Mechanical properties of epoxy resin/hydroxyl-terminated polyester blends: effect of two-phase structure

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Abstract: In this paper, the effect of two-phase structure on the mechanism of rubber-toughening of epoxy resins was studied. Three types of hydroxyl-terminated polyesters with different molecular weights were synthesized in order to modify epoxy resins to obtain single-phase (P-1), critical phase separation (P-2) and two-phase (P-3) structures. The results of dynamical mechanical analysis and scanning electron microscopy distinguished the dissolved and phase-separated polyesters in the epoxy matrix. The P-1 system showed the highest dissolved content of polyester in the epoxy matrix, while the P-3 system exhibited the lowest content. Both dissolved and phase-separated polyesters proved to be capable of increasing the toughness of modified epoxy resins. The phase-separated polyester was found to contribute much more to the improvement of toughness.

Keywords: rubber-toughening; epoxy; fracture behaviour; yielding

INTRODUCTION

Epoxy resins are some of the most widely used thermoset materials, exhibiting good adhesion, high strength, and resistance to creep, heat, and chemicals. However, a major drawback of cured epoxy systems is that they are brittle and exhibit poor resistance to impact and crack propagation. Therefore, in the last few decades, much attention has been paid to improving the toughness.1,2

Rubber toughening is one of the popular methods for improving the toughness of epoxy resins. It is generally agreed that a small amount of a reactive rubber can greatly improve the fracture toughness of epoxy resins by forming discrete rubbery particles that are chemically bonded to the matrix. In this mechanism of rubber toughening,3–5 it is required that the rubber phase separates as a discrete particulate phase during the cure. Extensive studies6–9 have shown that the phase separation process is a result of the decrease in configurational entropy due to the increase in molecular weight as the epoxy cures. This changes the free energy of mixing leading to a decrease in the solubility of the rubber that provides the driving force for phase separation. Various morphological parameters, such as particle size, particle size distribution, inter-particle distance and matrix to particle adhesion, play an important role in toughening.10–12 These morphological parameters depend on chemistry, molecular weight and concentration of the liquid rubber12,13 as well as on the curing conditions.14

However, the dissolved rubber is also expected to modify the mechanical properties of the epoxy resins. Bussi and Ishida15,16 studied the mechanical properties of blends of diglycidyl ether of bisphenol-A-based epoxy resin and internally epoxidized polybutadiene rubber. Upon pre-reaction of the rubber with excess diepoxide monomers, a 40 % improvement in the critical stress intensity factor was obtained. It was demonstrated that this improvement was due to the incorporation of the rubber into the epoxy network rather than to the presence of phase-separated rubber particles. This means that when the rubber is dissolved in the epoxy matrix, the ductility of matrix can be improved, resulting in increasing toughness. It is thus important to properly characterize these two-phase structure systems and distinguish the contribution of the dissolved rubber and of the phase-separated rubber to the toughening of epoxy resins. Whether the phase separation of a flexible polymer from the network is required for toughening or not will directly determine the selection of toughening agent and curing conditions. In this paper, three types of hydroxyl-terminated polyesters with different molecular weights were synthesized to modify epoxy resin so that single-phase, critical phase separation and two-phase structures could be obtained in the blends. The influence of phase-separated polyester
and dissolved polyester on toughening was investigated and distinguished by comparing these three systems.

**EXPERIMENTAL**

**Materials**

The epoxy system used in this study was diglycidyl ether of bisphenol A (DGEBA) epoxy resin (DER331) cured with methylhexahydrophthalic anhydride (MHHPA) and catalyzed by a tertiary amine, benzyl dimethylamine (BDMA). DER331 was purchased from Dow Chemical Company, MHHPA (CP) from Lonza Company and BDMA (CP) from Shanghai Third Agent Factory.

Hydroxyl-terminated polyesters, used as modifier, were synthesized based on sebacic acid and propylene glycol. Sebacic acid (CP) was purchased from Cathy Biotechnology Group and recrystallized in ethanol before use. Propylene glycol (AR) and xylene (AR) were purchased from Shanghai Third Agent Factory.

