

Novel Dibutyltin Oxide-Tributyl Phosphate Condensate as Accelerator for the Curing of the Epoxy Resin/4,4'-Diamino Diphenyl Sulfone System. II. Toughening of the Resin with Hydroxyl-Terminated Poly(tetramethylene) Glycols

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Received 4 April 2000; accepted 28 July 2000

ABSTRACT: When a crystalline $\text{Bu}_2\text{SnO-Bu}_3\text{PO}_4$ condensate was used as a catalyst for the curing of the Epon 828/DDS system, the addition of hydroxyl group to epoxy group took place. On the basis of this reaction, direct employment of poly(tetramethylene) glycols (PTMG) as toughener for the epoxy resin system was successful. Morphology of the modified resin depended on the molecular weight and the concentration of PTMG. With the incorporation of a small amount of PTMG, the critical fracture energy of the cured resin was improved greatly, while the flexural strength and the modulus were less influenced. A slight enhancement in glass transition temperature (T_g) of the modified resin was found up to the PTMG concentration of 5 phr; further increase of the PTMG concentration caused a significant lowering of T_g . © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 1237–1242, 2001

Key words: epoxy resin; poly(tetramethylene) glycol; fracture toughness; morphology

INTRODUCTION

Epoxy resins are the basis of the matrix of advanced composites and structure adhesives. They have superior thermomechanical performance and excellent processability. However, owing to their highly crosslinked structure, they are brittle in nature. Toughening of epoxy resins has attracted great research efforts since the late 1960s. Now it is a common practice to improve toughness of the cured resins by introducing a second phase.^{1,2}

Carboxyl-terminated butadiene-acrylonitrile copolymers (CTBN) are the most widely used

modifiers for epoxy resins. The liquid rubbers have the advantage of low viscosity. When they are used as tougheners, chain extension of the liquid rubbers is effected by the reaction of the functional carboxyl group with the epoxy group, and phase separation takes place during the cure.³ Reactivity of the functional group is of critical importance for both the chain extension and the adhesion between the two phases.

Hydroxyl-terminated polyethers, especially poly(tetramethylene) glycols (PTMG), are commercially available products, and are widely used as the soft segment of polyurethane. In the case of epoxy resins with polyamine as the curing agent, hydroxyl-terminated polyethers, in spite of their chain flexibility, have not been used as tougheners because the activity of the hydroxyl group is not high enough for the reaction with the epoxy group.

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Contract grant sponsor: Natural Science Foundation of China; contract grant number: 29673006.

Journal of Applied Polymer Science, Vol. 80, 1237–1242 (2001)
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In order to make polyether useful as a toughener for epoxy resins, the terminal hydroxyl group can be converted into a carboxyl group⁴ or an amino group⁵ to increase the reactivity with the epoxy group.

It has been reported in a previous article⁶ that, by using a crystalline $\text{Bu}_2\text{SnO-Bu}_3\text{PO}_4$ condensate (Sn-P-c) as a catalyst, the addition of the hydroxyl group to the epoxy group proceeds more easily as compared with the addition reaction of 4,4'-diaminodiphenyl sulfone (DDS) with the epoxy group. Based on this finding we can expect success in using hydroxyl-terminated polyether directly as toughener for the epoxy resin/DDS system in the presence of the named catalyst.

The epoxy resin/DDS thermosets have a rigid network and high glass transition temperature. Therefore, it is difficult to toughen them with a rubbery second phase. It has been reported that the fracture energy was increased from 121 to 338 J/m^2 by incorporation of 15 phr CTBN.⁷

In this article, we report the toughening of the Epon 828/DDS system with hydroxyl-terminated PTMG, with the aid of the crystalline $\text{Bu}_2\text{SnO-Bu}_3\text{PO}_4$ condensate. Influences of the modifier on the morphology and mechanical properties of the cured resins will be discussed in detail.

