to the epoxy group, then react with it, even though the crosslinked network was essentially established.

The addition of prepolymers into the epoxy resin changed the structure, thus affecting the properties of

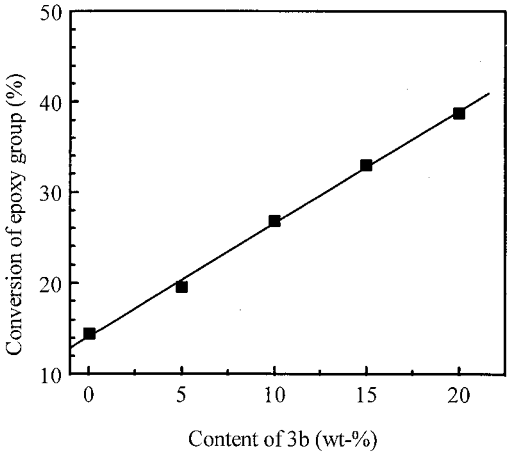


Fig. 1. The effect of **3b** concentration on conversion of epoxy resin. Conditions: temperature, 140°C; time, 2 h; 3 wt% of BF_3–H_2NEt as cure agent.

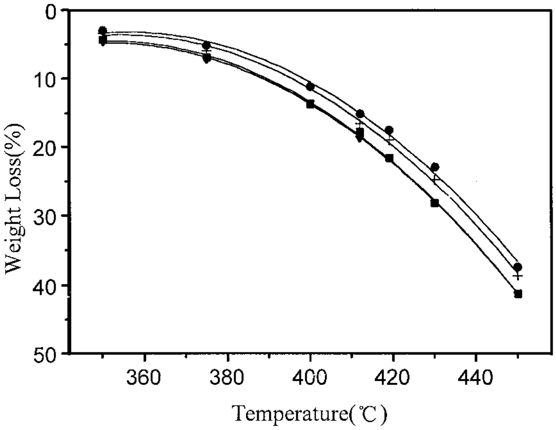


Fig. 3. The relationship between decomposition temperature and weight loss. Conditions: temperature, 140°C; time, 4 h; 3 wt% of BF_3–H_2NEt as cure agent; heating rate, 10/min. (●) 10 wt% of **3b**; (■) 20 wt% of **3b**; (+)10 wt% of **4b**; (▽) 20 wt% of **4b**.

the matrix. T_g is a measure of physical heat resistance of polymer materials. In general, the polycarbonates formed from cationic ring-opening polymerization of spiro orthocarbonate had low T_g. Therefore, a big decrease of T_g of the matrix prepared from epoxy resin and spiro orthocarbonate was observed in many cases. However, when the matrix was modified with prepolymer **3b** or **4b**, the T_g slightly decreased as the content of the prepolymer increased. The following two factors increasing T_g must be considered: (1) the introduction of iminoester linkage of the prepolymers would strengthen the interaction among macromolecules; (2) ring-opening polymerization of compound **2** with volume expansion could reduce the free volume of the polymer network, especially after the crosslinking network was essentially established, because it will restrict the rotation of the polymer chain segments.

The thermal decomposition behaviors are shown in Figs. 3, 4 and Table 2. Thermal stability of the matrix decreased gradually with the increase of the prepolymer **3b** or **4b** content in the curing system (see Fig. 2). However, almost no difference of the decomposition temperature between **3b** and **4b** at the same weight loss (especially before 20% of weight loss) and the same content of prepolymers indicated that the thermal stability of the matrix was mainly determined by type of linkages. The carbonate ester and iminoester linkages are not as stable as the ether linkage produced by the polymerization of the epoxy group.