**Synthesis of hydroxyl-terminated polyesters**

The hydroxyl-terminated polyesters were synthesized by a two-step polymerization process as presented in Fig. 1. The reaction of sebacic acid and a large excess of propylene glycol (1:6 mol ratio) was carried out in xylene at 150–180 °C for 6 h and oligomers with hydroxyl-terminated groups were formed. The solvent and excess propylene glycol were then removed under vacuum (100 Pa) at 150–180 °C. In the second step, ester exchange polycondensation occurred in the presence of catalyst under vacuum (100 Pa) at 150–180 °C. The more glycol was generated, the higher the molecular weight of produced polyester. Controlling the amount of glycol generated in the reaction could control the molecular weight of the products.

**Sample preparation of epoxy/polyester blends**

The weight ratio of the epoxy resin to MHHPA to BDMA components in the epoxy matrix was 100:88:0.14. The three types of polyester prepared, labelled P-1, P-2 and P-3 and with the characteristics shown in Table 1, were added into the solution. The added polyesters were 2.5, 5, 7.5, 10, 15 and 20 wt% of the total weight of epoxy matrix. Epoxy resin, curing agent, catalyst and polyester were mechanically mixed together, using a mixer (LC Series, Zhejiang Yangtse River Mixer Co., Ltd., China) with a stirring speed of 100 r min⁻¹, into a homogeneous solution and then put into a vacuum oven for degassing. After that the blends were cast into moulds coated with silicone mould release agent, and the moulds then placed in an oven for curing. The curing procedure was as follows: 90 °C for 3 h, 110 °C for 2 h, 130 °C for 1 h, and 140 °C 12 h. After curing, the samples were allowed to cool spontaneously to room temperature.

**Measurements**

Fourier-transform infrared (FTIR) spectra were measured on a Nicolet Nexus 470 FTIR spectrometer. Samples were ground to a fine powder, mixed with KBr powder and pressed into a pellet.

The molecular weight of the polyesters was measured on a Perkin Elmer 200 gel permeation chromatograph (GPC), with a flow phase of dimethylacetamide and a temperature of 25 °C, against monodisperse polystyrene standards.

The glass transition temperature, \( T_g \), was measured on a NETZSCH DSC-204 differential scanning calorimeter at a heating rate of 10 °C min⁻¹.

Scanning electron microscopy (SEM) analysis of impact fracture surfaces was carried out on a JEOL JMS-5600LV instrument.

The dynamic mechanical analysis (DMA) of the modified epoxy was carried out on a NETZSCH C DMA-242 instrument over the range –130 to

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**Figure 1.** Brief synthesis route of hydroxyl-terminated polyesters.

**Table 1.** Molecular weight, \( T_g \) and the area of the OH and C=O absorption peaks of the hydroxyl-terminated polyesters

<table>
<thead>
<tr>
<th>Polyester</th>
<th>( M_n (g\text{mol}^{-1}) )</th>
<th>( M_w (g\text{mol}^{-1}) )</th>
<th>( M_w/M_n )</th>
<th>( T_g (°C) )</th>
<th>( A_{OH} )</th>
<th>( A_{C=O} )</th>
<th>( A_{OH}/A_{C=O} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-1</td>
<td>6430</td>
<td>10 400</td>
<td>1.61</td>
<td>–49.8</td>
<td>676</td>
<td>2459</td>
<td>0.2790</td>
</tr>
<tr>
<td>P-2</td>
<td>8550</td>
<td>23 500</td>
<td>2.75</td>
<td>–49.0</td>
<td>274</td>
<td>3111</td>
<td>0.0882</td>
</tr>
<tr>
<td>P-3</td>
<td>24 000</td>
<td>58 100</td>
<td>2.42</td>
<td>–49.0</td>
<td>86</td>
<td>3815</td>
<td>0.0225</td>
</tr>
</tbody>
</table>

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*Polym Int 54:1408–1415 (2005)*

1409
+220 °C at 3 °C min⁻¹. The samples (1.5 mm × 5 mm × 30 mm) were used in the double cantilever mode.

