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Thermal Behavior of Bismaleimide-Amine/ Vinyl Ester Resin-Styrene Blends

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ABSTRACT

Curing of 4,4'-bismaleimido-diphenyl methane-4,4'-diaminodiphenyl methane (1:0.3 molar ratios) (BM-A) was carried out in the presence of vinyl ester-styrene resin. The BM-A could be cured at lower temperatures. The char yields of the cured resins depended on the percentage of bismaleimide-amine in the blend.

INTRODUCTION

Bismaleimides cure without the evolution of volatiles by the thermal polymerization at temperatures above 250°C [1]. These severe curing conditions not only increase the processing costs but also produce large internal strains in standard bismaleimide composites. It is therefore desirable to have low temperature processible bismaleimide resins.

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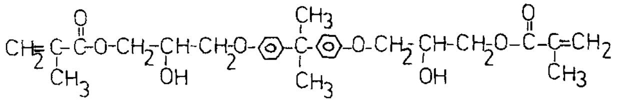
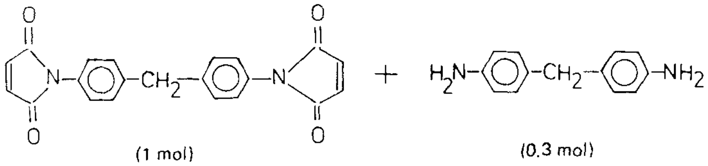
The reluctance of 1,2-disubstituted monomers (for example, maleimides) to polymerize by radical mechanisms is well documented in the literature. This has been attributed to steric hindrance which increases the activation energy required for the addition reaction [2]. However, 1,2-disubstituted olefins readily copolymerize with monosubstituted olefins, and this forms the basis for polyester laminate technology. It is therefore reasonable to expect that bismaleimides in the presence of vinyl-terminated oligomers may copolymerize at lower temperatures. The present investigations were undertaken with the aim of developing low temperature processible bismaleimide resin formulations by blending them with vinyl ester resins containing 40% styrene as a reactive diluent.

Vinyl ester resins are thermosetting resins produced by the addition reaction of an epoxy resin (diglycidyl ether of bisphenol A) with methacrylic acid [3]. The terminal unsaturation in these resins is the cross-linking site:



4,4'-Bismaleimidodiphenyl methane was used in the present work. In order to increase the solubility of bismaleimide in methyl ethyl ketone, it was chain extended by reacting it with 4,4'-diaminodiphenyl methane (1 mol of bismaleimide + 0.3 mol of diamine):



The thermal behavior of blends of chain-extended bismaleimide and vinyl ester resin (having 40% styrene) was evaluated by thermogravimetric analysis.

EXPERIMENTAL

Materials

Diglycidyl ether of bisphenol-A (DGEBA) was procured from Ciba Geigy (Araldite LY 556). Methacrylic acid (Fluka AG), maleic anhydride (BDH), 4,4'-diaminodiphenyl methane (Fluka), methyl ethyl ketone (E. Merck), imidazole (Sigma), and hydroquinone (Sarabhai Chemicals) were used as received.

Synthesis of 4,4'-Bismaleimidodiphenyl Methane (Bismaleimide)

Bismaleimide was prepared by cyclodehydration of bismaleamic acid precursor with acetic anhydride and sodium acetate by using a method reported earlier [4, 5].

To a well-stirred solution of 4,4'-diaminodiphenyl methane (0.1 mol) in dry acetone, 0.22 mol of maleic anhydride was gradually added over a period of 10 min. The solution was refluxed for 3 h in nitrogen atmosphere. Cyclodehydration of the amic-acid intermediate to bismaleimide was carried out by treating it with fused sodium acetate and acetic anhydride and refluxing the solution for a further 4 to 5 h. Yellow-orange precipitates of bismaleimide were obtained by adding this solution to water. The precipitates were repeatedly washed with sodium bicarbonate solution (to remove acetic acid) and finally with water, and then dried at 60-70°C in an air oven. Purification was done by passing a chloroform solution of bismaleimide through a silica gel column. Yellow crystals of 4,4'-bismaleimidodiphenyl methane (mp 152-154°C) were obtained (yield = 69-70%).