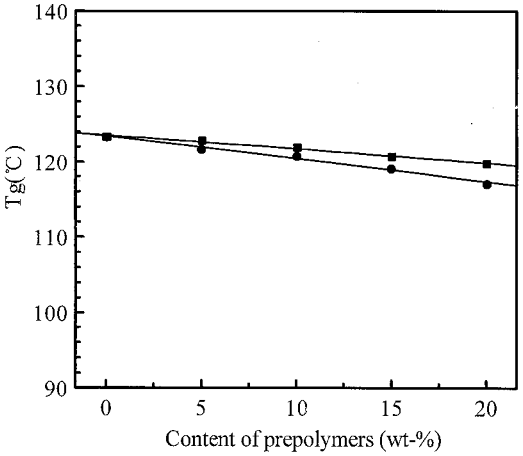


Fig. 2. The effect of prepolymer **3b** (■) and **4b** (●) concentration on T_g of epoxy resin matrix. Conditions: temperature, 140°C; time, 4 h; 3 wt% of BF_3–H_2NEt as cure agent.

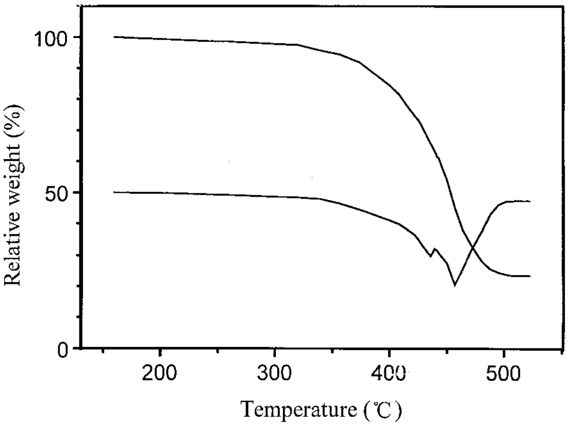


Fig. 4. DTG and TG curve of the matrix modified with 20 wt% of **3b**. Conditions, temperature, 140°C; time, 4 h; 3 wt% of BF_3–H_2NEt as cure agent; heating rate, 10°C/min.

Table 2
TG and DTG data of the epoxy resin matrix

Composition			
E-51 (wt%)	Prepolymer (wt%)	T_{max} [b] (°C)	W_r [c] (wt%)
E-51 (0)		465	48.0
E-51 (90)	**3b** (10)	464	22.0
E-51 (80)	**3b** (20)	463	28.5
E-51 (90)	**4b** (10)	456	22.4
E-51 (80)	**4b** (20)	455	30.3

[a] Conditions: temperature 140°C; time: 4 h; 3 wt% of BF_3-H_2NEt; heating rate: 10°C/min.

[b] T_{max}: maximum value of decomposition temperature related to epoxy resin on DTG curve.

[c] W_r: residual carbon calculated based on the maximum values of weight loss on TG curve.

The decomposition process of the matrix modified with and without prepolymer was examined by TG/DTG Instrument. Only one peak appeared on DTG curve of the epoxy resin. However, DTG curve of the matrix modified with prepolymers showed two peaks (see Fig. 4); one peak at lower temperature was due to decomposition of the polymeric linkages produced from prepolymer. The other was related to epoxy resin. The maximum values of decomposition temperature related to epoxy resin are listed in Table 2. The T_{max} of the modified matrix was lower then that of the epoxy resin matrix (see Table 2), indicating the occurrence of copolymerization between epoxy group and spiro orthocarbonate group. However, the prepolymer **4b** had slightly bigger effect on T_{max} than **3b** had (see Table 2). This may reflect the difference of decomposition mechanism between E-51/**3b** and E-51/**4b**. By examination of residual carbon (see Table 2), which was defined as the weight percentage of the residue at around 500°C to initial weight of the matrix, comparison with the residual carbon of the pure epoxy resin, a big decrease of the residual carbon for the matrix modified with the prepolymer, was obtained. However, the matrix modified with 20 wt% of **3b** or **4b** had higher residual carbon than the matrix containing 10 wt% of prepolymers had. The former was the result of copolymerization between the epoxy group and spiro orthocarbonate. The latter may be attributed to high crosslinking density of the E-51/prepolymer (20 wt%) matrix. As we mentioned, each prepolymer molecule had more than two units of compound **2**, thus the prepolymer could act as a crosslinking agent.

