

STUDIES ON EPOXY RESINS MODIFIED WITH POLY (BUTYLENE TEREPHTHALATE)-b- POLY (TETRAMETHYLENE GLYCOL)*

WANG Xia (王 霞) ZHAO Binyi (赵炳熒) LI Zhengyi (李贞宜)
and YU Yunzhao (余云照)

(*Institute of Chemistry, Academia Sinica, Beijing 100080*)

ABSTRACT

Poly(butylene terephthalate)-b-poly(tetramethylene glycol) (PBT-b-PTMG) was used as rheology modifier for the epoxy resin. The segmental copolymer formed spherulites in the epoxy medium. This copolymer was very effective in endowing yield stresses to the liquid resin. The PTMG segment brought in a lowering of the dissolution temperature of the spherulites in the epoxy gel. The cured resin with PBT-b-PTMG as modifier was two-phase materials. The rheology modifier improved the mechanical properties of the cured resin as well. The flexible PTMG segments, however, were not in favour of the toughening effect of the modifier. This was attributed to the large domain size of the dispersed phase.

INTRODUCTION

Rheological behaviour of many industrial materials is of critical importance. For instance, adhesives of inadequate viscosity may run away from the glue line, and result in starved bonding. Therefore adhesives and sealants for automobile assembly are usually formulated to display yield stresses to prevent sag during the curing^[1]. Conventionally, mineral fillers are used as rheology modifiers. Degradation of sag resistance during storage and irreversible change of viscosity upon shearing are the troublesome problems in these conventional systems.

The objective of the present investigation is to explore an approach of endowing yield stresses to the fluid resins, by using polymers as rheology modifier. It is known that swollen microgel particles can be used for adjusting the rheological behavior of coatings^[2,3]. In the previous paper^[4] it has been reported that poly(butylene terephthalate) (PBT) was effective in modifying the rheological properties of the

*The project is supported by Ford-China Research and Development Fund.

Received January 17, 1996

epoxy resin. The resin was made thixotropic by PBT spherulites, and the toughness was improved significantly as well.

This article is to report the rheological and mechanical properties of epoxy resins with poly(butylene terephthalate)-b-poly(tetramethylene glycol) (PBT-b-PTMG) as modifier. The poly(tetramethylene glycol) (PTMG) blocks were introduced into the PBT molecular chains to investigate the influence of the flexible segments on the properties of the modified epoxy resins.

EXPERIMENTAL

1. Materials

Epoxy resin used in the study was diglycidyl ether of bisphenol A (DGEBA), designated as E-51. Epoxy value was 5.1 meq/g. Curing agent for the epoxy resin was 4, 4'-diaminodiphenyl methane (DDM), a chemical reagent from Fengguang Chemical Factory, Hubei province.

PBT-b-PTMG was prepared by melting polycondensation, starting from dimethyl terephthalate, butylene glycol and poly(tetramethylene glycol) of molecular weight 1000. The copolymer of PBT/PTMG weight ratio 40/60, designated as B40×1000, was a good thermoplastic elastomer. The structural parameter and properties of this copolymer is given in Table. 1.

Table 1 Description of the copolymer B40×1000

PBT/PTMG weight ratio	$\bar{M}_n$ of PTMG segment	$[\eta]$ (dl/g)*	Tensile strength (MPa)	Ultimate elongation (%)	mp. (°C)
40/60	1000	1.2	21	500	178

* In m-cresol, 30°C

2. Preparation

PBT-b-PTMG was dissolved in the epoxy resin (DGEBA) by stirring at 165°C. The solutions were kept at 60°C for 4h, and then cooled to room temperature. Likewise, PBT was dissolved in the DGEBA at 220°C, and the solutions were kept at 180° for 4 h before cooling to room temperature. The blends were mixed with the curing agent DDM, and the mixtures were deaerated in vacuum, and then cast into a mould and cured. The curing conditions were 100°C for 4h and 165°C for 4h. Single edge notched specimens were machined for the three points bending tests.