Preparation of Bismaleimide-Amine Adduct

Chain extension of bismaleimide with 4,4'-diaminodiphenyl methane was carried out by refluxing an acetone solution of bismaleimide with amine (1:0.3 molar ratio) for 3-4 h until a homogeneous solution was obtained. Acetone was removed under vacuum at a temperature of 45-55°C using a rotary evaporator. A shining powder of bismaleimide-amine adduct was obtained.

Preparation of Vinyl Ester Resin

In a two-necked round-bottom flask fitted with a reflux condenser, 50 g DGEBA, 20.13 g methacrylic acid, 0.0702 g hydroquinone, 14.03 g of methyl ethyl ketone, and 0.119 g of imidazole were added. The flask was placed in an oil bath maintained at 100°C and the reaction mixture was vigorously stirred with the help of a magnetic stirrer. The course of the reaction was followed by titrating a known weight of the solution with standard sodium hydroxide and determining the acid number. The reaction was stopped when the acid number was around 1.2-1.5. The vinyl ester resin thus obtained was diluted with 40% styrene (w/w).

Curing of Bismaleimide-Vinyl Ester Resin Blends

The curing of bismaleimide-amine/vinyl ester-styrene was done by taking 100, 87.5, 75, 50, 25, and 0% (w/w) of bismaleimide. Homogenous solutions of the resins were prepared in methyl ethyl ketone, and benzoyl peroxide (1%) was added as the initiator. Curing was done in shallow aluminum dishes in an air oven in the temperature range from 100 to 120°C.

Thermal Characterization

A DuPont 1090 Thermal Analyzer was used to evaluate the thermal behavior of the resins. The measurements were done in nitrogen atmosphere (flow rate, 100 cm^3/min). A sample size of 10 ± 2 mg was used.

RESULTS AND DISCUSSION

The curing of various resin blend samples was done for 2 h at 100°C. Samples having 50% or more of bismaleimide-amine at the end of this period were cured to give a hard, deeply colored product. The neat vinyl ester resin containing 40% of styrene as the reactive diluent remained soft and somewhat tacky. The surface of resin blend containing 25% bismaleimide-amine was also undercured. This may be due to susceptibility of these systems to air inhibition since the curing was done in an air oven. It was therefore decided to further cure all samples for 1 h at 120°C. Undercuring of the surface was considerably reduced by such a thermal treatment.

The extent of residual cure was evaluated by recording the DSC scans of these samples. In a neat bismaleimide-amine (BM-A) sample, no significant curing was observed by heating the sample at 100-120°C. In a neat BM-A (uncured) sample, an exotherm corresponding to polymerization was observed in the temperature range from 120 to 230°C with a maximum at 181.9°C. This exotherm corresponds to a heat of polymerization of 31.6 J/g (Fig. 1). A small exothermic peak in the temperature range from 78.6 to 140°C (with a maximum at 104.9°C) was observed in a neat (cured) vinyl ester resin-styrene sample. The residual heat of polymerization was 10.6 J/g. No such exotherm was observed in other samples. These DSC results clearly indicate that bismaleimide resin can be cured effectively in the presence of vinyl ester resin-styrene at a much lower temperature.

The thermal stabilities of the various cured resin blends thus obtained were evaluated by thermogravimetric analysis in nitrogen atmosphere (Fig. 2). Total loss in weight was observed around 435°C in the neat vinyl ester resins-styrene system. However, as the content of bismaleimide in the blend increased, the thermal stability of