The critical strain energy release rate, $G_{\text{IC}}$, was measured on an Instron 5567 instrument. Five specimens (75 mm × 42 mm × 3 mm) were tested for each sample. The $G_{\text{IC}}$ and the critical intensity factor, $K_{\text{IC}}$, were defined by Eqns (1) and (2) below, according to the literature:18

$$G_{\text{IC}} = \frac{K_{\text{IC}}^2}{E (1 - \mu)^2}$$

$$K_{\text{IC}} = \sqrt{\frac{3 P_{\text{C}} W_{\text{m}}}{W t^3 t_n (1 - \mu)}}$$

where $E$ is the elastic modulus, $\mu$ is Poisson's ratio (taken as 0.35), $W$ is the width of the specimens, $W_{\text{m}}$ is the twisting moment, $t$ is the thickness of the specimens, $t_n$ is the thickness of the V-shape channel and $P_{\text{C}}$ is the loading.

The Charpy impact strength was tested according to ISO 179:1993(E) and performed on an XCJ-40 impact tester. The dimensions of the test specimen were 120 mm × 15 mm × 10 mm and 10 specimens were tested for each sample. The compressive properties were measured according to ASTM D695 on the Instron 5567, and the diameter of the specimens was 12.7 mm and the length was 25.4 mm. The stress–strain curves were obtained with an anvil displacement speed of 1.3 mm min⁻¹.

RESULTS AND DISCUSSION

Characterization of the hydroxyl-terminated polyesters

The three types of polyester were numbered respectively as P-1, P-2 and P-3. Their relative molecular weights and $T_g$ are given in Table 1.

The IR spectra are presented in Fig 2. The absorption peaks between 3450 and 3500 cm⁻¹ were due to the vibration of the terminal OH groups. The wavenumbers of the C=O and C–O bond absorption peaks in the ester groups were 1738 and 1176 cm⁻¹, respectively. The IR spectra of the polymers were found to be the same shape except for the OH absorption between 3450 and 3500 cm⁻¹. The ratio of the OH absorption area to the C=O absorption area ($A_{\text{OH}}/A_{\text{C=O}}$) reflected the content of the terminal OH group of polyesters. The results (given in Table 1) were consistent with the results of molecular weight indicated by GPC.

Table 2. Transparency of the different polyester/epoxy resins blends

<table>
<thead>
<tr>
<th>Polyester content (wt%)</th>
<th>System</th>
<th>2.5</th>
<th>5</th>
<th>7.5</th>
<th>10</th>
<th>15</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-1</td>
<td>T</td>
<td>T</td>
<td>T</td>
<td>T</td>
<td>T</td>
<td>T</td>
<td>T</td>
</tr>
<tr>
<td>P-2</td>
<td>T</td>
<td>S</td>
<td>S</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>P-3</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>N</td>
</tr>
</tbody>
</table>

$T =$ transparent; $S =$ semi-transparent; $N =$ opaque.

Figure 2. IR spectra of hydroxyl-terminated polyesters.

Figure 3. Impact fracture surface of P-2 polyester/epoxy resin blends with different initial polyester content: (a) 15 wt% (scale bar = 2 µm); (b) 20 wt% (scale bar = 1 µm).
Characterization of the microstructure

A comparison of the transparency of polyester (P-1, P-2 and P-3)/epoxy resin blends is given in Table 2. SEM results of the impact fracture surface of the polyester/epoxy resin blends are given in Figs 3 and 4. The three systems demonstrated different microstructures. The P-1 system always remained homogeneous as the content of polyester changed. In the P-2 system, no particles were observed by SEM at the polyester content of 5 or 10 wt%, and only a few small particles were observed when the content of polyester reached 15 wt% (Fig 3, not completely consistent with the samples’ transparency). This showed that the P-2 polyester-modified epoxy resins had critical phase-separation structure based on the compatibility between the P-2 polyester and epoxy matrix.

In the P-3 system, particles were clearly observable by SEM (Fig 4) when the content of polyester reached 5 wt%. The separated particles’ content and size increased with increasing the content of polyesters. However, when the content increased up to 15 wt%, particles disappeared and the structure of the system changed to be twin-continuous phase. Phase inversion occurred and the polyester phase changed to be continuous phase when the content of polyester reached 20 wt%.

