EFFECT OF STRUCTURE ON PROPERTIES
OF
BISMALEIMIDE RESINS

by

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DEDICATED

TO MY

PARENTS

CERTIFICATE

This is to certify that the thesis entitled, **"Effect of Structure on Properties of Bismaleimide Resins"**, being submitted by Mr. S.P. Gupta to the Indian Institute of Technology, Delhi, for the award of degree of Doctor of Philosophy, is a record of bonafide research work carried out by him. Mr. S.P. Gupta has worked under our guidance and supervision and has fulfilled the requirement for the submission of this thesis which to our knowledge has reached the requisite standard.

The results contained in this thesis have not been submitted in part or full to any other University or Institute for the award of any degree or diploma.

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ABSTRACT

The application of bismaleimides as matrix resins in advanced fibre reinforced composites has grown considerably in the past decade. These resins cure with no evolution of gaseous byproducts at relatively low temperatures to yield composites with excellent hot-wet strength retention.

There are however, certain limitations of bismaleimide resins. Most of the commercially available bismaleimide resins are solids and hence are difficult to handle in preimpregnated form. Prepregs based on glass/carbon fibres and bismaleimide resins are generally fabricated by using high boiling solvents such as N-methyl pyrolidone or dimethyl formamide. Complete removal of these high boiling solvents is often difficult from the prepregs. Residual solvent is responsible for deterioration in properties of composites at elevated temperatures. Therefore, it is necessary to synthesise bismaleimide with higher solubility in low boiling solvents such as acetone or methyl ethyl ketone. On curing, bismaleimide resins yield a highly cross-linked void free network polymer with high modulus, low strength and very low elongation at break. In other words, the cured resins are brittle having very poor impact properties. In order to improve the toughness of these resins it is necessary to reduce the cross-link density and

enhance the backbone flexibility without impairing the good thermal and flame resistance of the polymers. There is thus a need to modify the state-of-the art bismaleimide resins to develop polymers with good thermal and flame resistance and better impact strength.

In the present work an attempt has been made to modify the structure of bismaleimide resin by (a) changing the structure of bridging unit between maleimide end-caps; (b) reducing the cross-link density and (c) copolymerisation with allyl-type derivatives.

Effect of the bridging group between the maleimido group on properties was investigated by synthesizing bis(4-maleimidophenyl) methane (BM) and 2,5-bis(p-maleimido phenyl) 3,4-diphenyl thiophene (BPT) resins were prepared by reacting 4,4'-diaminodiphenyl methane (DADPM) or 2,5-bis(p-aminophenyl)- 3,4-diphenyl thiophene (TPTDA) (synthesized in laboratory) with maleic anhydride in DMF/acetone, using acetic anhydride and sodium acetate as cyclodehydrating agents. BPT resin was appreciably soluble in acetone or MEK whereas BM resin was insoluble. Melting point of BM and BPT resin was 156-157°C and 212°C respectively. Broad exothermic transition indicating curing reaction was observed in the temperature range of 200-350°C in BM and BPT resins. Uncured BPT and BM resins were stable upto 400°C. However, char yield at 800°C in nitrogen atmosphere was higher in BPT (60%) than BM (50%) resin. These results thus indicate that incorporation of 3,4-diphenyl thiophene group in BM resin increases solubility in organic solvent as well as thermal performance.

Reduction in cross-link density of bismaleimides was done by chain extension reaction (Michael addition reaction) with amines. Nucleophilic addition reaction to the maleimido double bonds was done with 4,4'-diaminodiphenyl methane (DADPM), tris(m-aminophenyl)phosphine oxide (TAP), ethylene diamine (EDA), 1,4-diaminobutane (DAB), 1,6-diaminohexane (HMDA), diethylene triamine (DETA), triethylene tetramine (TETA) in molar ratios 1:0.05 - 0.3. In chain extended BM resins thus obtained, no endothermic transition due to melting was observed and exothermic peak due to curing was in the range of 130-300°C. Δ H of BM resin decreased on chain extension. Thermal stability was not significantly affected by varying methylene content of amine used for chain extension (e.g. BM-D_1 and BM-HD_1).

