

Mechanical Properties of an Epoxy Resin Toughened by Polyester

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ABSTRACT: The epoxy resins were toughened by 4–24 phr polyester with average molecular weight 1.9×10^4 g/mol in this investigation. The mechanical properties were examined and dynamic mechanics analyses were performed for the epoxy resins before and after the modification. The toughening mechanism of polyester to epoxy resin is discussed in light of the scanning electronic microscopy observation of the fracture surfaces. The results showed that the impact strength and tensile strength of the modified epoxy resin were remarkably greater than those of the unmodified cured epoxy resin. The most suitable composition for the modified epoxy resin was the addition of 16 phr polyester,

which led to 138 and 46% increments in the impact strength and the tensile strength, respectively. And the mechanical properties depended greatly on the congregating state of polyester added. The polyester dispersing in the epoxy matrix was amorphous when its addition was less than or equal to 12 phr, and was sphere crystals when the addition was over 16 phr. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 3384–3389, 2003

Key words: epoxy blends; toughness; mechanical properties; microstructure

INTRODUCTION

Epoxy resin is extensively used for electronic–electric pouring and packaging, due to its excellent adhesive and dielectric properties. However, its usage has been greatly limited in complicated environments due to accompanying disadvantage, such as its worse toughness, particularly in the presence of sharp cracks, which cause warping and cracking of products loaded by impact, thermomechanical fatigue, shrinkage stress during the preparation and the service of the products. As the higher integrated components and the more toughness-needed materials are developed, especially, the larger scale and the more multiple pinned packages are required. Therefore, it is an emergent subject to develop new toughening-modified epoxies with high toughness.

In the past several years, rubber materials have been used to improve the toughness of the cured

epoxy resins.^{1–6} Much attention has been paid to the addition of novel synthesis elastomers.^{7–12} However, the toughening of the cured epoxy resins was obtained at the loss of modulus and the glass transition temperature of the composites. Namely, the modulus and heat resistance of the modified epoxy resins were reduced, which resulted from the lower modulus and the glass temperature of rubber materials.

The use of rigid, thermoplastic particles to toughen epoxy has been attempted, where the related toughening mechanism was proposed.^{13–17} These toughening mechanisms have been a subject of academic as well as industrial interest. However, it was difficult to choose the addition, the size in microstructure, and the contribution to mechanical properties of the second phase, since the curing of epoxy resin was a complicated period.

Polyethylene terephthalate (polyester, PET) is a kind of engineering thermoplastic with excellent tensile strength, high modulus, and glass transition temperature. In a previous article, aromatic polyesters, prepared by the reaction of phthalic or isophthalic acids and α,ω -alkanediols, were used to reduce the brittleness of epoxy resin.¹⁸ The results showed that the fracture toughness was increased with the increases in molecular weight of aromatic polyester. It needs to be noted that these synthesized aromatic

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polyesters had only small number-average molecular weight. Therefore, the use of polyester with great number-average molecular weight more than 1×10^4 g/mol to toughen epoxy is a relatively novel toughening approach in this article. The investigation was focused on the relationship between the addition of polyester, the mechanical properties, and the microstructure of the modified epoxy resin.

Experimental

Preparation of modified cured epoxy resins

A commercially available E-6101 bisphenol A type of epoxy resin with 0.43N/100 g of epoxy value and polyester (PET) with 1.9×10^4 g · mol⁻¹ of number-average molecular weight were added into a 250 mL enamelware cup with stirring and a heater. The mixing operations were carried out at 250°C for 20 min until the added polyester was resolved completely. After the mixing was cooled at 200°C, maleic anhydride (MA) used for curing agent and pathalic anhydride (PTA) used for compatilizer were added into the cup and stirred uniformly. The compositions of blends were listed in Table I. Then mixings were poured into the preheating mold at once, and placed it into a vacuum oven at 200°C for 4 h. Subsequently, the cured epoxy resins were brought out of the oven, and cooled to room temperature and then taken out from the mold.

