# EFFECT OF STRUCTURE ON PROPERTIES OF ITACONIMIDE RESINS, THEIR BLENDS AND COMPOSITES

by

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Itaconimide (Resins);

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# CERTIFICATE

This is to certify that the thesis entitled "**EFFECT OF STRUCTURE ON PROPERTIES OF ITACONIMIDE RESINS, THEIR BLENDS AND COMPOSITES**" being submitted by **Ms. Anjali Solanki** 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 her. Ms. Anjali Solanki has worked under our guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to our knowledge has reached the requisite standard.

This work has not been submitted, in part or full, to any other University or Institute for the award of any other degree or diploma.

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# ABSTRACT

Although extensive studies have been reported on addition polyimides i.e. nadimide and maleimide resins, very few papers have been published on imide derivatives of itaconic anhydride. In contrast to itaconimides, which contain 1,1-disubstituted double bond, nadimides as well as maleimide resins contain 1, 2-disubstituted double bond, that has a very low tendency to homopolymerize due to kinetic considerations. Therefore the rate of polymerization of itaconimide end-capped resins may be faster than the maleimide or nadimide resins. The present thesis deals with the effect of structure on curing characteristics and thermal behaviour of bisitaconimides and their blends.

The main objective of present investigations was to examine the effect of structure on curing characteristics and thermal behaviour of bisitaconimide resins. For this purpose, bisitaconimides of varying molecular masses and backbone structure were synthesized and characterised. In order to improve the processability of these resins, blends with other thermosets eg. epoxy, nadimides or allyl type reactive diluents were investigated. Mechanical properties and flammability of glass fibre-reinforced composites based on these resins were also evaluated.

The thesis had been divided into seven chapters. Chapter 1 reviews the current status of itaconimide resins.

The synthesis of bisitaconimides having ether, sulfone, phosphine oxide, amide linkages and fused aromatic ring structure in the backbone is given in chapter 2. Itaconimides were synthesized by reacting aromatic amines with itaconic anhydride using acetone, glacial acetic acid or N,N'-dimethyl formamide as solvent. The amines used were 4,4'-

diaminodiphenyl ether (E), 1,4-bis(4-aminophenoxy)benzene (H), 1,3-bis(4-aminophenoxy)benzene (R), 2,2'-bis(4-aminophenoxyphenyl)propane (P), tris(3-aminophenyl)phosphine oxide (T), bis(3-aminophenyl)methyl phosphine oxide (B), 4,4'-diaminodiphenyl sulfone ($S_p$), 3,3'-diaminodiphenyl sulfone ($S_m$), 1,3-bis(3-aminobenzamide)benzene (A) and 9,9-bis(4-aminophenyl)fluorene (F) and the corresponding bisitaconimides were designated as IE, IH, IR, IP, IT, IB, $IS_p$, $IS_m$, IA and IF respectively. In order to synthesize oligomeric itaconimides, aromatic tetracarboxylic acid dianhydrides i.e. pyromellitic dianhydride (M), 3,3', 4,4'-benzophenone tetracarboxylic acid dianhydride (C) and hexafluoro isopropylidene-2,2-bis(phthalic anhydride) (D) were used along with amines E, H and $S_p$. The synthesis of bisnadimides (using nadic anhydride and ether group containing amines E, H, R and P) and reactive diluents 4,4'-bis(4-allyl-2-methoxyphenoxy)benzophenone ($R_1$) and 4,4'-bis(4-allylphenoxy)benzophenone ($R_2$) is also described in chapter 2.

The characterisation of imide resins and reactive diluents was done using FT-IR, elemental analysis and vapour phase osmometry. The structure of imide resins and reactive diluents was confirmed by the above-mentioned techniques. In case of oligomeric bisitaconimides the IR spectra showed the presence of residual bisitaconamic acid along with bisitaconimide. Isomerisation of itaconimide to citraconimide was indicated by $^1$H-NMR studies where an additional proton resonance signal due to methyl group was observed at 2.06 ± 0.05 ppm. There was also a change in the intensity of protons due to olefinic protons of itaconimide (5.6 and 6.1 ppm). The presence of citrconimide vinyl proton resulted in an increase in intensity of 6.1 ppm resonance signal with respect to 5.6 ppm (due to vinylic protons of itaconimides). The percentage of citraconimide was estimated from the ratio of signals at 2.06 and 5.6 ppm (in itaconimides).