Epoxy resin has been extensively used as an adhesive. For an application view of spiro orthocarbonate, the effect of the prepolymers on the adhesive properties of the epoxy resin was investigated. When the samples were ruptured, resin residue could be found generally on both the surfaces of the two adherends, indicating that the matrix was broken. Only in a few cases did all of the matrix adhere onto the surface of the one adherend. The tensile and shear strengths at break between two adherends were measured. The results are shown in Figs. 5 and 6. It is observed that the tensile strength and shear strength slightly increased as the content of the prepolymers in the matrix increased (see Figs. 5 and 6). As we know, compound **2** underwent double ring-opening polymerization with expansion in volume. The addition of prepolymer **3** or **4** into the epoxy resin system would

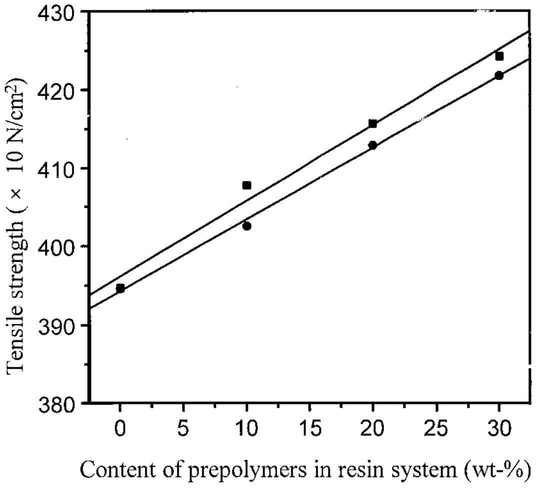


Fig. 5. The effect of **3b** (■) and **4b** (●) concentration on adhesive tensile strength. Conditions: temperature, 140°C; time, 4 h; 3 wt% of BF_3–H_2 NEt as cure agent; rate, 6 mm/min.

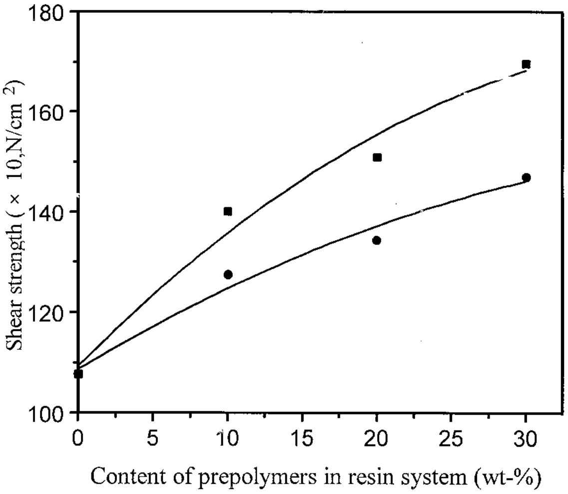


Fig. 6. The effect of **3b** (■) and **4b** (●) concentration on adhesive shear strength. Conditions, temperature, 140°C; time, 4 h; 3 wt% of BF_3–H_2Et as cure agent; rate, 6 mm/min.

Table 3
The effect of content of prepolymer **3b** on volume change of the curing system[a]

3b (wt%)	0	5	10	12	15	100
E-51 (wt%)	100	95	90	88	85	0
β^b (%)	−4.05	−3.74	−3.30	−3.25	−2.90	+ 4.12

[a] Conditions: temperature: 120°C; time: 6 h; 3 wt% of BF_3-H_2NEt as cure agent.
[b] (+) Expansion; (−) shrinkage.