EXPERIMENTAL

Materials

Bisphenol A type epoxy resin Epon 828 was supplied by the Shell Company. DDS is a chemical pure reagent that was supplied by Beijing Chemical Factory. PTMG of molecular weight of 700, 1000, and 2000 was supplied by DuPont Company and designated as PTMG-700, PTMG-1000, and PTMG-2000, respectively. They were all dried in a vacuum at 100°C for 2 h before use. Phenyl glycidyl ether (PGE) was supplied by Yueyang Chemical Corporation. It was distilled under vacuum, and the fraction of 95–96°C/2 mm Hg was used. Methanol was an analytical reagent and was used without previous purification. The crystalline condensate (Sn-P-c) of Bu_2SnO and Bu_3PO_4 was synthesized as described in a previous paper.⁶

Preparation of the Toughened Resins

Table I shows the composition of the toughened resins. In preparing the toughened resins, Epon

Table I Composition of the Toughened Epoxy Resins

Component	Parts by Weight (phr)	
Epon 828	100	
DDS	32	
Sn-P-c	2	
PTMG	Molecular weight 700	2, 5, 10
	Molecular weight 1000	2, 5, 10
	Molecular weight 2000	2, 5

828, Sn-P-c, and PTMG were previously mixed and stirred at 120°C for 60 min, then DDS was added. The mixture was stirred at 135°C until all DDS was dissolved, then degassed under vacuum and cast into a mold to effect the cure at 140°C for 270 min.

Characterization

The glass transition temperature (T_g) of the cured resins was measured on a TA 2100 Modulated Differential Scanning Calorimeter at a heating rate of 10°C/min under nitrogen atmosphere. The inflection temperature of the transition region of the DSC curve was designated as T_g .

The morphology of the specimens was investigated on a Hitachi S-530 Scanning Electron Microscope (SEM). The fracture surface of the specimens was obtained by fracturing a precracked specimen at room temperature. The surface was gold-sputtered in vacuum before observation.

A three-point bending test was conducted at room temperature according to the standard GB 1042-79, to determine the flexural properties of the cured resins. The specimens were $4 \times 6 \times 55 \text{ mm}^3$ rectangular bars. The measurement was carried out on an Instron 1122 Mechanical Analyzer. The support span was 48 mm, and the crosshead speed was 10 mm/min for the flexural strength determination, and 2 mm/min for the flexural modulus determination. The average value was taken from five specimens.

The I-type critical stress intensity factor, K_{IC} , and the critical fracture energy, G_{IC} , were determined using three-point bending specimens with a prepared crack. The tests were performed using an Instron 1122 Mechanical Analyzer at a crosshead speed of 2 mm/min. The reported values were the average from the results of five to seven

specimens. K_{IC} and G_{IC} were calculated according to eq. (1)⁸:

$$K_{IC} = (6F_c Y a^{0.5}) / \sqrt{10BW} \quad (1)$$

where F_c is the critical load for crack propagation. Y is the geometric factor calculated according to eq. (2):

$$Y = \frac{1.99 - \{a/W(1 - a/W)\} \times [2.15 - 3.93a/W + 2.7(a/W)^2]}{(1 + 2a/W)(1 - a/W)^{1.5}} \quad (2)$$

where B is the specimen thickness and W is the specimen width; a is the crack length, which is prepared using a razor blade and measured under an optical microscope as the average of three points; its magnitude should be 0.45 ~ 0.55 times of that of the specimen width.

The values of the critical stress intensity factor were converted to corresponding critical fracture energy according to eq. (3) in the plane-strain conditions:

$$G_{IC} = 880K_{IC}^2/E_b \quad (3)$$

where E_b is the elastic modulus.

RESULTS AND DISCUSSION

Reaction of the Hydroxyl Group with the Epoxy Group Catalyzed by Sn-P-c

The reactivity of the functional group is of critical importance in order for a liquid rubber to be used as the toughening agent for epoxy resin. In the cases of epoxy resins with polyamine as a curing agent, the hydroxyl group of the polyether is not active enough to react with the epoxy group, and,

consequently, the hydroxyl-terminated polyether was easily separated and formed a layer on the surface upon the curing of epoxy resin. The addition of the hydroxyl group to the epoxy group catalyzed by $\text{Bu}_2\text{SnO-Bu}_3\text{PO}_4$ condensate has been reported in the literature.⁵ The catalyst, Sn-P-c, used in this study has a lower degree of condensation than those used in previous studies.⁵ Therefore, it is more soluble in the epoxy resin.

In the previous article,⁶ we used DSC to demonstrate the reaction of the hydroxyl compound with the epoxy resin catalyzed by Sn-P-c. Here, we used PGE as a model compound to demonstrate the catalytic activity of Sn-P-c for this reaction. Thus, 1.00 g Sn-P-c, 0.76 g (0.005 mol) PGE, and 10 mL (0.25 mol) methanol were refluxed for 5 h. The product was analyzed using gas chromatography-mass chromatography (GC-MS). It was found that 80.8% of PGE reacted with methanol in this case.

