

Rheological and mechanical properties of poly(butylene terephthalate)-modified epoxy resins

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Poly(butylene terephthalate) (PBT) was used as modifier for epoxy resin. With the incorporation of 7.5 wt % PBT, the resin became a gel as shown by rheological measurements in steady shear, thixotropic loop and dynamic shear mode. The gel was very stable on storage. An abrupt change of rheological properties occurred at the dissolution temperature of the PBT spherulites. The PBT modifier did not impair mechanical properties of the cured resins, yet a moderate improvement in toughness was achieved.

1. Introduction

The need for rheology control in industrial materials is evident. Paints should be spread upon the shearing action, and not run away at rest; automotive adhesive should be delivered using a pump, but should be non-sag during curing, even on vertical surfaces. Therefore, rheology modifiers are usually incorporated to make the systems thixotropic.

Typical commercial rheology modifiers are fine particulate materials, such as fumed silica, which form a network structure through particle aggregation. These materials work well initially, but the effectiveness is gradually lost during storage, as the aggregation breaks down through wetting by fluid components.

The purpose of this study was to explore an alternative approach to rheology control, namely by means of molecular assemblies. It is known that, in some cases, the presence of a minor amount of macromolecules can exert so great an influence on rheological properties as to solidify a liquid system. Gel formation is a quite common feature of semicrystalline polymers above their critical gel concentration [1–8]. In the light of these phenomena, attempts have been made to develop materials with novel rheological properties.

In the present work, epoxy resin was used as an example to determine how far the flow behaviour and other properties can be influenced by a crystalline polymer. Poly(butylene terephthalate) (PBT) was chosen as a modifier because it has a solubility parameter very close to that of the epoxy resin. Thermo-reversible gelation and mechanical properties of PBT-epoxy resin systems have been studied by Robertson and co-workers [8–10]. However, no detailed rheological data have been reported so far.

2. Experimental procedure

2.1. Materials

The epoxy resin used in this study was glycidyl ether of bisphenol A (DGEBA), designated E51, produced by Yueyang Resins Factory. The epoxy value was 5.1 meq g^{-1} . Poly(butylene terephthalate) was PBT 101 produced by Beijing Institute of Chemical Industry, $[\eta] = 1.05$ in the 1:1 mixture of phenol:tetrachloroethylene at 25°C . The curing agents for the epoxy resins were triethylenetetramine, a chemical reagent from Beijing Chemicals Factory, and 1,8-diamino-*p*-menthane, a chemical reagent from Aldrich Chemical Company.

2.2. Preparation

PBT was dissolved in the epoxy resin by stirring at 220°C . The solutions were kept at 180°C for 4 h, and then cooled to room temperature. The blends were mixed with a curing agent, and the mixtures were deaerated *in vacuo*, and then cast into a mould and cured. Single-edge notched specimens were machined for the three-point bending tests.

2.3. Measurements

Rheological behaviour in simple shear was measured on a Rheometric Mechanical Spectrometer RMS 605 using a parallel plate geometry of radius 25 mm and a gap of 2 mm. Differential scanning calorimeter (DSC) scans were run on a Perkin-Elmer DSC 7 system at a heating rate of $20^\circ\text{C min}^{-1}$. Fracture toughness was determined using single-edge notched specimens [11]. Three-point bending tests were conducted on an Instron 1122 test machine at a crosshead moving rate of 2 mm min^{-1} . Fracture surfaces were

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examined under a Hitachi S-530 scanning electron microscope.

3. Results and discussion

3.1. Rheological behaviour of PBT-modified epoxy resins

PBT can dissolve in the epoxy resin at $\sim 220^\circ\text{C}$, and crystallize on cooling. The morphology of the PBT spherulites is dependent upon the crystallization conditions. Therefore, in order to study the influence of the PBT content on the rheological behaviour of the epoxy resin, the blends were prepared under a completely identical thermal regime. The solutions of different PBT concentration were heated at 220°C in an oven for 20 min to ensure complete dissolution. Then, the containers were transferred into another oven at 180°C and kept there for 4 h to build up the nuclei. The morphology of the PBT spherulites (Fig. 1) prepared under the above conditions was similar to that described by Nichols and Robertson [8].

