

Thermal and toughness property studies on a polybenzimidazole-modified epoxy resin system

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Abstract: The effect of polybenzimidazole (PBI) on a silica-filled epoxy resin matrix has been investigated. Polybenzimidazole (PBI) was incorporated into a difunctional epoxy resin matrix to the extent of 10%, before being cured with an anhydride hardener. The effects of PBI on the curing reaction and glass transition temperature (T_g) and on the toughness of the cured epoxy matrix have been studied using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and a universal testing machine (Instron). The results indicate that the PBI modifier enhanced not only the glass transition temperature of the difunctional epoxy matrix but also its toughness, by its catalytic action. Further investigations have been carried out on the fractured specimens, using scanning electron microscopy (SEM) to support the enhanced toughness property of the epoxy matrix.

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Keywords: polybenzimidazole; difunctional epoxy; anhydride hardener; catalytic; glass transition; toughness; SEM

INTRODUCTION

Among thermosetting resins, epoxy resins exhibit outstanding adhesive properties towards a wide variety of fillers, substrates and reinforcing agents, very low shrinkage during curing, chemical resistance, and electrical insulation. Because of these properties they find extensive applications in both the electrical industry and in structural composites. Even though epoxy resins exhibit several advantageous properties, they are inherently brittle due to the high crosslink density developed in the cured state.¹ Bucknall *et al.*² reported various techniques for enhancing the toughness of epoxy resin matrices. It was observed that toughness enhancement techniques resulted in loss of glass transition temperature of the cured epoxy matrix,³ but later it was proved that with suitable choice of modifiers and curing agents, the toughness of the epoxy matrix can be enhanced without sacrificing the glass transition temperature.⁴ Anhydride curing agents are well known for their production of high glass transition temperature epoxy matrices.⁵ Furthermore, a polybenzimidazole thermoplastic polymer has been reported as a high T_g polymer⁶ and as a catalyst,⁷ for curing epoxies.

In the present paper, investigations were carried out by using high T_g polybenzimidazole as a catalytic agent to accelerate the curing reaction of a difunctional

epoxy in the presence of an anhydride hardener. The castings obtained were studied for glass transition temperature using differential scanning calorimetry (DSC), thermal stability by thermogravimetric analysis (TGA) and toughness properties by an Instron universal testing machine.

EXPERIMENTAL

Materials

Materials used were a difunctional epoxy resin, namely the diglycidyl ether of bisphenol-A (DGEBA) coded CY-205 from Ciba Geigy Ltd, an anhydride curing agent coded HY 905 (ricacid (5-methyl phthalic anhydride) from Ciba Geigy Ltd, and polybenzimidazole (poly [2,2'-(diphenyl) 5,5'-di(benzimidazole)]) (PBI), a catalytic modifier synthesized in-house, and a silica filler.

Preparation of blends

Finely-ground polybenzimidazole particles (10% by weight) were added to the epoxy resin, followed by the addition of silica filler (40%). A stoichiometric quantity of curing agent was added while stirring well. The resultant blend was poured into an aluminium mould and heated to 150°C for 3 h; this was followed by post curing at 180°C for 30 min and at 210°C for

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Temperature (°C)	Time of gelation (min)	
	Unmodified epoxy resin system	10% PBI modified epoxy resin system
120	510	358
150	310	165
180	175	115
210	70	40

Table 1. The effects of PBI on gel time of epoxy-hardener systems at a variety of temperatures

30 min. The specimens obtained were used for various tests.

Determination of gelation time

The effect of PBI on gelation time of the epoxy-anhydride system, at a variety of temperatures was studied by the cup plate gel time (ASTM 242) method. After mixing the resin, hardener, filler and catalyst, the surface of the reaction mixture was probed with a needle, and the time required for the reaction mixture to become non-adherent to the needle was recorded. The values obtained are presented in Table 1.

Thermal characterization

DSC

The glass transition temperature of the cured sample (7.00 mg) was studied using a differential scanning calorimeter (DSC-2910, TA Instruments), under a nitrogen atmosphere at a flow rate of about 60 ml min⁻¹. To record a stabilized glass transition temperature (T_g), the samples were preheated in the calorimeter and then scanned over the temperature range 30–350°C at a heating rate of 10 K min⁻¹. The obtained data are reported in Fig 1.

TGA

The thermal stability of pure PBI, cured-PBI incorporated epoxy and unmodified epoxy-anhydride samples (sample size about 7.20 mg) were studied using a thermogravimetric analyser (TGA-model-951, DuPont 1090). Tests were run at a heating rate of 10 K min⁻¹ under nitrogen atmosphere at a flow rate of about 60 ml min⁻¹. The thermograms are shown in Fig 2.

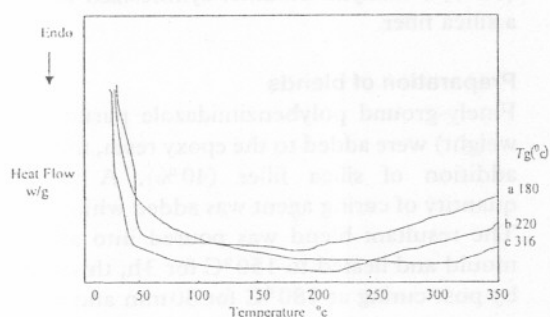


Figure 1. DSC thermograms of cured resin systems: curve a, unmodified epoxy-hardener (T_g 180°C); curve b, PBI modified epoxy-hardener matrix (T_g 220°C); curve c, PBI (T_g 316°C).