The SEM results showed that the molecular weight of polyester was the key factor in determining the compatibility between polyester and cured epoxy resins, while the content of polyester influenced the number and size of the separated rubber particles.

DMA results

In the DMA experiments, the tan δ curves exhibited two major relaxations. The high-temperature or α transition corresponded to the major $T_g$ of the epoxy-rich continuous phase, above which significant chain motion took place. The low-temperature (about $-30^\circ C$) or β transition was attributed predominantly to the motion of the phase-separated polyester. The tan δ versus $T$ curves of the polyester/epoxy resin blends with polyester content of 5, 10 and 20 wt% are presented in Figs 5 and 6. It can be seen that from the P-1 system to the P-3 system the $T_g$ of matrixes increased with increasing the molecular weight of polyester. This phenomenon demonstrated that there was less polyester dissolved into the matrix when the molecular weight of polyester increased for any fixed adding content. Simultaneously, the β transitions became stronger from the P-1 system to the P-3 system, which meant that the content of phase-separated polyester increased from the P-1 system to the P-3 system. These results were consistent with those from the SEM.

The above-mentioned results showed that, for all the systems in this study, the phase-separation structure depended on the molecular weight of polyester. Furthermore, the degree of phase separation became stronger as the content of polyesters added into the systems increased.
Fracture and impact behaviours

The $G_{IC}$ values of the modified epoxy resins are shown in Fig 7. Compared with P-1 polyesters, P-2 and P-3 polyesters had higher molecular weight ($M_w$) and lower OH-terminated group content. So the cross-linking density of P-2 and P-3 modified epoxy resins was higher than P-1 modified epoxy resins, which contributed less to toughening of the materials. In addition, the particle matrix interaction would decrease with increasing molecular weight of polyester, because increased $M_w$ would decrease the compatibility between polyester and matrix. However, the P-2 and P-3 systems that had phase-separation structures showed better toughness than the P-1 system for any given polyester content. Therefore the

Figure 5. High-temperature range of the tan $\delta$ versus $T$ curve of polyester/epoxy resin blends with different polyester content: (a) 5 wt%; (b) 10 wt%; (c) 20 wt%.

Figure 6. Low-temperature range of the tan $\delta$ versus $T$ curve of polyester/epoxy resin blends with different polyester content: (a) 5 wt%; (b) 10 wt%; (c) 20 %.
phase-separation structures were the deciding factor in the improvement of toughness of P-2 and P-3 systems. However, both dissolved and separated polyester particles were expected to improve the toughness of the blends. The results of DMA and SEM proved that there was less polyester dissolved into the matrix of P-2 P-3 systems than that of the P-1 system. Therefore phase-separated particles were the major source of the greatly increased toughness in P-2 and P-3 systems.

As shown in Fig 7, the $G_{IC}$ increased with increasing content of polyester, in an approximately linear relationship. Both parts of polyester were expected to improve the toughness of the blends in a complimentary manner. The linear relationships between the $G_{IC}$ and the content of polyester were curve-fitted and their slopes are listed in Table 3. The slope indicated the additional toughness in proportion to the addition of polyester. Therefore it could be defined as the ‘toughening capacity’ per content of added polyester. For the P-1 system, the ‘toughening capacity’ only resulted from the dissolved polyester. For the P-2 and P-3 systems, the ‘toughening capacity’ resulted from the cooperation of both dissolved polyesters and separated polyester particles. The slopes of the P-2 and P-3 systems were several times more than that of the P-1 system, i.e. the ‘toughening capacity’ of P-2 and P-3 polyester was several times more than that of P-1 polyester in this study. It was therefore concluded that phase separation was the major source of the greatly increased toughness in P-2 and P-3 system.

![Graph](image1.png)

**Figure 7.** Effect of polyester content on the $G_{IC}$ of different polyester/epoxy resin blends.

**Table 3.** Line equations and slopes of simulated lines of $G_{IC}$ versus polyester content

<table>
<thead>
<tr>
<th>System</th>
<th>Line equation</th>
<th>Slope</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-1</td>
<td>$y = 34.8 + 6.8x$</td>
<td>6.8</td>
</tr>
<tr>
<td>P-2</td>
<td>$y = -11.3 + 31.5x$</td>
<td>31.5</td>
</tr>
<tr>
<td>P-3</td>
<td>$y = 3.1 + 35.4x$</td>
<td>35.4</td>
</tr>
</tbody>
</table>

The results indicated that both dissolved polyester and the phase-separated polyester contributed to the increase of toughness but the latter had much more ‘toughening capacity’. It was proved that the particle phase in the polyester/epoxy blends played a significant role in toughening.