Steady shear measurements showed that the neat epoxy resin and the PBT-modified epoxy resins were non-Newtonian fluids. A plot of apparent viscosity versus shear rate is given in Fig. 2. It can be seen that when the PBT content was below 5 wt % the viscosity curves were similar to each other in shape, while the viscosity of the fluids increased gradually with the PBT content. The change in the rheological behaviour

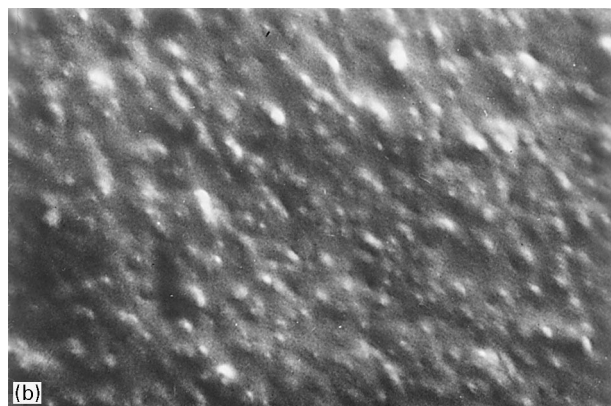
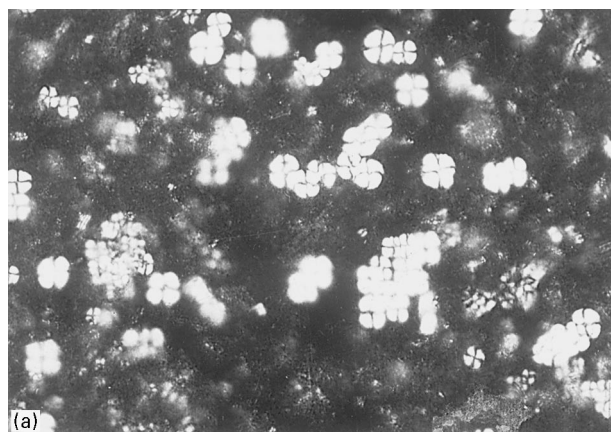


Figure 1 Morphology of the EP-7.5 PBT gel. (a) Micrograph taken with polarized light, (b) scanning electron micrograph of the fracture surface, cured with TETA.

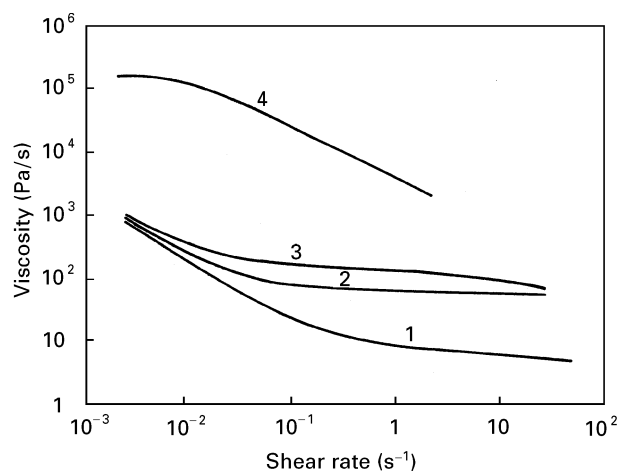


Figure 2 Viscosity versus shear rate for the PBT-modified epoxy resins at 26°C . 1, 0 wt % PBT; 2, 2.5 wt % PBT; 3, 5 wt % PBT; 4, 7.5 wt % PBT.

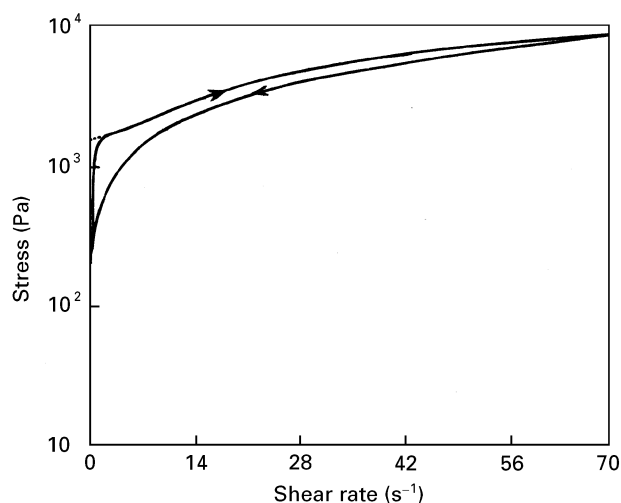


Figure 3 Thixotropic loop for the EP-7.5 PBT gel.

was abrupt when the PBT content increased from 5 wt % to 7.5 wt %. There was a viscosity increase by two orders of magnitude at the low shear-rate end. This change was connected with the gelation of the system.

The resin modified with 7.5 wt % PBT was soft, but practically did not flow. Rheological measurements for the resins containing over 10 wt % PBT were unsuccessful because of slip between the plates and the sample.

