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STUDIES ON THE CURING BEHAVIOUR OF BISMALEIMIDES AND EPOXY-RESIN BLENDS

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ABSTRACT

This paper describes the effect of diglycidyl ether of bisphenol A (DGEBA) on the curing behaviour of a chain-extended bismaleimide resin. 4,4′-Bismaleimidophenyl sulfone (BS) resin was treated with 4,4′-diaminodiphenyl ether or 4,4′-diaminodiphenyl methane to yield BS–M and BS–E resins which were then solution-blended with DGEBA containing stoichiometric amounts of amine as hardener. A decrease in the curing temperature of BS–M or BS–E was observed on blending with DGEBA. The thermal stability of the cured resin was reduced on blending.

INTRODUCTION

Epoxy resins have been used as binders for carbon fibres in the fabrication of composites which are now well-established construction materials in the aerospace industry. However, on prolonged exposure to the environment, these composites absorb moisture, thereby leading to a reduction in the T_g and in the service temperature to 120°C. In order to overcome the shortcomings of epoxy resins, a family of bismaleimide resins with epoxy-like processing and excellent hot-wet strength were developed. Composite structures with 120–232°C thermal envelopes have been designed using bismaleimide as the matrix material [1]. However, bismaleimides are high-modulus, low-strength materials with a very low elongation-at-break. The room temperature shear-strength of laminates fabricated from bismaleimides is inferior to those based on epoxy resins. There is a need to develop matrix resins with better performance characteristics.

The blending of polymers is an attractive proposition for tailor-making the products. Bismaleimide–epoxy blends of optimum composition may yield resins with better properties than state-of-the-art materials. Such blends have been reported in the literature. The Hysol division of Dexter Corporation has developed a broad line of 232–288°C [2,3] service adhesives, EA 9655 and EA 9102, which are bismaleimide-modified epoxy

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resins, processed like conventional heat-cured epoxy resins. Resins with good heat resistance were obtained by blending the epoxy with bismaleimide–anhydride copolymer [4]. Keremid 601 was blended with 1,2-polybutadiene epoxide in the presence of an organic peroxide to prepare electric insulators with good high-frequency properties, heat resistance, adhesion and dimensional stability [5].

An epoxy-modified bismaleimide film-adhesive with improved tack and flow properties was developed for 232°C service applications with potential short-term service to 260°C [6]. The mechanical properties and phase behaviour of inter-penetrating networks formed by co-curing two thermosets, a tetra-functional epoxy/amine and a bismaleimide formulation, have been investgated [7]. In contrast to most epoxy systems modified with rubbers or thermoplastics, phase separation was not observed in these inter-cross-linked epoxy–bismaleimide networks. A homogeneous structure for the network was suggested by the results of both dynamic mechanical analysis and scanning electron microscopy. Recently, the Narmco × 5250 series of bismaleimide-resin-based composites with superior properties has been reported. They have the excellent high-temperature performance expected from a bismaleimide, along with a toughness greater than that in currently used high-temperature epoxy resin systems [8,9].

Though considerable work has been carried out on bismaleimide–epoxy blends, the thermal characterisation of such blends has not been investigated in detail. We here report the curing characteristics of these blends using the DSC technique.

EXPERIMENTAL

Preparation of bismaleimide–epoxy resin blends

4,4′-Bismaleimidophenyl sulfone (BS) resin was prepared according to the method reported earlier [10–12]. The chain extension of BS resin was done using 4,4-diaminodiphenyl ether (E) or 4,4′-diaminodiphenylmethane (M). These chain-extended BS–M and BS–E resins were blended with diglycidyl ether of bisphenol-A using 5%, 10%, 15%, 20%, 30% and 50% (w/w) of epoxy resin. Solution blending was carried out using acetone as a solvent. In order to bring about curing of the epoxy resin, the stoichiometric amount of diamine (M or E) was also added to the acetone solution. After thorough mixing, a homogeneous solution was formed. The acetone was then removed using a rotary evaporator.

The blends were designated on the basis of the composition and nature of the constituents. Thus, for example, the blend containing 5% epoxy resin and 95% BS–M was designated D_1 : SM. Similarly a blend of 15% epoxy and 85% BS–E was designated D_3 : SE. The details of blend designations are given in Table 1.