Based on the above results, we are sure that Sn-P-c is effective for the reaction between the hydroxyl group and the epoxy group. Therefore, it is possible to use the commercially available hydroxyl-terminated polyether as toughener for the epoxy resin/amine thermoset when Sn-P-c is used as the catalyst. The schematic for the reaction of PTMG with epoxy resin is shown in Figure 1.

Morphology of the Modified Resins

An important condition for the polymers to be useful as tougheners is that they can dissolve in the resin before cure, and can separate from the resin as molecular weight of the resin increases during the cure. PTMG was soluble in the Epon 828/DDS mixture at the beginning, and phase separation took place as the reaction went on. Therefore, it could be a useful toughener for the cured Epon 828/DDS resin.

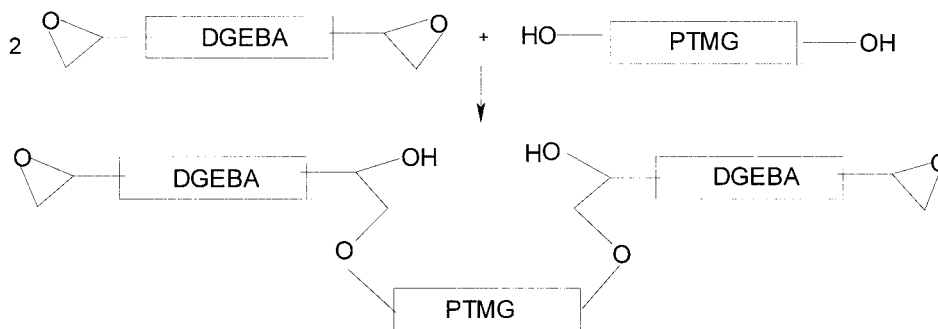


Figure 1 Schematic for the reaction between PTMG and epoxy resin.