The prepregs fabricated from MEK solution of BM or chain extended BM resin had poor tackiness. Hence it was considered of interest to use reactive diluents in BM formulations which can act as processing aids. In order to introduce s - triazine units in bismaleimide formulations blending with 2,4,6-tris(4'-allyl 2'-methoxy phenyl) cyanurate (TAIC) and triallyl cyanurate (TAC) was done. TAIC was synthesized by reacting eugenol [4-allyl 2-methoxy phenol] and cyanuric chloride. Commercially available triallyl cyanurate (TAC) was used as such. Addition of 5-25% TAC to chain extended bismaleimides, reduced temperature of the exothermic transition (due to curing). In these studies benzoyl peroxide (0.05-2% w/w) was used as an initiator. A decrease in curing temperature and ΔH was observed by addition of TAC. The activation energy for curing reaction of chain extended BM with aliphatic amines having 10% TAC was found to be in the range of 105-168 KJ/mole. In BM-M/TAIC blends, an endothermic peak associated with TAIC was observed in the range of (111.9-122.0°C), and the heat of curing was in the range of (11-13.5 J/g). Thermal stability was not affected by the addition of TAC to chain extended BM resins. However, a significant reduction in initial decomposition temperature (IDT) and temperature of maximum rate of weight loss (T_{max}) was observed by the addition of TAIC to BM-M resins. Higher char yield was obtained in these resins.

Dry blending of BM with DADPM (1:0.3 molar ratio) and addition of TAC resulted in a decrease in melting transition. TAC only marginally affected the curing temperature. Activation energy for curing of BM:DADPM/TAC blends was found to be in the range of 129-152 KJ/mole.

Bis(4-allyl 2-methoxy phenyl)sebacate(SEg), bis(4-allyl 2-methoxy phenyl)terephthalate(TEg), bis(4-allyl 2-methoxy phenyl)adipate(AEg) and bis(o-allyl phenyl)sebacate(APS) were prepared by reacting eugenol or o-allyl phenol with sebacoyl, terephthaloyl and adipoyl chloride in 20% aq. NaOH solution or pyridine.

In the DSC scans of reactive diluents, the melting peak was at 76.3°C (SEg), 99.7° (AEg) and 179.4° (TEg). The heat of fusion were found to be 87.6 (SEg), 104 (AEg) and 119 J/g (TEg). In the DSC taces of BM-M resin with reactive diluents the low temperature curing exotherm disappeared on addition of APS, SEg and AEg. Isothermal curing of BM-M/SEg blends at 200°C for 2 h resulted in 1-4% weight loss. The cured resins were tested for solubility in DMF. However, in BM-M/APS blends higher weight loss was observed. Addition of 5-15% of these allyle type reactive diluents (i.e SEg, APS, AEg) did not influence thermal stability of cured BM-M resin. However further increase in concentration to 35%, IDT and T_{max} vlues were reduced . Char yield was in the range of 30-48%.

Blends of BM:DADPM (molar ratio 1:0.3) and TEg were also investigated. An exotherm, due to curing was observed in the temperature range of 206-305°C with peak position at 240 ± 10°C depending on TEg constant of blends. Thermal stability of these blends (BM : DADPM/TEg) was slightly better than BM : DADPM blends.

Fabrication and characterization of glass fibre and carbon fibre reinforced composites using chain extended BM resins and 10% (w/w) of reactive diluents (TAC and APS) was also done using compression molding technique at 180-185°C (50-100 psi) for 1h and then at 200-205°C (100 psi) for 1h. Post curing was done at 220±5°C for 10-16h. Laminates having 25-42% resin content were prepared. Higher values for ILSS (4.59 x 10^3psi) in laminates fabricated from BM-M/TAC was observed as compared to BM-D_1, BM-HD_1/TAC and BM-M/APS (ILSS = 3.02-3.49 x 10^3 psi) resins formulation. Glass transition temperature, using DMA technique was found to be 280° in BM-M/TAC/glass fibre and 285°C in BM-M/TAC/carbon fibre laminates. A 35.5, 29.0, 23.0% reduction in ILSS was observed in BM-M, BM-D_1, BM-HD_1 based laminates on heat aging at 220 or 200°C. The % weight gain in the laminates in boiling water for (6,12,18 h) was found to be 4.58, 5.17, 6.58 respectively.

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FIGURE CAPTIONS