Measurement in mechanical properties

Impact strength of the resulting cured epoxy resins were measured by the Charpy impact strength measurement set, produced by Hebei province of People's Republic of China, using no-notch specimens. The size of specimen was 120 × 15 × 10 mm. Impact strength was calculated as follows:

TABLE I
Composition of Blend

Materials	Supplied by	Composition (phr)
EP	Yueyang Chemical Co. Ltd., People's Republic of China	100
PET	Xinjiang Petroleum Chemical Factory, People's Republic of China	0-24
MA	Xi'an Chemical Reagent Factory, People's Republic of China	30
PTA	Xi'an Chemical Reagent Factory, People's Republic of China	3-10

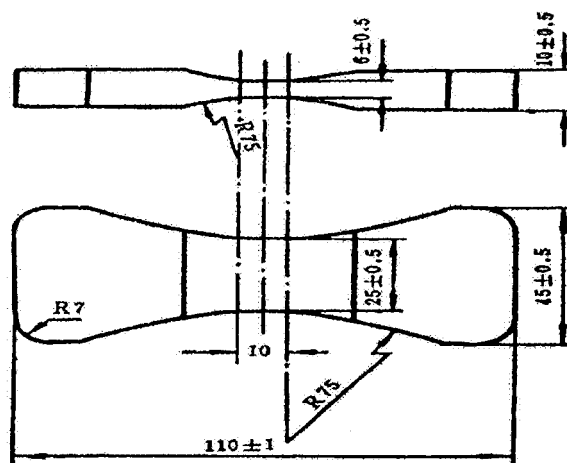


Figure 1 Specimen size of tensile strength.

$$\sigma_t = \frac{P}{a \times b} \quad (1)$$

where P is the maximum impact force at the final failure of the samples, a and b are width and thickness of the used specimen, respectively.

Tensile strength was measured by a 1195 Instron Mechanical Testing Machine (UK). Tensile velocity was controlled at 0.5 mm/min. The size of the testing specimens is shown in Figure 1. The tensile strength is given by

$$\sigma_T = \frac{P_1}{a \times b} \quad (2)$$

where P_1 is the maximum tensile load, the meaning of a and b are same as eq. (1).

At least five specimens were used for the tests of impact and tensile strength.

The sizes of cured samples used to dynamics mechanics analysis (DMA, Dupont product, USA) were 40 × 10 × 4 mm. The temperature varied from -125 to +250°C. The heating speed was 5°C/min. The resonance frequency was 5 Hz.

Some fracture surface of the impact specimens was observed with a S-2700 scanning electron microscope (SEM) (Hitachi, Japan), which were coated previously by sputtering with gold metal to achieve a conducting and protecting layer.

RESULTS AND DISCUSSION

The mechanical properties of the cured epoxy resins

In the present case, the toughness of the cured unmodified epoxy resin, measured as impact strength, was 6.91 kJ/m² as shown in Figure 2. First, there were

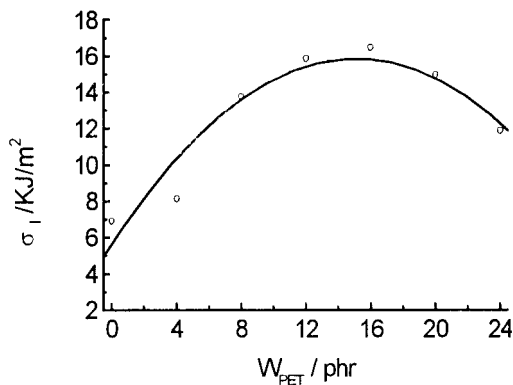


Figure 2 Impact strength of cured epoxy resins dependence on the addition of polyester.

remarkably enhanced in impact strength (σ_1) when the addition of polyester was varied from 4 to 8 phr, and the corresponding values in impact strength were 8.13 and 13.74 kJ/m², respectively. With the addition of polyester increased, such as 12 and 16 phr, there was a further moderate increase in σ_1 , the corresponding values were 15.83 and 16.44 kJ/m², respectively. The maximum impact strength of the modified epoxy resin with 16 phr polyester had increased by 138% compared to that of the unmodified epoxy resin. However, when the addition of polyester was over 16 phr, such as from 20 to 24 phr, the impact strengths of the cured modified epoxy resins obviously decreased, from 14.94 to 11.85 kJ/m², which were still of an increase compared with that of the unmodified cured epoxy resin.