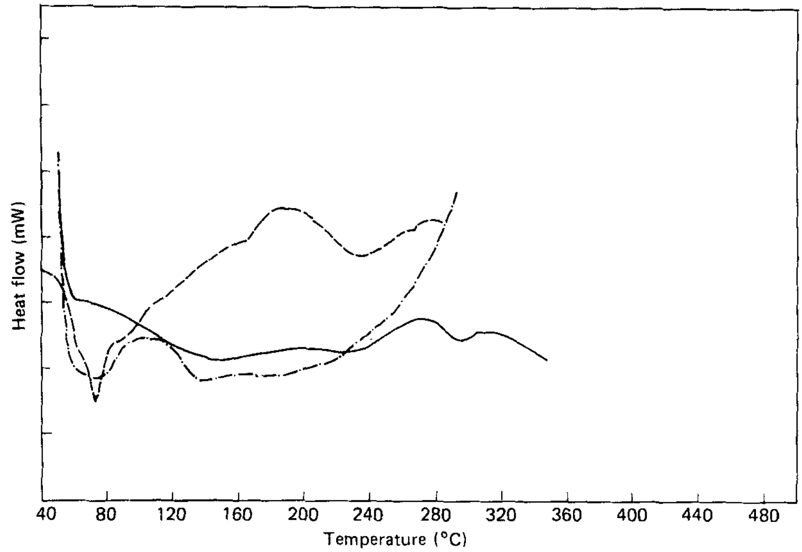


FIG. 1. DSC scans of various resin samples in air atmosphere at a heating rate of 10°C/min. (- -) Neat bismaleimide-amine adduct (uncured). (—) Bismaleimide-amine adduct cured at 100°C (2 h) and 120°C (1 h). (- · · -) Vinyl ester-styrene resin cured at 100°C (2 h) and 120°C (1 h).

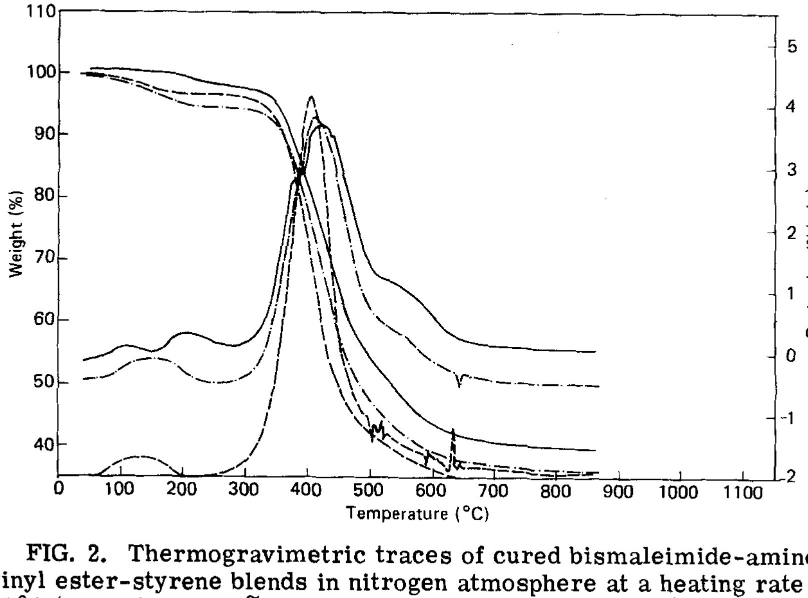


FIG. 2. Thermogravimetric traces of cured bismaleimide-amine/ vinyl ester-styrene blends in nitrogen atmosphere at a heating rate of 10°C/min. (—) 87.5% Bismaleimide-amine. (- · · -) 75% Bismaleimide-amine. (- -) 50% Bismaleimide-amine.