In order to investigate the effect of reaction conditions on isomerisation, N,N'-bis(4,4'-itaconimidophenyl) ether was synthesized using different solvents and temperature (chapter 3). The citraconimide content depended on the reaction conditions and was found to be 77 % in toluene, 29.5 % in acetone, 24 % in chloroform and 7.2 % in tetrahydrofuran. A decrease in melting point (DSC) and exothermic peak temperature ($T_{exo}$) was observed as the citraconimide content in the samples increased. Thermal stability of resins, as determined by thermogravimetric analysis was similar irrespective of citraconimide content upto 30 %.

The thermal characterisation of imide resins was done using DSC and TGA techniques (chapter 4). In bisitaconimides melting endotherms were observed at as low a temperature as 83°C (IP) to as high as 232°C (IA). In the DSC scans of samples IF, IT and IB, only curing exotherms were observed. The curing exotherms in IE, IR, IA and IH were observed immediately after melting. In oligomeric bisitaconimide resins two broad melting endotherms were observed at 60-115°C (loss of adsorbed water) and 115-280°C (thermal cyclisation of residual amic-acid to imide). A corresponding mass loss was observed in TG traces of uncured bisitaconimides. The presence of bisitaconamic acid was also indicated in the IR spectra.

Bisnadimides NR, NP, NE and NH showed melting endotherms at 50-100°C higher than the corresponding bisitaconimides. The curing exotherms were also observed at much higher temperatures than the bisitaconimides. The melting point was 174°C for NP and 292°C for NH. The curing exotherms were observed above 289°C. Thus melting as well as curing of bisnadimides occurs at higher temperatures compared to corresponding bisitaconimide resins.

The cured bisitaconimides were stable upto 392°C and major decomposition occurred after this temperature. In the TG traces of cured bisitaconimides (200°C for 2h), one or two-step decomposition was observed. The mass loss in the first step was 2-6.9 %. The char yield at 800°C of these cured resins depended on backbone structure, the highest value (66 %) was observed in itaconimide having phosphine oxide group in the backbone and lowest (35 %) for IP which had labile isopropylidene group in the backbone. Incorporation of aromatic tetracarboximide moieties in the backbone of IE, IH and $IS_p$ resins resulted in an increase in the char residue.

In bisnadimides, cured at 200°C for 2h, major mass loss was observed above 425°C. However the mass loss in the first step is due to cyclopentadiene evolved as a result of reverse Diels-Alder reaction. The char yield at 800°C was 33-37 % in all nadimides. A comparison of bisnadimides and bisitaconimides of similar structure revealed that curing of bisitaconimides can be carried out at lower temperatures than bisnadimides, but the thermal stability and char yields of cured resins were similar.

Studies on blends of bisitaconimides with other thermoset resins (i.e. bisnadimides and epoxy resins) and reactive diluents are described in chapter 5 of the thesis. In order to improve the processability of bisnadimide resins and thermal stability of bisitaconimides, several blends of bisnadimide and bisitaconimide were prepared by changing the structure of the resin and blend composition. Depending upon the blend composition significant changes in melting transition and curing exotherms were observed in such blends and the curing temperatures of nadimide resins could be reduced by incorporation of itaconimide without affecting their thermal stability.

Blends of epoxy/amine (10 and 20 %)-bisitaconimide (IE) showed a decrease in melting point (DSC) and thermal stability (TGA) when compared with bisitaconimide alone. Effect of addition of 4,4'-bis(4-allyl-2-methoxyphenoxy) benzophenone ($R_1$) and 4,4'-bis(4-allylphenoxy) benzophenone ($R_2$) on curing behaviour of IE resin was studied by incorporating 10-50 % w/w of $R_1$ or $R_2$. A decrease in melting point and peak exothermic temperature was observed on increasing the weight percentage of the reactive diluents. Char yield decreased in blends having higher amounts of reactive diluents.

The properties of glass fibre-reinforced bisitaconimides and their blends are given in chapter 6. The resin content of the laminates was in the range 22-37 %. The mechanical properties (i.e. flexural properties and inter-laminar shear strength (ILSS)) of composites based on 20 % epoxy-amine or 5 % reactive diluent and bisitaconimide were better than bisitaconimide alone. Epoxy resins are known to have lower thermal stability than addition polyimides and therefore laminates with low percentage of epoxy-amine (20 %) were fabricated. Similarly high percentage of reactive diluent decreased the thermal stability of the imide resins. Limiting oxygen index (LOI) and smoke density of blends of bisitaconimides with epoxy-amine or reactive diluents was similar. A decrease in ILSS was observed on hygro-thermal ageing or heat ageing of the laminates for 500h at 200°C. General discussion and summary are given in chapter 7 of the thesis.

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