Thermochimica Acta, 93 (1985) 217-220
Elsevier Science Publishers B.V., Amsterdam

THERMAL CHARACTERISATION OF IMIDE RESINS

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ABSTRACT

The paper describes the curing behaviour of several bismaleimides, chain extended bismaleimides and reactive diluent modified bismalemides. Cure kinetics of the resins was evaluated by isothermal curing using DSC. High temperature performance of the resins and glass fabric/carbon fibre reinforced composites was evaluated by thermogravimetric analysis and dynamic mechanical analysis.

INTRODUCTION

Maleimide end-capped monomers and oligomers are prime candidates as matrix resins for fibre-reinforced composites, because of their good performance at elevated temperatures and hot wet environments. However the applications of these polymers for structural composites is somewhat limited due to their brittleness. Michael addition reaction of diamines and bismaleimide leads to chain extension reaction thereby reducing the brittleness of the product. Structural modifications of these polymers can thus be achieved by varying either the structure of the bismaleimide or the amine used for chain extension. Copolymerisation of bismaleimides with double bond containing compounds is yet another way of modifying the polymer backbone and this may affect the processing conditions and thermal behaviour.

In our earlier papers we have reported the synthesis and charcterisation of bismaleimides, chain extended bismaleimides and curing of imides in presence of vinyl ester resins[1-8]. In this paper we report thermal behaviour of bismaleimides, chain extended bismaleimides and triallylcyanurate modified imide.

EXPERIMENTAL

4,4'-Bis(maleimidophenyl methane) (BM) (m.p. 156-157°C) and 4,4' - Bis(maleimidophenyl ether) (BE) (m.p. 179-181°C) were prepared by the cyclodehydration of bismaleamic acid precursor with acetic anhydride and sodium acetate using a modification of the method described by Searle[9].Chain extension of BM and BE was done by using 4,4' - diamino diphenyl ether (E), 4,4' - diamino diphenyl methane (M), 4,4'-diamino diphenyl sulfone (DDS_p), 3,3' - diaminodiphenyl sulfone (DDS_m), 9,9 bis (p-aminophenyl) fluorene (BAF) and tris (m-aminophenyl) phosphine oxide (TAP).

Bismaleimide - amine adducts were prepared by refluxing bismaleimide (BM)/ (BE) with various amines in molar ratio of 1:0.3 and 1:0.4 in acetone for 3-4h till

Proceedings of ICTA 85, Bratislava

a homogeneous solution was obtained. Acetone was removed by using rotary evaporator and shining powder of bismaleimide-amine adduct was obtained.

Bismaleimides as well as their adducts were separately placed in shallow aluminium dishes and cured at 220 ± 5°C for 4-1/2 h in an air oven. Effect of triallyl-cyanurate on the curing of these bismaleimides and chain-extended bismaleimide was also investigated.

A Du Pont 1090 thermal analyser having a TGA module 951 and DSC module 910 was used to evaluate the thermal behaviour of the resins. The measurements were done in air (static) or in nitrogen atmosphere (flow rate 100 cm^3/min) at a heating rate of 10°C/min.

Ten pieces of 6"x6" glass fabric (Pilkington Fibre Glass Co., Rp-6 epoxy compatible weighing 200 g/m^2) were coated with a 45% (W/W) solution (DMF or methyl ethyl ketone) of chain extended bismaleimide having different weight percentage of triallylcyanurate (5-15%). The dried prepregs were stacked and pressed between glazing sheets covered with an aluminium foil. Molding was done on a Carver Laboratory Press at a temperature of 180°C and a pressure of 100 psi. Post curing was done at 220°C.

Glass transition temperature of laminates was determined using Du Pont 982 dynamic mechanical analyser. Mechanical Properites of the laminates were determined according to ASTM standards using Instron tensile testing machine.

RESULTS AND DISCUSSION

In the DSC scans of various resins, endothermic transition associated with melting (Tm) and exotherm due to curing reaction were observed. The temperature corresponding to exothermic peak (T_{exo}) and onset of curing reaction (T_i) (obtained extrapolation) depended on the structure of the resin sample (Table 1). Chain extension of BM or BE resin with various diamines resulted in a decrease in T_i and T_{exo} values. The reduction was significant if the amine contained electron donor groups (E or M).

