BISMALEIMIDES
SYNTHESIS, CHARACTERISATION AND APPLICATIONS

by
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DEDICATED

TO

MY

PARENTS

CERTIFICATE

This is to certify that the thesis entitled "Bismaleimides : Synthesis, Characterisation and Applications" being submitted by Miss Sangita to the Indian Institute of Technology, Delhi for the award of the degree of Doctor of Philosophy in Materials Science, is a record of bonafide research work carried out by her. Miss Sangita has worked under our guidance and supervision and has fulfilled the requirements for submission of this thesis which to our knowledge has reached the requisite standard.

The results contained in the 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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A B S T R A C T

Advanced composite materials exposed to temperature above 150°C have to be fabricated from resin matrices whose thermal/moisture resistance is superior to that of conventional epoxy matrix system. In the past few years, several imide prepolymers end-capped with reactive maleimide groups having excellent thermal and thermooxidative stability have been developed. The main objective of the present work was to develop bismaleimide resin with good processing characteristics and improved heat and flame resistance than the state-of-the-art resins. In order to attain this goal it is necessary to have information about the effect of structure on properties of these resins.

In order to study the effect of structure on thermal behaviour, four bismaleimides were synthesized by reacting maleic anhydride with 3,3'-diaminodiphenyl sulfone (S_m), 4,4'-diaminodiphenyl methane (M), 4,4'-diaminodiphenyl ether (E) and bis(m-aminophenyl) methyl phosphine oxide (BAP) and have been designated as BS, BM, BE and BP respectively. The incorporation of phosphine oxide and sulfone groups in the backbone is expected to affect the thermal stability and to increase the flame resistance. The characterisation of resins was done by IR, ^{1}H-NMR and mass spectroscopy. These investigations supported the assigned structure of bismaleimides.

Chain extended bismaleimides having lower melting point than the corresponding imide monomer could be obtained by Michael type addition reactions in acetone or methyl ethyl ketone. The aromatic amines used for chain extension reaction included 3,3'-bis(p-aminophenyl) phthalide (AP), BAP and tris(m-aminophenyl) phosphine oxide (TAP). These amines were synthesized in the laboratory. Commercially available diamines such as M, E, S_m, 4,4'-diaminodiphenyl sulfone (S_p) and 9,9-bis(p-aminophenyl) fluorene (BAF) were also used for the preparation of chain extended resins. The molar ratios of bismaleimide to amine was kept as 1:0.3 in these chain extension reactions.

These chain extended bismaleimides have been named on the basis of bismaleimide and amine used for chain extension e.g. the resin BS-M stands for bismaleimide BS, chain extended with M. Characterization of these resins was done by elemental analysis and IR spectroscopy.

The effect of structure on thermal behaviour of bismaleimides and chain extended bismaleimides was studied using DSC and TGA techniques. Curing behaviour of these resins depend on the structure of bismaleimides as well as of aromatic amine used for chain extension reaction. Exothermic transition indicative of curing was observed in DSC traces in the temperature range of 166-350^{o}C for

bismaleimide resins. The melting temperature was lowest in BM (156°C) and highest in BS (208°C).

A significant lowering of melting (T_m) and curing temperatures was observed when amines E, M, BAF, BAP and TAP were used for chain extension reaction. In BS-amine adducts bimodal character of exotherm was observed only when amines E, M and BAF were used for chain extension. Similar curing behaviour was observed in BP-amine adducts. The presence of electron withdrawing groups in the backbone increased the curing temperatures.

Heat of curing (ΔH) ranged from 108-221 J/g in bismaleimides and from 33-196 J/g in chain extended resins. The effect of advancement of resin on the curing characteristics was also studied in BP and BP-amine adducts. A reduction in T_m with the broadening of melting peak was observed in partially cured (at 200°C for 30 min.) resins. A considerable reduction in ΔH values was observed in advanced resins.

Activation energies of BS-amine adducts were determined by isothermal and multiple heating rate method. A value of 65 KJ/mole was obtained by isothermal method in the temperature range of 150-199°C in BS-TAP resin. In BS-E (temperature range 116-150°C) and BS-S_m (temperature range 209-261°C), the values were 74 and 75 KJ/mole respectively.