The transient gel of epoxy resin modified with 7.5 wt % PBT (designated EP-7.5 PBT gel) was thixotropic, as indicated by thixotropic loop experiments, in which the shear rate was increased from 0 s^{-1} to 70 s^{-1} over a time interval of 50 s, and then the shear rate was brought back to zero. The curves of shear stress versus shear rate made a thixotropic loop, as shown in Fig. 3. The apparent yield stress, 1600 Pa, obtained by extrapolation as shown by the dotted line in the figure, was high enough for making sag-resistant formulations. The thixotropic loop indicated the structure break-down at high shear rate. The recovery must be very quick because a second run which immediately followed gave a thixotropic loop that

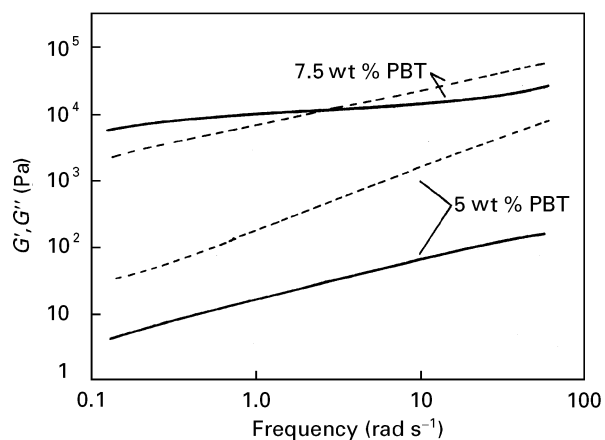


Figure 4 Dynamic moduli versus frequency for epoxy resins modified with PBT. (—) G' , (---) G'' .

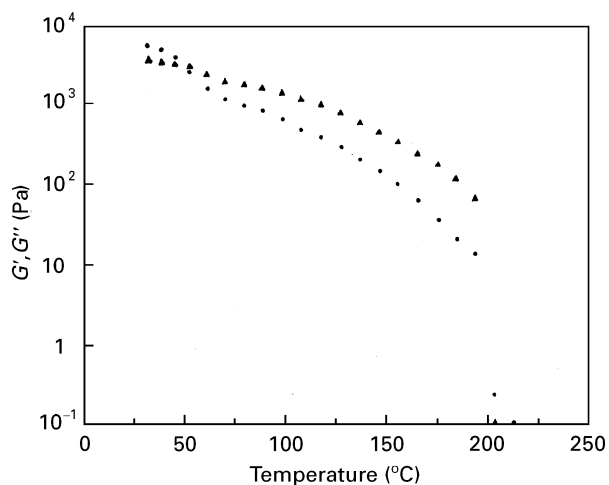


Figure 5 Rheometric mechanical spectra for the EP-7.5 PBT gel at 2 rad s^{-1} . (●) G' , (▲) G'' .

completely coincided with that given by the previous run.

The gel was very stable on storage. No change was found after several months at room temperature or after an accelerated test at 60°C for 10 days.

The rheological behaviour of the EP-7.5 PBT gel was also characterized by dynamic measurement in the linear viscoelastic regime. The frequency dependence of the moduli is shown in Fig. 4. The storage modulus, G' , proportional to the stress in phase with the strain, provided information on the elasticity of the material. For the neat epoxy resin, G' was negligible. For the resin modified with 5 wt % PBT, G' was one order of magnitude below G'' , the loss modulus. For the EP-7.5 PBT gel there was a cross-over in G' and G'' . This is characteristic of gelation.

By following the change in dynamic properties with temperature, the rheometric mechanical spectra (RMS) were obtained. Fig. 5 shows the spectra of G' and G'' versus temperature for the EP-7.5 PBT gel. The gradual decrease of G' in the temperature range from room temperature to $\sim 180^\circ\text{C}$ might be explained by the relaxation of the interspherulite linking, and the steep change of the properties around 199°C was attributed to the dissolution of the PBT

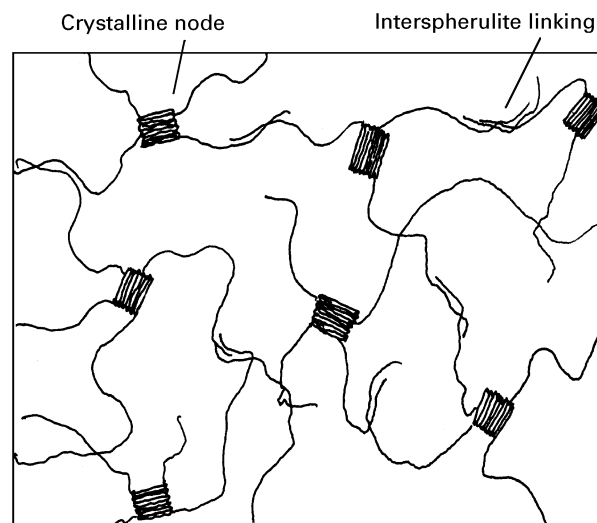


Figure 6 Schematic diagram for the network structure in the EP-7.5 PBT gel.