In the DSC scan of triallylcyanurate (TAC) two exotherms were observed (T_{exo} at 189 and 299°C resp.) Addition of TAC to BM reduced the Tm but no significant change in the curing exotherm was observed (Table 2). In BM-TAP system, the T_{exo} and T_i values increased on increasing the concentration of TAC.

Thermal stability of cured resins was evaluated by TGA and initial decomposition temperature (T_i), temperature of maximum rate of weight loss (T_{max}) and char yield (Y_c) (%) at 800°C in nitrogen atmosphere was noted down (Table 3).

The mechanical properties of the glass fibre reinforced/carbon fibre reinforced laminates were also evaluated. Interlaminar shear strength of 355 kg/cm^2 and flexural strength 2970 kg/cm^2 was obtained with laminate based on BE-E and glass fibre.

TABLE I

Results of DSC Scans of various bismaleimide - amines

S.No	Bismaleimide	Amine	Molar ratio	Tm (°C)	T_i (°C)	T_{exo} (°C)	Δ H (J/g)
1.	BM	-	-	156	194	260	221
2.	BE	-	-	181	219	262	164
3.	BM	E	1:0.3	-	203	245	33.3
4.	BM	E	1:0.4	80	180	264	29.6
5.	BE	E	1:0.3	-	113	154	36.7
6.	BE	E	1:0.4	-	131	171	30.6
7.	BM	M	1:0.3	83	118	162	32.9
8.	BM	M	1:0.4	75	84	136	24.4
9.	BE	M	1:0.3	-	117	152	18.8
10.	BM	DDSm	1:0.4	129	201	248	99.4
11.	BE	DDSm	1:0.4	-	195	242.2	113
12.	BM	DDSp	1:0.3	147	198	259	158
13.	BM	DDSp	1:0.4	137	227	266	152
14.	BE	DDSp	1:0.4	-	199	239	144
15.	BM	BAF	1:0.4	79	100	135	34.1
16.	BE	BAF	1:0.4	-	122	149	25.5
17.	BM	TAP	1:0.3	-	125	190	100
18.	BM	TAP	1:0.4	-	128	194	119
19.	BE	TAP	1:0.4	-	130	194	95.2

TABLE 2

Effect of triallyl cyanurate (TAC) on the curing characteristics of bismaleimide amines.

S.No	Bismaleimide	% of TAC	Tm (°C)	T_i (°C)	T_{exo} (°C)	Δ H (J/g)
1.	BM	5	154	238	266	109
2.	BM	10	151	249	273	-
3.	BM	15	148	236	264	153
4.	BM	20	147	236	265	171
5.	BM	25	143	236	263	176
6.	BM-TAP	5	-	167	205	95
7.	BM-TAP	15	-	180	219	144
8.	BM-TAP	25	-	193	232	227

TABLE 3

TGA results of various bismaleimide - amines (cured at 220 ± 5°C)

S.No	Bismaleimide	Amine	Molar ratio	IDT (°C)	T_{max} (°C)	T_f (°C)	Y_c (%)
1.	BM	E	1:0.3	373.3	433	520	42.89
2.	BE	E	1:0.3	387.7	413.6	499	45.20
3.	BM	M	1:0.3	372	424	523	49.28
4.	BM	M	1:0.4	377.5	434.3	522.7	41.00
5.	BE	M	1:0.3	373.4	417.6	511	44.7
6.	BM	DDSp	1:0.3	418	445.6	501.6	50.5
7.	BM	DDSp	1:0.4	400	431.4	498.4	47.8
8.	BM	BAF	1:0.4	390.4	420.4	522.7	45.6
9.	BE	BAF	1:0.4	392.3	417.4	500	47.7
10.	BM	TAP	1:0.4	363.3	399.7, 520.4	-	58.67
11.	BE	TAP	1:0.4	373	396.4, 511.2	-	61.1

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ACKNOWLEDGEMENT

The Financial assistance provided by DST-UNDP for carrying out this research work is gratefully acknowledged.