3. Measurements

Controlled shear stress rheometry was conducted on a Bohlin Rheometer CS-50 using a parallel plate geometry of radius 25mm and gap 1 mm. The rheological

characteristic under constant shear rate and dynamic measurement in linear visco-elastic regime were run on a Rheometric Mechanical Spectrometer Model RMS 605 using a parallel plate geometry of radius 25mm and gap 2mm. The spherulites in the PBT-b-PTMG-epoxy gels were examined using an Olympus BH-2 polarising microscope. The morphology of the cured resins was studied on a Hitachi S530 scanning electron microscope. Dynamic mechanical analysis was run on a DMA 7 system at a heating rate of 5°C/min. Differential scanning calorimetry (DSC) scans were run on a Perkin-Elmer DSC 7 system at a heating rate of 20°C/min.

Fracture toughness of the cured resin was measured in terms of the critical strain energy release rate G_{IC} . The values were calculated from the critical value of stress intensity factor K_{IC} using the equation:

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

where E is the flexural modulus and ν is the Poisson's ratio. The K_{IC} was determined by three-point bending tests using single edge notched specimen. (Fig. 1).

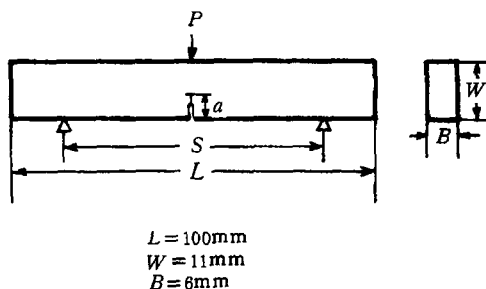


Fig. 1 Specimen for the determination of fracture toughness

The tests were run on an Instron 1122 testing machine at a crosshead speed of 2 mm/min. The values were calculated using the following equation^[5]:

$$K_{IC} = \frac{3P_C S}{2B^2 W} \sqrt{a} \cdot f(a/W)$$

where P_C is the load, S is the span between supports, B and W are the thickness and the width of the specimen, and a is the notch depth. $f(a/W)$ is a function of geometry, and given by:

$$f(a/W) = 1.93 - 3.07(a/W) + 14.53(a/W)^2 - 25.11(a/W)^3 + 25.8(a/W)^4$$

Flexural strength was determined using uniform beam specimen at a crosshead rate 5mm/min.

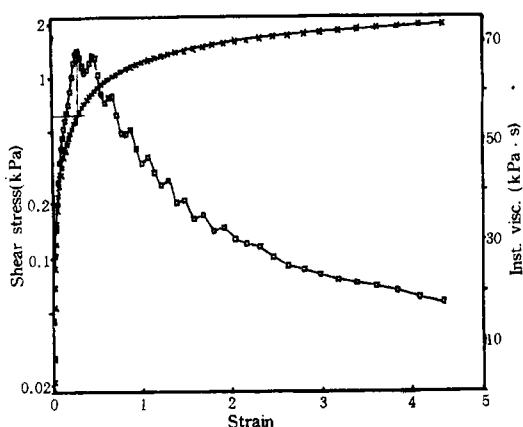


Fig. 2 Determination of yield stress for the E51 epoxy resin modified with 7.5 wt% B40 $\times$ 1000 copolymer

RESULTS AND DISCUSSION

1. Rheological behaviour of modified epoxy resins

PBT-b-PTMG copolymers are very effective rheology modifier for liquid epoxy resins. A small amount of the copolymer can turn the fluid resin into a gel. Fig. 2 shows a diagram of yield stress test for the epoxy resin modified with 7.5 wt% of the B40 $\times$ 1000 copolymer. The measurement was conducted on a controlled stress rheometer in which the shear stress was increased stepwise. The shear stress, when the instant viscosity began to fall off, was taken as the yield stress.