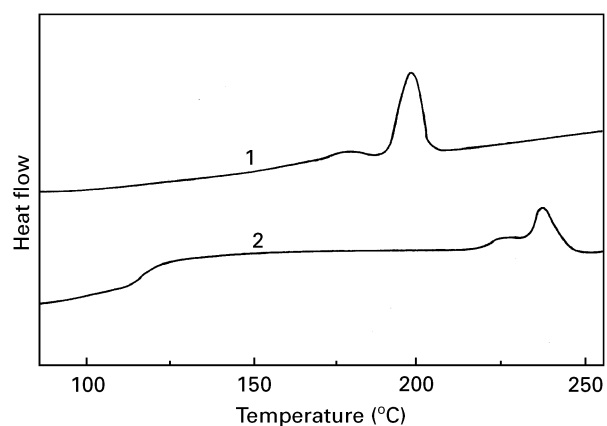


Figure 7 DSC thermograms for the EP-7.5 PBT gel: 1, before curing; 2, cured with TETA.

spherulites. Thus a schematic diagram for the network structure in the gel has been suggested as in Fig. 6.

3.2. Thermal analysis of PBT-modified epoxy resins

The transition in PBT-modified epoxy resins was studied by DSC. Typical thermograms are shown in Fig. 7, and the influence of PBT content on the dissolution temperature is given in Table I. For the systems containing 5–10 wt % PBT, the endothermic peak, i.e., the dissolution temperature, was about 40°C below the melting temperature of neat PBT, independent of the PBT content. The dissolution temperatures determined by DSC were in good agreement with the temperature at which the abrupt change in rheological properties took place, found by RMS. The heat transition data were not used for evaluation of the crystallinity of PBT because the heat of fusion could not be separated from the heat of mixing.

With the purpose of eliminating the solvent effect of epoxy resin on the melting of PBT, the resins were cured with an aliphatic polyamine before DSC analysis. As shown in Fig. 7, in this way the endothermic peak was brought to the temperature at which the

TABLE I Dissolution temperatures for PBT-modified epoxy resins

PBT content (wt %)	Dissolution temperature	
	DSC (°C)	RMS (°C)
2.5	182	190
5	197	195
7.5	199	194
10	197	–

TABLE II Heat of transition determined by DSC (curing conditions: RT, 72 h and 120 °C, 3.5 h)

Material	Peak temperature (°C)	ΔH (J g ⁻¹) normalized to 100% PBT
EP-7.5 PBT	199	76.4
EP-7.5 PBT cured with triethylenetetramine	238	86.2
EP-7.5 PBT cured with cyanoethylated TETA	237	55.5

TABLE III Mechanical properties of PBT modified epoxy resins curing conditions: 80 °C, 2h and 160 °C, 2h

	I	II
Composition (by wt)		
DGEBA	100	100
1,8-diamino- <i>p</i> -menthane	28	28
PBT	0	2.5
Flexural strength (MPa)	130	140
Modulus (GPa)	1.64	1.52
K_{IC} (MPa m ^{-1/2})	0.63	0.85
G_{IC} (J m ^{-1/2})	214	416

melting of PBT should take place, independent of the kind of curing agent used. Nevertheless, evaluation of crystallinity was still impossible, in that the heat of transition depended on the curing agent used (see Table II). It is likely that the crystallinity changed during the curing process.

3.3. Mechanical properties of PBT-modified epoxy resins

It is of practical importance to know the influence of the rheology modifier on the mechanical properties of

the cured resins. PBT-modified epoxy resins are two-phase materials. Scanning electron micrographs of the fracture surfaces indicated that the bonding at the interface was very good (Fig. 1b). It was therefore expected that the PBT spherulites should not impair mechanical properties of the modified resins.

To study the influences of the PBT modifier experimentally, the content of the modifier was limited in the range where thorough deaeration of the mixture was possible, to ensure preparation of void-free specimens. Mechanical properties of a PBT-modified epoxy resin are given in Table III. It can be seen that a slight lowering in the modulus and a slight increase in flexural strength resulted from incorporation of 2.5 wt % PBT. Meanwhile, a moderate improvement in the toughness was achieved.

Acknowledgement

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