Figure 8 shows the impact strength of the polyester/epoxy resins blends. The results were consistent with those of fracture behaviour: the P-2 and P-3 systems that had phase-separation structures showed better toughness than the P-1 system for any given polyester content.

**Compression yielding behaviour**

Yielding and the resulting unstable deformation are characteristic behaviours of polymers.19 Some brittle materials that will break before yielding in tensile tests will yield under compression and twisting loading. Lower yielding strength usually means better toughness.20–22

Figure 9 shows the compression load versus displacement curves of the polyester-modified epoxy resins. All the P-1 systems showed the yielding phenomenon as the content of polyester changed. In the P-2 systems, the yielding phenomenon was no longer obvious when the content of polyester reached to 15 wt%, and it disappeared altogether at the content of 20 wt%. In the P-3 systems, the yielding phenomenon was not very clear when the content of polyester was 10 wt%, and it disappeared at the content of 15 wt%. It was thus shown that a brittle-tough transition occurred due to the presence of phase separation.

According the compression theory of polymer materials,23–25 the compression modulus is determined by the strength of the second bonding interaction between the polymer’s chains and the compression yielding strength is mainly determined by the stiffness of the chains. As shown in Fig 10, the compression modulus of modified epoxy resin decreased with increasing polyester molecular weight (from P-1
Figure 9. Load versus displacement curves of polyester/epoxy resin blends: (A) 2.5 wt%; (b) 5 wt%; (c) 7.5 wt%; (d) 10 wt%; (e) 15 wt%; (f) 20 wt%.

to P-3) and with increasing polyester content. The increased molecular weight reduced the compatibility between polyesters and epoxy resin. Therefore it reduced the strength of the second bonding interaction between chains and decreased the elastic modulus.

Figure 10. Effect of polyester content on the compression modulus of polyester/epoxy resin blends.

Figure 11. Effect of polyester content on the compression strength of polyester/epoxy resin blends.

As shown in Fig 11, the compressive yielding strength decreased with increasing polyester molecular weight for any fixed polyester content. The polyester particles chemically bonded to the matrix created stress concentrations that acted as initiation sites for plastic deformation of the matrix and energy was thus dissipated. Therefore the presence of rubber particles made it easier for the modified epoxy resins to yield, i.e. the particle phase separation improved the toughness of the materials.

Along with the results of the fracture test, the study of compression yielding behaviour strongly supported the rubber toughening mechanism: the phase separation was the major source of the improved toughness.

CONCLUSION
In order to study the effect of two-phase structure on the mechanism of rubber-toughening of epoxy resins, single-phase, critical phase separation and two-phase structures were obtained respectively by introducing three types of hydroxyl-terminated polyesters (P-1, P-2 and P-3) with different molecular weight into the epoxy resins. The results of DMA and SEM indicated that the highest content of polyester was dissolved into the matrix of the P-1 systems, while the least content of polyester was dissolved into the matrix of P-3 systems.

The compression tests showed that phase-separated rubber particles reduced the yielding strength and made the materials easier to yield by creating stress concentration that induced the plastic deformation of the matrix. The fracture and impact behaviours proved that the toughness of the epoxy/polyester blends increased with the addition of polyester. Both dissolved polyesters and separated polyester particles were expected to improve the toughness of the blends. However, the P-2 and P-3 systems had a better toughness than the P-1 systems due to the presence of phase separation. Hence the slopes of the curves of $G_{IC}$ against the content of polyester could represent the 'toughening capacity' of both dissolved and phase-separated polyester. The fracture and compression behaviours demonstrated that the phase-separated polyester particles contributed much more to the improvement of toughness than the dissolved polyester. It was therefore concluded that the particle phase separation plays a significant role in improving toughness of modified epoxy resins.

REFERENCES