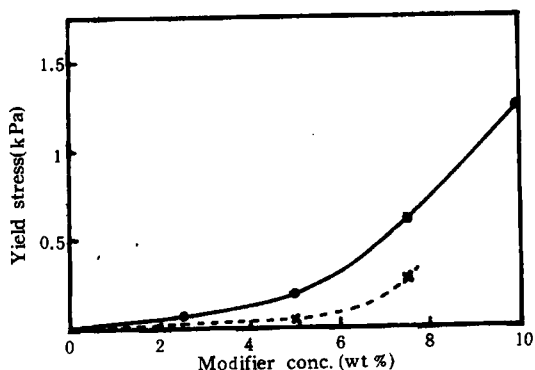


Fig. 3 Yield stress vs. concentration of rheology modifiers for the E51 epoxy resin
—B40 $\times$ 1000; --- PBT

In Fig. 3, a diagram of yield stress vs. content of the modifier is given. It is seen that the yield stress increases consistently with the concentration of the modifier, and the block copolymer was more effective than PBT. The E51 epoxy resin was

rendered a yield stress 50.2 Pa by 2.5 wt% of the copolymer B40 × 1000. This value is high enough for a layer of 1 mm thickness to keep away from sag. Commercial thixotropic adhesives have a yield stress in the range 50—500 Pa usually.

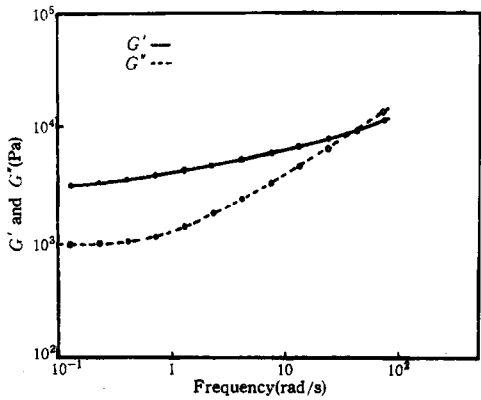


Fig. 4 Dynamic moduli vs. frequency for the epoxy resin containing 10 wt% B40 × 1000

The epoxy resin modified with 10 wt% B40 × 1000 was in a critical gel state as demonstrated by dynamic measurements. The frequency dependence of storage modulus G' and loss modulus G'' for the epoxy gel is shown in Fig. 4. G' is negligible for the neat E51 epoxy resin. For the epoxy resin containing the B40 × 1000 copolymer, there is a cross-over of G' and G'' curves, which is the characteristic of the critical gel state^[6,7].

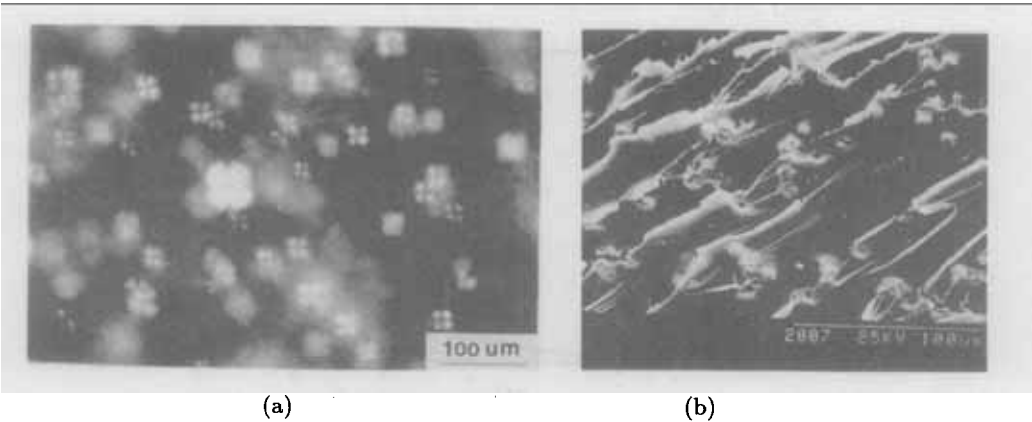


Fig. 5 Morphology of the E51 epoxy resin containing 10wt% B40×1000 copolymer: (a) micrograph of the gel taken with polarized light, (b) SEM micrograph of the fracture surface

The rheological behaviour of the modified epoxy resin can be accounted for by the network formed by the overlap of spherulites of the modifier in the epoxy medium.