TABLE 1

Details of bismaleimide–epoxy resin blends

Resin system	Composition (w/w)	Hardener (phr)	Designation
BS–M:DGEBA	95:05	M1.45	D_1:SM
BS–M:DGEBA	90:10	2.90	D_2:SM
BS–M:DGEBA	85:15	4.35	D_3:SM
BS–M:DGEBA	80:20	5.80	D_4:SM
BS–M:DGEBA	70:30	8.70	D_6:SM
BS–M:DGEBA	50:50	14.50	D_{10}:SM
BS–E:DGEBA	95:05	(E)1.47	D_1:SE
BS–E:DGEBA	90:10	2.94	D_2:SE
BS–E:DGEBA	85:15	4.41	D_3:SE
BS–E:DGEBA	80:20	5.88	D_4:SE
BS–E:DGEBA	70:30	8.80	D_6:SE
BS–E:DGEBA	50:50	14.70	D_{10}:SE

Thermal characterisation

DSC analysis was done using a DuPont 1090 thermal analyser with a 910 DSC module. A heating rate of 10 °C min^{-1} was used in static air atmosphere. The exothermic transition associated with curing was characterised by determining: T_i, the temperature at which polymerisation begins; T_1, the onset temperature of curing; T_{exo}, the exothermic peak temperature; and T_2, the temperature for the completion of reaction. The heat of curing ΔH was calculated by measuring the area under the exothermic peak.

RESULTS AND DISCUSSION

Curing behaviour of epoxy resin

The epoxy resin, DGEBA, was cured using diamines M and E as hardeners. The stoichiometric amount of amine was added to the epoxy resin for curing, e.g. 0.5 mol of aromatic diamine for curing 1 mol of epoxy resin. An exotherm was observed in the DSC trace above 60–80 °C with T_{exo} at 160 and 152 °C, for diamines M and E respectively. The heat of polymerisation ΔH for D:M was found to be 332 J g^{-1}, and that for D:E was found to be 172 J g^{-1}.

Curing behaviour of epoxy resin–bismaleimide blend

The exothermic transition associated with the curing reaction was observed above 100 °C. With the addition of a small amount of epoxy resin

TABLE 2

Thermal characteristics of BS–M/epoxy resin and BS–E/epoxy resin blends

Resin designation	T_i (°C)	T_1 (°C)	T_{exo} (°C)	T_2 (°C)	ΔH (J g^{-1})
D:M	74	122	160	230	338
D_1:SM	111	115	198	248	31
D_2:SM	116	137	193	240	28
D_3:SM	106	108	192	240	33
D_4:SM	105	128	188	245	34
D_6:SM	121	128	176	212	41
D_{10}:SM	110	133	177	235	32
D:E	84	114	152	315	172
D_1:SE	99	110	187	244	30
D_2:SE	111	111	182	243	28
D_3:SE	124	124	177	250	32
D_4:SE	106	106	170	241	36
D_6:SE	110	110	167	237	50
D_{10}:SE	110	130	179	230	32

(D_1 : SM), the T_{exo} value of BS–M was reduced from 246 °C to 198 °C. Similarly, the T_{exo} value fell from 245 °C to 187 °C in D_1 : SE. The T_{exo} values decreased further with increasing epoxy component (Table 2). Thus, the curing of bismaleimide resins can be done at lower temperatures with the addition of even 5% of epoxy resin.

Thermal stability of bismaleimide–epoxy resin blends

The thermal stability of bismaleimide–epoxy resin blends was assessed after heating them at 180 °C for 1 h and at 220 °C for 1 h. In the case of D_1 : SM or D_1 : SE, the IDT, T_{max} and %char-yield values decreased significantly. With the increase in concentration of epoxy resin in the blend, the thermal stability reduced. On increasing the epoxy concentration from 30 to 50% in the blends, the IDT and T_{max} values reduced further but the char yield remained unchanged or was not significantly affected.

These results, therefore, indicate that the curing temperatures of epoxy resin blends are lower than those of neat bismaleimides. However, the thermal stability of the cured resin is also decreased.

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