Figure 3 showed that the tensile strength (σ_T) of the cured epoxy resins was as function of the increased polyester. The tensile strength of the unmodified epoxy resin was 36.7 MPa. A significant enhancement in the tensile strength was achieved with the increase addition of polyester. Similar to change law in impact strength, that is, tensile strength was firstly increased and then

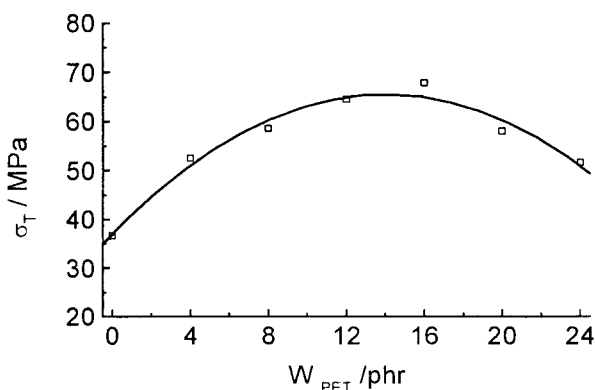


Figure 3 Tensile strength of cured epoxy resins as function of the addition of polyester.

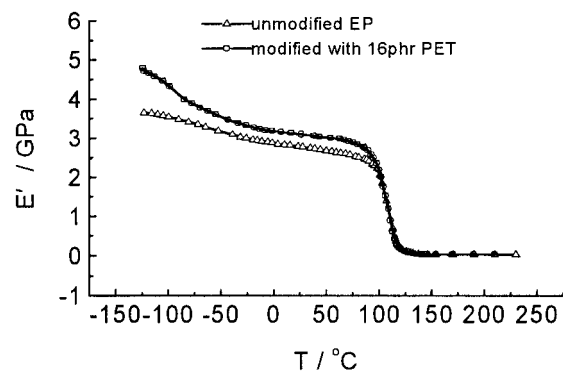


Figure 4 Flexural modulus for the unmodified and modified epoxy resins.

decreased with the increase in addition of polyester. The maximum tensile strength of the modified epoxy resin also emerged at the point of addition of 16 phr polyester, and the maximum value was 67.85 MPa, which led to increment of 46 % relative to that of unmodified epoxy resin. The tensile strength decreased when the addition of polyester was over 16 phr.

Dynamic mechanic analysis

The flexure storage modulus (E') of the modified epoxy resin by 16 phr polyester and the unmodified cured epoxy resins as function of the temperature are shown in Figure 4. It was worthy to be pointed out that the relationship between E' and T of the unmodified epoxy resin was almost linear below the glass transition temperature (about 111°C), which revealed that the microstructure of the unmodified epoxy resin has uniform microstructure. However, that of the modified epoxy resin exhibited similar linear tendency but with two slopes below its glass transition temperature, which suggested that the morphology within the modified epoxy resins had two kinds of phase structures.

The loss factor ($\tan\delta$) curves was shown in Figure 5. Two major relaxation can be observed in both the modified and the unmodified epoxy resins: a major high-temperature or α transition corresponds to T_g of the cured epoxy resins. T_g of the modified epoxy resins was almost unchanged relative to that of unmodified epoxy resin and both was about 111°C.

The low-temperature or β transition depended on the toughness of the cured epoxy resins. The higher the height of peaks, the better the low-temperature toughness. Therefore, the modified epoxy resin possessed better low-temperature toughness.

These results indicated that the low temperature toughness can be improved by the addition of polyester at no-sacrifice heat resistance (T_g of both $\sim 111^\circ\text{C}$).