Maltese cross for the spherulites was observed on a polarized optical microscope. A photograph is shown in Fig. 5a.

The network in the epoxy gel is sensitive to shearing. This can be demonstrated by thixotropic loop tests. Fig. 6 illustrates a thixotropic loop for the E51 epoxy resin modifier with 10wt% B40 $\times$ 1000 copolymer. The shear rate is increased from zero to 3 s⁻¹ over a time interval of 30s, and then brought back to zero. The curves of shear stress vs. shear rate make a loop.

The thixotropic loop indicates the structure break-down at high shear rate. The structure recovery must be very quick as the immediately followed second run gave a loop completely coincided with that given by the previous run. The apparent yield stress obtained by extrapolation of the rising ramp of the loop was much higher than the value obtained by the controlled stress measurement.

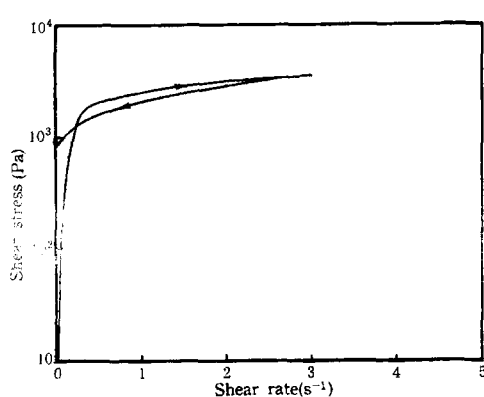


Fig. 6 Thixotropic loop for the epoxy gel containing 10 wt% B40 $\times$ 1000 copolymer

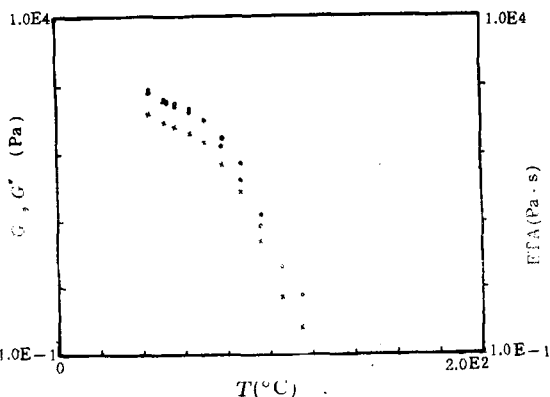


Fig. 7 RMS spectra for the epoxy gel containing 10 wt% B40 $\times$ 1000 copolymer
● G' ; ○ G'' ; $\times$ η'

2. Morphology and transitions in modified epoxy resins

The epoxy gels thus formed are thermoreversible. In Fig. 7 rheometric mechanical spectra (RMS) of G' , G'' and η' vs. temperature for the epoxy gel containing 10 wt% B40 $\times$ 1000 copolymer are shown. The steep change of the properties around 90°C is connected with the dissolution of the spherulites. This was confirmed by the endothermic peak at 88°C in the DSC thermogram (Fig. 8, a) and the disappearance of the Maltese cross in the microscope field upon heating.

The effect of structure parameters on the dissolution temperature is shown in Table. 2. It is seen that the dissolution temperature was pulled down seriously by the PTMG segment.

The cured resin modified with the B40 × 1000 copolymer was two phase material as indicated by the SEM micrograph (Fig. 5b). The domain size of the dispersed phase is in the range of 10–13 μm . The modifier exerted a slight influence on the glass transition of the matrix resin. T_g of the resin with 7.5 wt% of the B40 × 1000 copolymer was 9 degrees lower than that of the neat resin, as determined by dynamic mechanical analysis.