reduce the shrinkage of the curing system. This was confirmed by the results listed in Table 3. The greatest the addition of prepolymer **3b** into the curing system, the less the volume shrinkage (see Table 3). Therefore, the polymerization of prepolymer **3** or **4** during the curing process, especially after the formation of three-dimensional network, could reduce the stress between joints. This is why the addition of prepolymer into epoxy resin enhances the adhesive strength. The results shown in Fig. 7 verified further that adhesive strength increased as volume shrinkage decreased. In fact, it is not necessary to add enough prepolymer **3** or **4** for compensating completely the shrunken volume of epoxy resin during the curing process. The very important point is to compensate the volume change of the curing resin system after the crosslinking reaction occured. In addition, in comparison with the pure epoxy resin, a greater homogeneous three-dimensional network structure was formed because more epoxy groups were taking part in the cure reactions. Possibly, the iminoester group of prepolymers was also contributive to increasing adhesive strength.

The prepolymers studied in this research were capped with compound **2**. In our experiment conditions, it was not found that the molecular weights of the prepolymers obviously affected the adhesive properties of the epoxy resin. However, in comparison with E-51/**4b**, slightly better improvement of adhesive strength was observed for E-51/**3b** (see Figs. 5 and 6). This must be attributed to the presence of diphenylene-methane group in **3**. Better compatibility of the prepolymer **3** with epoxy resin will produce a more homogeneous matrix, thus reducing the decrease of tensile strength of the matrix. It is interesting to note that elongation of the modified matrix increased slightly (see Table 4). This is probably attributed to

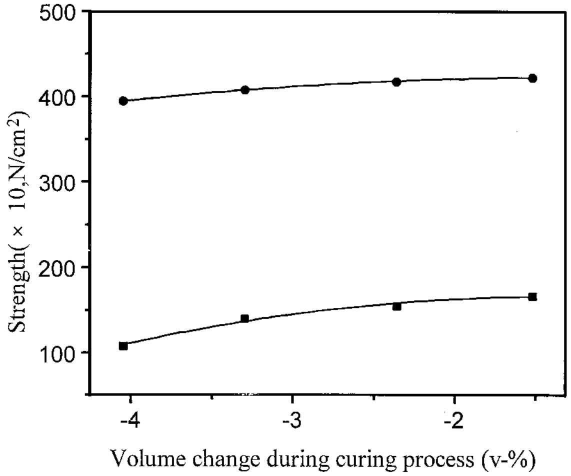


Fig. 7. The effect of volume change during curing process on adhesive tensile strength (●) and adhesive shear strength (■). Conditions: E-51/**3b**; 3 wt% of BF_3–H_2NEt as cure agent; temperature, 140°C; time, 4 h; rate, 6 mm/min.

Table 4
Mechanical properties of the matrix modified with prepolymer **3b** and **4b**[a]

Composition				
E-51 (wt%)	Prepolymer (wt%)	Yang modulus ($\times 10^4$, N/cm^2)	Flextural strength ($\times 10^3$, N/cm^2)	Elongation (%)
100	–	9.44	8.49	8.50
90	**3b** (10)	8.84	8.23	8.88
90	**4b** (10)	8.77	8.08	8.95

[a] Conditions: temperature: 140°C; time: 4 h.

the presence of polyurethane and polycarbonates in the matrix.

4. Conclusion

Higher conversion of the epoxy group was achieved when epoxy resin was cured in the presence of the prepolymers prepared from compound **2** and MDI (or HDI). The copolymerization behaviors of spiro orthocarbonate with epoxy group affected the structure, and the properties of the matrix obtained. When the content of the prepolymers in the resin system was increased, the T_g of the matrix slightly decreased in comparison with the epoxy resin matrix, the thermal stability of the matrix modified with prepolymers was decreased, because of lower decomposition temperature of carbonate ester and/or iminoester linkage. However, the residual carbon of the modified matrix increased as the content of the prepolymer increased. The addition of the prepolymers into the resin system reduced the volume contraction of the epoxy resin during the curing process, and the adhesive tensile strength and shear strength increased. The tensile strength of the matrix modified with prepolymers slightly decreased, however, the toughness was improved.

Acknowledgements

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