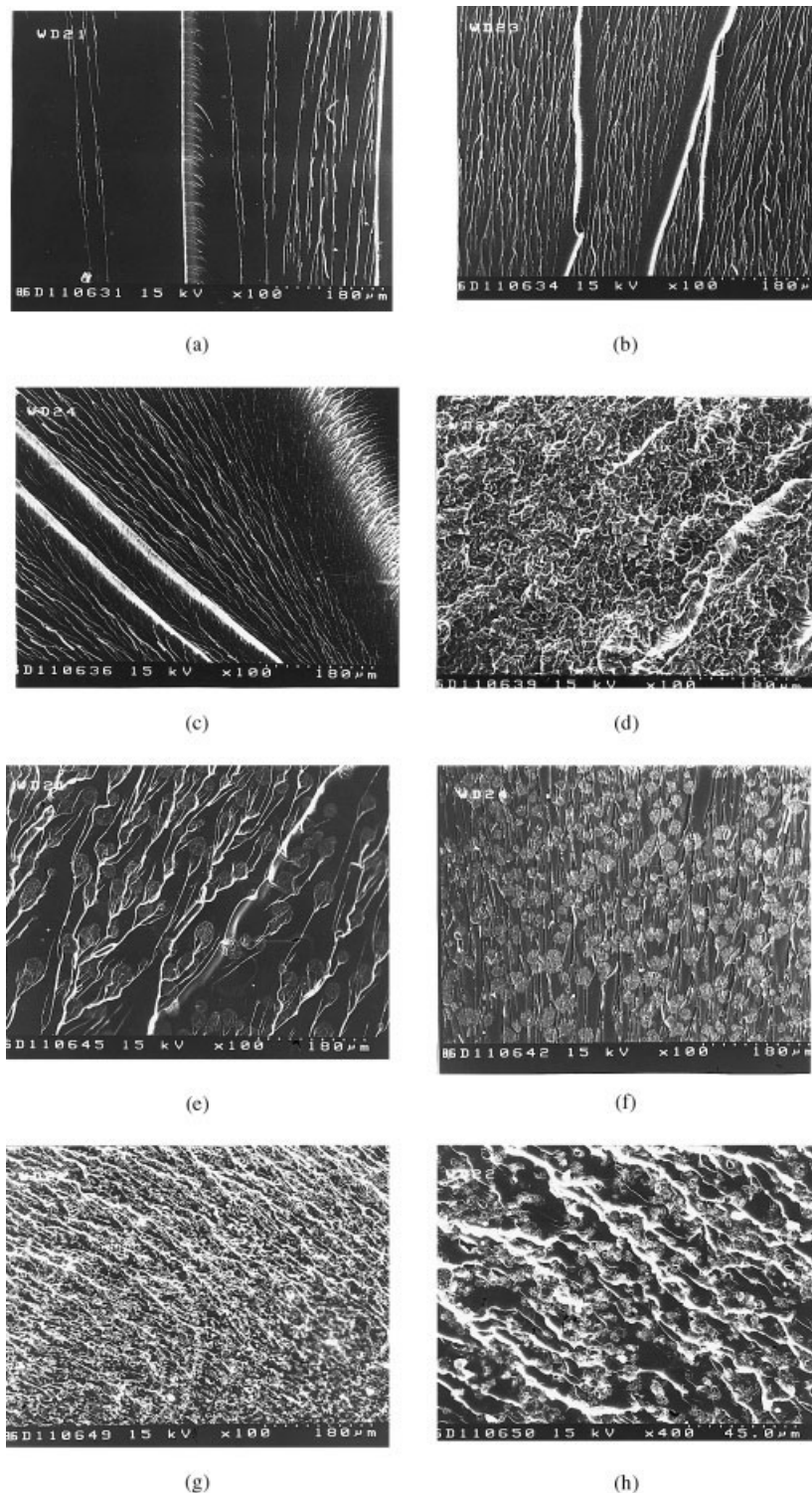


Figure 6 SEM micrograph of the fracture surface of unmodified cured epoxy resin and those modified with polyester. (a) Unmodified. (b) Modified with 4 phr polyester. (c) Modified with 8 phr polyester. (d) Modified with 12 phr polyester. (e) Modified with 16 phr polyester. (f) Modified with 20 phr polyester. (g) and (h) Modified with 24 phr polyester: $\times 100$ and $\times 400$, respectively.

Analysis of toughening mechanism

The morphologies of the fracture surfaces of the modified epoxy resins with polyester were shown in Fig-

ure 6. The crack propagation showed approximately linear shape with a small quantity of dendritic structure. No plastic formation emerged on the fracture

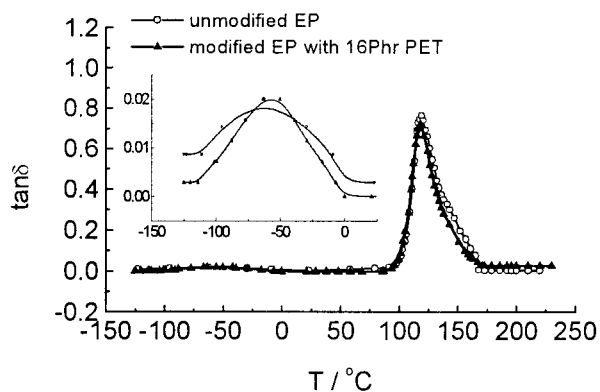


Figure 5 $\text{Tan}\delta$ curves of unmodified and modified epoxy resins.

plane, and the fracture plane was smooth and featureless. This was a kind of typical brittle rupture.