Determination of toughness properties

The plane-strain fracture toughness (K_{IC}) of the cured unmodified and of PBI-modified epoxy resin samples were determined as per the ASTM-E-399-74 test method. Three-point bend specimen samples were prepared by machining a central 'V' notch of 3 mm depth on one edge of the sample followed by a sharp notch of 0.2 mm using a razor blade. The specimens were loaded in three-point bending configuration with a span length of 40 mm in a Universal testing machine (Instron model 6025) at a cross-head speed of 1 mm min⁻¹ at 23°C and 55% relative humidity. Six specimens were tested in each case and the average K_{IC} values obtained are reported.

Fractographic studies

The obtained fractured specimens were used for fractographic analysis. The fractured areas of the specimens were coated with a gold/palladium alloy by vapour deposition and examined with a scanning electron microscope (SEM) (Jeol JSM-840-A) at about 6.0 kV. The micrographs are presented in figs 3 and 4.

RESULTS AND DISCUSSION

The results presented in Table 1 indicate that the gel time of curing reaction between epoxy resin and anhydride hardener was accelerated by the PBI modifier. This indicates that 10% addition of PBI accelerated the reaction and reduced the gel time to about half that of the unmodified system, at a variety of temperatures.

The DSC thermograms exhibited in Fig 1 clearly

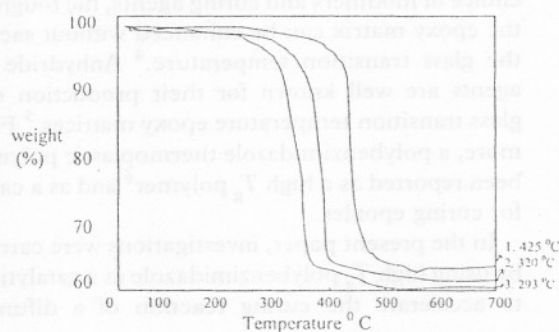


Figure 2. TGA thermograms of pure PBI (curve 1), cured PBI modified epoxy resin system (curve 2) and unmodified epoxy-anhydride system (curve 3).

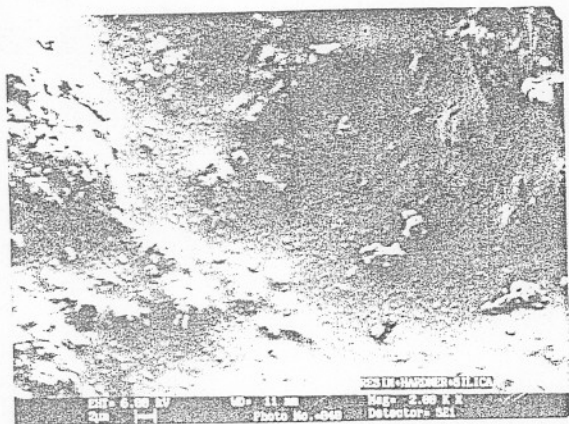


Figure 3. Scanning electron micrograph of the fractured surface of the unmodified epoxy resin system.

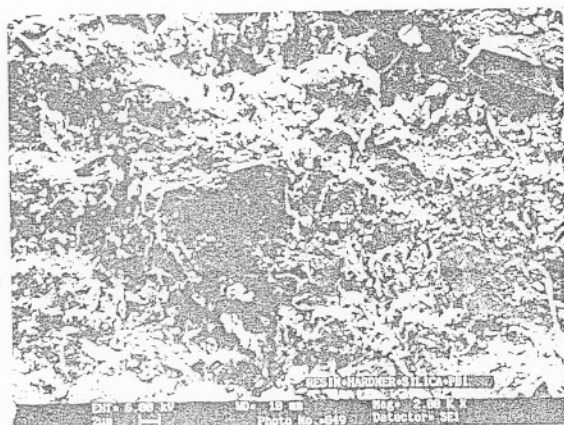


Figure 4. Scanning electron micrograph of the fractured surface of the PBI-modified epoxy resin system.

indicate that the glass transition temperature (T_g) of the unmodified cured epoxy resin–hardener matrix is 180 °C, of the PBI modified epoxy resin–hardener matrix is 220 °C and of pure PBI is 316 °C. It is evident that the PBI raises the glass transition temperature of the epoxy resin–hardener matrix system from 180 °C to 220 °C

Furthermore, the TGA thermograms exhibited in Fig 2 indicate that the onset temperature of decomposition or degradation of PBI, PBI modified epoxy–hardener and unmodified epoxy–hardener system, is

425 °C, 320 °C, and 293 °C, respectively, at 5% weight loss. Fracture toughness values (K_{IC}) of the PBI modified resin system show enhancement in the K_{IC} value from 0.59 to 0.83 MPam^{1/2}.

The enhancement in the toughness value for the PBI modified epoxy resin system was supported by fractographic analysis. The scanning electron micrographs exhibited in Figs 3 and 4 indicate that more rough surface was developed by PBI in the epoxy matrix (Fig 4) than in the unmodified resin system (Fig 3). It is a well known fact⁶ that the rougher the surface the higher will be the energy absorption. Hence, more energy was absorbed by PBI-modified resin systems.

CONCLUSIONS

Polybenzimidazole not only accelerated the curing reaction between the difunctional epoxy resin and anhydride hardener (CY-205 and HY-905), but also increased the glass transition temperature (T_g) of the matrix up to 220 °C, when 10% was added. It also considerably enhanced the toughness of the epoxy matrix.

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