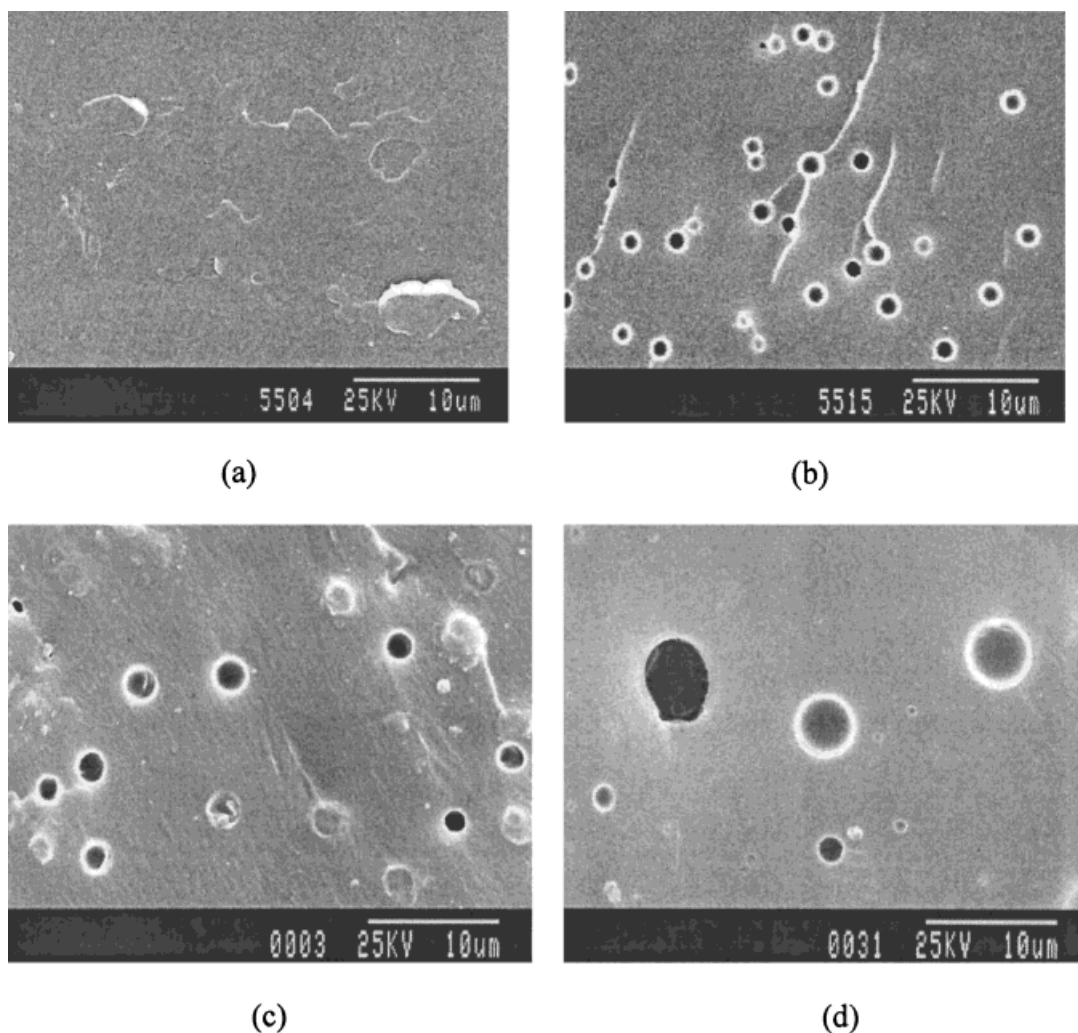


Figure 2 SEM micrographs of the fracture surface initiated by a precrack at room temperature for the cured Epon 828/DDS/Sn-P-c resins: (a) neat resin, (b) modified with 5 phr PTMG-700, (c) modified with 5 phr PTMG-1000, (d) modified with 5 phr PTMG-2000.

As shown in Figure 2, the cured resins modified with PTMG were two-phase materials with spherical PTMG particles dispersed in the resin matrix. The size of the dispersed phase depended on the compatibility of the components. Molecular weight and concentration of the modifier are the major parameters that influence the morphology, as summarized in Table II.

It is usually the case that the compatibility of the components declines with the increase of the molecular weight. PTMG-700 and PTMG-1000 were well compatible with the Epon 828/DDS resin. However, PTMG-2000 was less compatible. For the cured resin containing 5 phr PTMG-2000, big particles of around 10 μm were found, which

Table II Particle Size of the Dispersed Phase in the PTMG-Modified Epoxy Resins

PTMG	Concentration of PTMG (phr)	Particle Size Range (μm)
Without modifier	0	No second phase
PTMG-700	2	0.5 ~ 0.7
	5	1.0 ~ 2.0
	10	2.0 ~ 4.0
PTMG-1000	2	0.4 ~ 0.7
	5	0.8 ~ 3.3
	10	2.6 ~ 4.0
PTMG-2000	2	0.9 ~ 2.5
	5	1.2 ~ 10

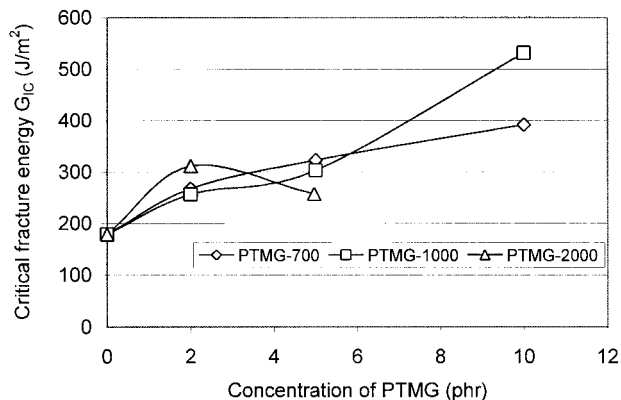


Figure 3 Influence of PTMG on the fracture toughness of Epon 828/DDS/Sn-P-c thermosets.

are believed to be disadvantageous for the toughness. For the resin containing 10 phr PTMG-2000, creaming was observed during the cure, and a sticky layer was observed on the top of the cured resin.