Thermal stability of bismaleimides and bismaleimide-amine adducts was studied by using TGA. Thermal behaviour of these resins depended on the structure of bismaleimide and chain extended bismaleimides. A two step decomposition was observed in uncured BP and BE resins. This behaviour was retained in BP resin after curing. The char yields of uncured resins varied from 39% (BS) to 64%(BP). Char yields increased on curing of these resins, for example in cured BP resin a char yield of 69% was obtained in nitrogen atmosphere. On the basis of char yields, the relative stability of bismaleimide was :

BP > BM > BE > BS

The chain extended bismaleimides had lower IDT values than the bismaleimides from which these adducts were prepared. A two step decomposition behaviour was retained in BP-amine adducts. This behaviour was also observed when bismaleimides BM and BE were chain extended with phosphorus containing triamine. Char yields were higher in bismaleimide-TAP adducts. The char yield of partially cured chain extended BP resins varied from 58-66%. Better char yields in BP-S_m and BP-S_p resins in comparison to BP-TAP were obtained. IPDT values were higher in cured samples than uncured resins. On the basis of char yields and IPDT values, the thermal stability of partially cured BP and their Michael adducts was in the

following order :

$$BP > BP\text{-}S_p \simeq BP\text{-}S_m > BP\text{-}TAP > BP\text{-}E > BP\text{-}M \simeq BP\text{-}BAF$$

From these studies it could be concluded that condensed phase char forming reactions are enhanced in the presence of phosphorus. Meta or para orientation of sulfone group in chain extended BE and BM had negligible effect on the thermal stability of resins.

Chain extension reaction of bismaleimide BE with BAP, TAP, AP and E amines in molar ratios ranged from 0.1 - 0.5 was also carried out in DMF. Thermal stability of such resins cured at 200°C depended on the structure of the amine and also on molar concentration of amine used. A systematic decrease in decomposition temperatures and IPDT on increasing the molar ratio of BE:amine from 0.1 - 0.5, was observed. The char yields in nitrogen was higher when TAP was used for curing. Thermogravimetric analysis of cured resins was also done in air atmosphere. A total loss in weight was observed above 750°C. No significant decrease in initial decomposition temperature was observed in air atmosphere.

Bismaleimide : vinyl ester resin blends were also investigated with an aim to improve the processability and mechanical properties of glass fibre reinforced composites. Chain extended resins BS-M, BS-BAP, BS-TAP and BM-M were

blended with various percentages of vinyl ester (VE) and styrenated VE resin. The effect of VE resin on curing characteristics of bismaleimides depended on the backbone structure and percentage of VE resin used. Significant reduction in ΔH was observed on blending with VE resin. The temperature of completion of curing (T_2) reduced in all chain extended resins by blending.

Thermal stability of cured (at 200°C for 30 min.) resin blends was also evaluated. These resins were stable upto 300°C. IDT was reduced on blending bismaleimide with VE resin. Addition of even 1% of VE resin reduced the char yield at 800°C. Further increase in VE content did not affect the char yield significantly. These results thus clearly indicate that chain extended bismaleimides can be cured at low temperatures in the presence of VE. The better thermal properties can be retained by using a low weight percent of VE resin.

Mechanical properties of glass and carbon reinforced imide/blends were evaluated. Bismaleimides BM/BE and amine mixtures and chain extended resins BE-TAP, BE-E, BS-M and BS-TAP were used for fabrication. Better mechanical properties were obtained with chain extended resins. The mechanical properties of BE:amine/glass fibre-reinforced laminates were in the following order :

BE:TAP > BE:BAP > BE:AP > BE:E

Mechanical properties were best in BE-TAP resin. These results have been corroborated by fabrication of laminates at National Aeronautical Laboratory, Bangalore. The mechanical properties of these composites were superior to the commercially available Technochemie M-751 laminates. Heat ageing of some of these laminates at 235°C for 500h showed reduction in mechanical properties. However, better retention of flexural strength at elevated temperature was observed in BE-E/carbon fibre and BE-TAP/glass fibre reinforced composites. Flexural strength and ILSS improved by adding 10% VE to BS-TAP resin. The limiting oxygen index (LOI) was significantly reduced on addition of 10% VE resin. Glass transition temperature as determined by dynamic mechanical analysis was also affected by structure of resin and percentage of vinyl ester resin.

Aspartimide oligomers from BE:BAF were also prepared. Char yields of aspartimide oligomers increased by 12% (from 46-58.5%) after heating the samples at 200°C for 306 h.

C O N T E N T S