The fracture surface for the cured epoxy blend with 4 phr polyester was quite different from that of the unmodified epoxy resin, as shown in Figure 6(b). Compared with that of the cured unmodified epoxy resin, the lubricity mirror plane was replaced by the numerous dichotomous microcracks. The formation of microcracks was resulted from the decomposing and absorbing impact energy or the emergence of the deflection of crack propagation when the crack tips encounter the amorphous polyester molecular chain segments. Good toughening effect of polyester to epoxy resin has been exhibited.

The microcracks became very thin and dense when addition of polyester was 8 phr, as shown in Figure 6(c), which can decompose or absorb more impact energy. So there was better toughening effect. The dispersed phase of polyester produces great plastic deformation when the sample was loaded by impact force.

For the epoxy blend with 12 phr polyester, the rough and many dimples were emerged in the fracture surfaces, as shown in Figure 6(d). The fracture surface has been transformed toughness rupture. The toughening mechanism can be explained by cavitation/shear banding.

The fracture surface morphology of the modified epoxy resin was drastically changed at the addition of 16 phr polyester. The excessive addition of polyester led to the two-phase structure: the emergence of sphere crystals dispersed phase of the polyester was in the epoxy resin matrix, as shown in Figure 6(e). The DMA results shown in Figure 4 also supported this conclusion. At this time, the sphere crystals dispersed phase of the polyester had greater volume and less number, and the blends obtained great impact and tensile strength, as shown in Figure 1 and Figure 2. Based on the gridding statistics, the average diameter of the sphere crystals was $30\ \mu\text{m}$ and the average

distance of sphere center-sphere center was $48.6\ \mu\text{m}$, as listed in Table II.

When the addition of polyester was increased to 20 phr, the diameter of sphere crystals was decreased to about $18\ \mu\text{m}$, but the number of sphere crystals was remarkably enhanced, and the distances between sphere center and sphere center became short and about $24.0\ \mu\text{m}$, as shown in Figure 6(f).

With further increasing addition of polyester, such as at 24 phr, the diameter of sphere crystals was decreased to about $4.5\ \mu\text{m}$ and the number of sphere crystals become so much that they impenetrate the cured system, as shown in Figure 6(g) and Figure 6(h). The distances between the sphere centers were very short and about $7.5\ \mu\text{m}$.

Because the flexible amorphous molecular chains of polyester dispersed in the matrix were transformed for sphere crystals. The plastic deformation ability of sphere crystals was less than that of the amorphous flexible molecular chains. The more the addition of polyester, the more the number of polyester sphere crystals or the less the number the amorphous flexible molecular chains of polyester. Therefore, the impact strength of the modified epoxy resins decreased with the increased addition of polyester.

It can be seen that the toughening effects of polyester to the epoxy resin depended mainly on the congregating state of polyester in the epoxy matrix. When the addition of polyester was less than or equal to 12 phr, the congregating state of polyester was amorphous. Over 16 phr polyester, the sphere crystals emerged.

CONCLUSIONS

Polyester with number-average molecular weight $1.9 \times 10^4\ \text{g/mol}$ was an effective modifier for improving the toughness and tensile strength without the loss in the modulus and thermal properties of the cured epoxy resins. The different additions of polyester resulted in the different morphology of polyester dispersing in the epoxy resin matrix.

When the addition of polyester was less than or equals to 12 phr, the polyester had excellent compatibility with the epoxy matrix and exhibits amorphous state. And when the addition of polyester was over 12 phr, the polyester dispersed phase was sphere crystals. The addition of 12 phr polyester resulted in the

TABLE II
The Average Distance Between the Polyester Sphere Crystals

W_{PET} (phr)	16	20	24
b (μm)	48.6	24.0	7.5

W_{PET} : the addition of polyester, b : the average diameter of the sphere crystals.

emergence of cavitation/shear banding. The addition of polyester less than 12 phr leads to microcracks mechanism. The addition of 16 phr polyester possessed the maximum value of both impact and tensile strengths of the modified epoxy resins.

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