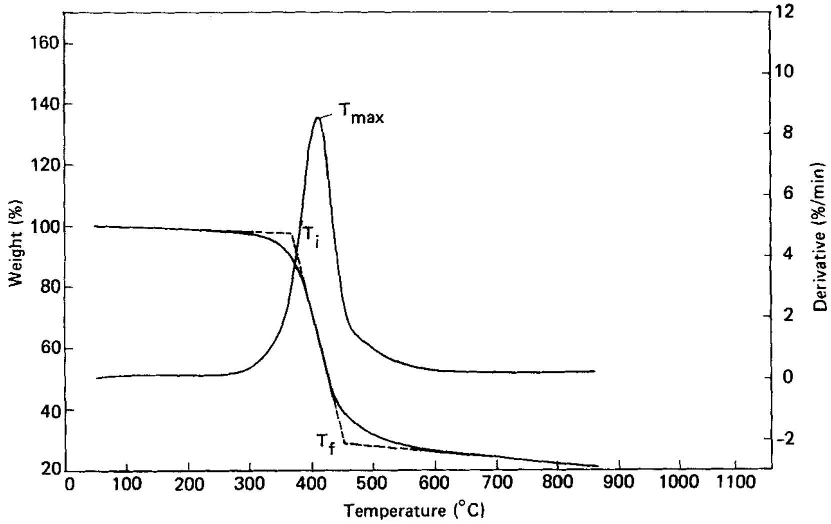


FIG. 3. Thermogravimetric trace of cured bismaleimide-amine/vinyl ester styrene blend (containing 25% bismaleimide-amine) in nitrogen atmosphere showing the evaluation of T_i, T_f, and T_{max}.

TABLE 1. Results of Thermogravimetric Analysis of Bismaleimide-Amine/Vinyl Ester-Styrene Blends

Sample	Bismaleimide content (%)	IDT (°C)	T_f (°C)	T_{max} (°C)	Char yield (Y_c) (%), 800°C
a	0	386.5	440	418.8	0
b	25	369.6	453.0	410.8	23.7
c	50	364.6	464.8	407.5	33
d	75	361.8	494.6	414.2	37
e	87.5	362.8	512.9	420.1	40
f	100	372.0	533.4	432.0	45

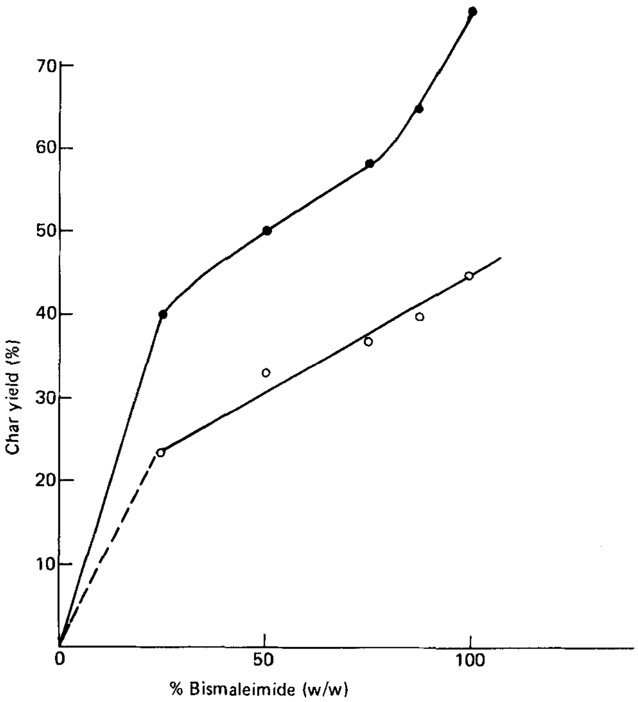


FIG. 4. Effect of percentage of bismaleimide-amine on the anerobic char yield of cured bismaleimide-amine/vinyl ester styrene blends. (○) Char yield at 800°C. (●) Char yield at 450°C.

the cured resin increased. The relative thermal stabilities of the resins were assessed by comparison with the initial decomposition temperature (IDT) which was obtained by extrapolation. The temperature of maximum rate of weight loss (T_{max}), the final decomposition temperature (obtained by extrapolation) (T_f), and the char yields (Y_c) at 450 and 800°C were also obtained from thermogravimetric traces (Fig. 3). The results thus obtained are summarized in Table 1. Char yields and T_f increased as the bismaleimide-amine content was increased in blends (Fig. 4). IDT and T_{max} values decreased with an increase in bismaleimide-amine content up to an optimum concentration (~75% w/w), beyond which increases in these values were obtained.

These results clearly indicate that bismaleimide-amine can be cured at low temperatures in the presence of vinyl ester resin-styrene.

The better thermal properties associated with bismaleimide-resin can be retained by using a low weight-% of the vinyl ester resin-styrene in the blend.

ACKNOWLEDGMENTS

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