

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

by

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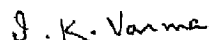
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This is to certify that the thesis entitled "EFFECT OF STRUCTURE ON PROPERTIES OF ITACONIMIDE RESINS, THEIR BLENDS AND COMPOSITES" being submitted by Ms. Anjali Solanki to the Indian Institute of Technology, Delhi, for the award of degree of **Doctor 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 (R₁) and 4,4'-bis(4-allylphenoxy)benzophenone (R₂) 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 ¹H-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 citraconimide 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.

CONTENTS

	Page No.
LIST OF FIGURES	(i-iii)
CHAPTER 1: INTRODUCTION AND LITERATURE SURVEY	
1.1 INTRODUCTION	1
1.2 SYNTHESIS OF ITACONIMIDES	2
1.2.1 Preparation of itaconic anhydride	2
1.2.2 Preparation of addition polyimides	3
1.3 ISOMERISATION OF ITACONIC ANHYDRIDE AND ITACONIMIDES	6
1.4 CHARACTERISATION OF BISITACONIMIDES	10
1.5 THERMAL POLYMERISATION	14
1.5.1 Thermal stability	18
1.6 MODIFICATION OF ADDITION POLYIMIDES	21
1.7 APPLICATIONS OF ADDITION POLYIMIDES	23
1.8 OBJECTIVES OF THE PRESENT WORK	23
1.9 APPROACHES	25
CHAPTER 2: SYNTHESIS AND CHARACTERISATION	
2.1 INTRODUCTION	29
2.2 EXPERIMENTAL	33
2.2.1 Materials	33
2.2.2 Synthesis of amines	34

2.2.2a <i>Preparation of 1,3-/1,4-bis(4-aminophenoxy) benzene</i>	34
2.2.2b <i>Preparation of bis(3-aminophenyl) methyl phosphine oxide</i>	35
2.2.3 Preparation of itaconic anhydride	36
2.2.4 Synthesis of bisitaconimides	37
2.2.5 Synthesis of high molecular mass bisitaconimides	40
2.2.6 Synthesis of bisnadimides	41
2.2.7 Synthesis of allyl type reactive diluents	42
2.2.8 Characterisation	42
2.3 RESULTS AND DISCUSSION	43
2.3.1 Bisitaconimides	43
2.3.2 High molecular mass bisitaconimides	52
2.3.3 Bisnadimides	52
2.3.4 Allyl type reactive diluents	58

CHAPTER 3: ISOMERISATION OF ITACONIC ANHYDRIDE AND

ITACONIMIDE

3.1 INTRODUCTION	60
3.2 EXPERIMENTAL	62
3.2.1 Synthesis of amic-acids and imides	62
3.2.2 Thermal characterisation	63
3.3 RESULTS AND DISCUSSION	64
3.3.1 Characterisation of amic-acids	64
3.3.2 Characterisation of bisitaconimides	65

3.3.3 Thermal studies	70
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CHAPTER 4: BISITACONIMIDES: THERMAL CHARACTERISATION

4.1 INTRODUCTION	77
4.2 EXPERIMENTAL	77
4.2.1 Materials	77
4.2.2 DSC studies	78
4.3 RESULTS AND DISCUSSION	78
4.3.1 Effect of structure on curing behaviour of addition polyimides	78
(a) Bisitaconimides and bisnadimides containing ether group	78
(b) Bisitaconimides containing phosphorus or sulfone group	82
(c) Bisitaconimides having amide group or fused aromatic ring	83
(d) High molecular mass bisitaconimides	85
4.3.2 Thermal behaviour of cured bisitaconimide resins	89
(a) Bisitaconimides and bisnadimides containing ether group	89
(b) Bisitaconimides containing phosphorus or sulfone group	93
(c) Bisitaconimides having amide group or fused aromatic ring	95
(d) High molecular mass bisitaconimides	95

CHAPTER 5: THERMAL BEHAVIOUR OF BISITACONIMIDE BLENDS

5.1 INTRODUCTION	100
5.2 EXPERIMENTAL	101
5.2.1 Bisitaconimide/bisnadimide blends	101

5.2.2 Bisitaconimide(IE)/epoxy-amine(DG) blends	102
5.2.3 Bisitaconimide(IE)/reactive diluents (R ₁ and R ₂) blends	102
5.3 RESULTS AND DISCUSSION	103
5.3.1 Bisitaconimide/bisnadimide blends	103
5.3.1a <i>DSC studies</i>	103
5.3.1b <i>Thermogravimetric studies</i>	105
5.3.2 Bisitaconimide (IE)/epoxy-amine (DG) blends	107
5.3.3 Bisitaconimide(IE)/reactive diluents (R ₁ and R ₂) blends	109
CHAPTER 6: GLASS FIBRE-REINFORCED BISITACONIMIDES	
6.1 INTRODUCTION	115
6.2 EXPERIMENTAL	116
6.2.1 Materials	116
6.2.2 Fabrication of glass fibre-reinforced composites	116
6.2.3 Characterisation and testing of laminates	117
(a) Determination of resin content	117
(b) Determination of flexural strength and modulus	118
(c) Inter-laminar shear strength	118
(d) Determination of LOI and smoke density	119
6.3 RESULTS AND DISCUSSION	120
6.3.1 Composites based on bisitaconimides	120
6.3.2 Composites based on bisitaconimide/epoxy resin	122
6.3.3 Composites based on bisitaconimide/ reactive diluent	123

6.3.4 Effect of thermal ageing on ILSS	124
6.3.5 Effect of hygrothermal ageing on ILSS	125
CHAPTER 7: GENERAL DISCUSSION AND SUMMARY	
7.1 INTRODUCTION	127
7.2 SYNTHESIS OF ADDITION POLYIMIDES AND REACTIVE DILUENTS	127
7.3 EFFECT OF REACTION PARAMETERS ON EXTENT OF ISOMERISATION	131
7.4 THERMAL BEHAVIOUR OF IMIDE RESINS CONTAINING ETHER LINKAGE	132
7.5 THERMAL BEHAVIOUR OF IMIDE RESINS HAVING SULFONE OR PHOSPHINE OXIDE GROUP	135
7.6 THERMAL BEHAVIOUR OF IMIDE RESINS HAVING AMIDE / FUSED AROMATIC RING STRUCTURE	135
7.7 THERMAL BEHAVIOUR OF CHAIN EXTENDED BISITACONIMIDES	137
7.8 THERMAL BEHAVIOUR OF BISITACONIMIDE BLENDS	138
7.9 GLASS FIBRE-REINFORCED BISITACONIMIDES	140
7.10 SUGGESTIONS FOR FUTURE WORK	142
REFERENCES	143
LIST OF PAPERS	150
BIODATA	151