Table 2 Dissolution temperature of the epoxy gels containing 10 wt% modifier

Modifier	Wt. ratio of PBT/PTMG	$\overline{M}_n$ of PTMG segment	Dissolution temp. ¹⁾ (°C)
B20 × 1000	20/80	1000	70
B30 × 1000	30/70	1000	80
B40 × 1000	40/60	1000	88
B30 × 2000	30/70	2000	93
PBT	100/0	—	194

1) determined by RMS

In the DSC thermogram of the cured resin with the modifier (Fig. 8b), there is a broad endothermal with the peak at 176°C. This is attributed to the melting of the crystalline copolymer, overlapped by the glass transition of the epoxy resin.

3. Mechanical properties of modified epoxy resins

The morphology modifiers acted as tougheners in the cured resins. Mechanical properties of the cured resins are given in Table 3. It is seen that both PBT and PBT-b-PTMG improved flexural strength, maximum deflection and toughness.

Since reactive rubbers are effective tougheners for the epoxy resin, it was supposed that introduction of the flexible segment into the modifier may bring in an additional toughening mechanism. However, the results were not as expected. The block copolymer was not as effective as PBT in improving the mechanical properties of the epoxy resin.

Table 3 Mechanical properties of PBT-b-PTMG modified epoxy resins

Composition (by wt)				Flexural strength	Maximum	G_{IC}
DGEBA	DDM	PBT-b-PTMG	PBT	(MPa)	deflection (mm)	(J/m ²)
100	28	0	—	90.2	7.8	580
100	28	3	—	106	9.9	660
100	28	5	—	115	8.4	670
100	28	7.5	—	107	11.6	750
100	28	—	7.5	121	12.6	910

Morphology of the multiphase polymers may play a dominating role for mechanical performances. In the epoxy resins modified with the B40 $\times$ 1000 copolymer, the domain size of the dispersed phase (10–13 μ m, in Fig. 5b) is not in favour of the mechanical properties. It is likely that the PTMG segment (solubility parameter 17 (J/cm³)^{1/2}) does not well compatible with epoxy resin (solubility parameter 19.9–22.3 (J/cm³)^{1/2}).

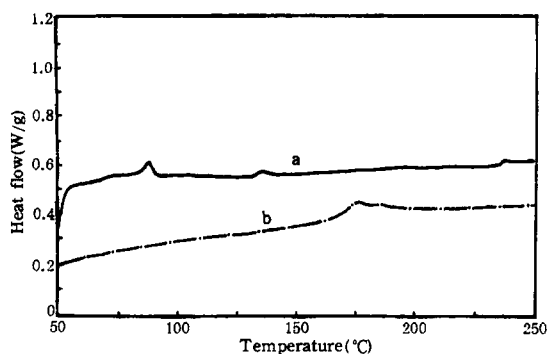


Fig. 8 DSC thermogram for the epoxy resin containing 7.5 wt% B40 $\times$ 1000 copolymer
(a) before curing; (b) cured with DDM

Keywords:

Epoxy resin; PBT-b-PTMG; Yield stress; Gel; Toughening

REFERENCES

- [1] Li, C.; Mazich, K. A. and Dickei, R.A., *J. Adhesion*, **1990**, *32*: 127.
- [2] Funke, W., *British Polym. J.*, **1989**, *21*: 107.
- [3] Raquois, C.; Tassin, J.F.; Resaiguis, S., et al., *Prog. Org. Coat.*, **1995**, *26*: 239.
- [4] Wang, X.; Li, Y. and Yu, Y., *J. Mater. Sci.*, *submitted*.
- [5] Yee, A. F. and Pearson, R.A., *J. Mater. Sci.*, **1986**, *21*: 2462.
- [6] Burchard, W. and Ross-Murphy, S. B., "Physical Networks-Polymers and Gels", Chapt. 1, Elsevier Applied Science, London and New York, **1990**.
- [7] Ross-Murphy, S.B., in "Polymer Gels-Fundamentals and Biomedical Applications", ed. Derossi, D., et al., Plenum Press, New York, **1991**.