Effect of PTMG on Properties of the Cured Resins

Figure 3 shows the effect of PTMG with different molecular weights on the fracture toughness of the cured resins. When PTMG-700 and PTMG-1000 were used as toughener, the critical fracture energy of the cured resins increased consistently with the concentration of the modifier. PTMG-2000 showed significant toughening effect at very low concentrations; by using 2 phr of PTMG-2000 as the toughening agent, the critical fracture energy of the cured resin reached 311 J/m², as compared to 178 J/m² for the unmodified resin. However, as the concentration of PTMG-2000 in-

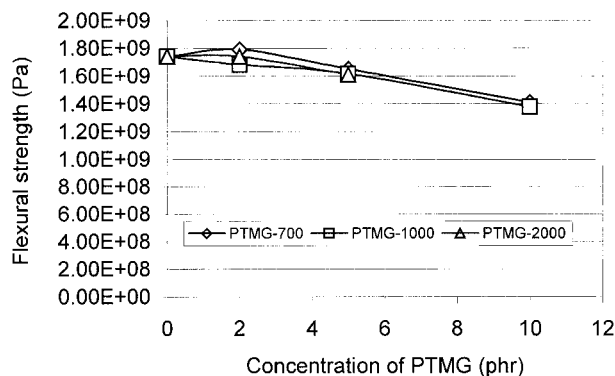


Figure 4 Influence of PTMG on flexural strength of the Epon 828/DDS/Sn-P-c thermosets.

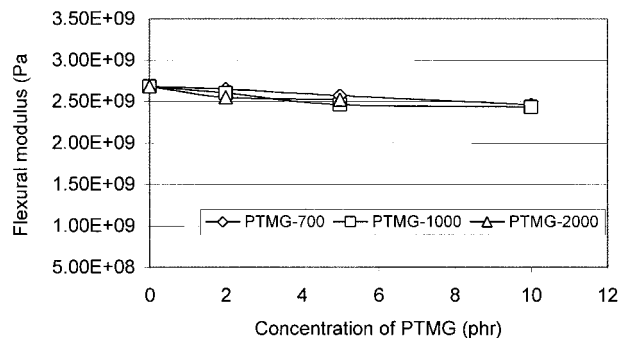


Figure 5 Influence of PTMG on flexural modulus of the Epon 828/DDS/Sn-P-c thermosets.

creased to 5 phr, a reversed effect resulted. This may be accounted for by the unfavorable morphology.

Incorporation of PTMG did not cause a notable loss in the flexural strength of the cured resins at low concentrations (Fig. 4), while the flexural modulus was reduced consistently with the increase of the modifier (Fig. 5).

The T_g was improved slightly by PTMG up to a concentration of 5 phr (Fig. 6). As the concentration of the modifier increased to 10 phr, a significant lowering of T_g resulted. The effect of PTMG was two-sided: the presence of the hydroxyl group may have promoted the curing of epoxy resin with DDS,⁶ on the other hand, the inclusion of a soft segment may have reduced the stiffness of the network.

A small amount of low molecular weight hydroxyl compound, such as glycerol, also improved the T_g , but the obtained material was single phase. No improvement in the fracture toughness could be achieved, as shown in Table III.

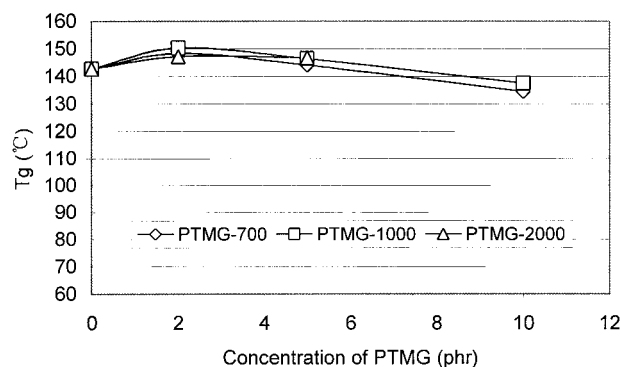


Figure 6 Influence of PTMG on T_g of the Epon 828/DDS/Sn-P-c thermosets.

Table III Effect of Additives on Properties of the Cured Epoxy Resins

Additive	None	Glycerol	PTMG-2000
Concentration of additive (phr)	—	0.31	2
Flexural strength (MPa)	171.1	173.7	168.0
Flexural modulus (GPa)	2.54	2.50	2.45
Maximum deflection (mm)	9.43	8.26	11.89
Fracture energy G_{IC} (J/m ²)	178	185	311
T_g by DSC (°C)	142.7	148.2	147.1
Morphology	Single phase	Single phase	Two phase

The authors express their thanks to the Natural Science Foundation of China for providing financial support for this work (Grant 29673006).

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