PREPARATION AND PROPERTIES OF ENDO-5-NORBORNENE-2,3-DICARBOXIMIDE (NADIMIDE) END-CAPPED IMIDE RESINS

by

ANJU SRIVASTAVA

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CERTIFICATE

This is to certify that the thesis entitled "**PREPARATION AND PROPERTIES OF ENDO-5-NORBORNENE-2,3-DICARBOXIMIDE (NADIMIDE) END-CAPPED IMIDE RESINS**" being submitted by **Ms. Anju Srivastava** 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. She has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis which to my 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.

I. K. Varma

Prof. (Ms.) I.K. Varma
Centre for Polymer Science
and Engineering
Indian Institute of Technology
Hauz Khas,
New Delhi-110016.

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ANJU SRIVASTAVA

ABSTRACT

The thesis deals with synthesis and characterisation of endo-5-norbornene-2,3-dicarboximide (nadimide) end-capped imide resins. These resins have been investigated in the past as matrices for advanced fibre reinforced composites. The main aim of the present work was to study the effect of structure of preformed nadimides on thermal characteristics and performance.

The thesis has been divided into five chapters. A comprehensive and critical literature survey of nadimides is given in chapter I of the thesis. Synthetic routes for nadimides, allyl nadicimides and polymerisation of monomeric reactants (PMR approach) have been reviewed. The basic chemistry involved in the synthesis is the nucleophilic reaction of amino group with one of the carbonyl groups of endo-5-norbornene-2,3-dicarboxylic anhydride (nadic anhydride) to yield the intermediate amide acid which is subsequently cyclodehydrated to imide, either thermally or chemically. An account of curing of nadimides, thermal characteristics of cured resins, and fibre reinforced composites based on these resins has been given. The scope of the present studies is also described.

The synthesis and characterisation of nadimides by using tris (3-aminophenyl) phosphine oxide (TAP)/1,3-bis (3-aminobenzamide) (ABB)/ 9,9-bis (p-aminophenyl) fluorene(APF), pyromellitic dianhydride (PMDA)/ 3,3′,4,4′-benzophenone tetracarboxylic acid dianhydride (BTDA)/2,2-bis (3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6F) is described in chapter II of the thesis. TAP was synthesised in the laboratory from triphenyl phosphine

oxide by nitration and subsequent reduction of the trinitro compound. Nadic anhydride (NA) was recrystallised from acetic anhydride and reacted with the amines in 2:1 and 1:1 molar ratios to give bisnadimides and mononadimides respectively. The reactions were carried in glacial acetic acid by refluxing at 120°C for 8-11 h and the imides were recovered by precipitation in water and purified. The mononadimides of ABB/APF (0.01 mol) containing free NH_2 groups were further reacted with PMDA/BTDA/6F (0.005 mol)in DMF at 60°C. The solution was heated for 4 h followed by chemical cyclisation to imide using sodium acetate and acetic anhydride as cyclodehydrating agents. Similar reactions were carried out with TAP based bisnadimide using acetone as solvent. The mononadimide of TAP (0.01 mol) was also reacted with 0.0075 mol each of the dianhydride to give nadimides with higher formulated molecular weight (FMW). Eighteen nadimide oligomers were synthesised with FMW in the range of 469 to 3100. Some of the phosphorus containing nadimides were soluble in chloroform, acetone, methyl ethyl ketone etc. indicating their ease in processability as compared to the traditional preformed nadimides whcih are soluble in high boiling solvents only.

Structural characterisation of these nadimides was done using elemental analysis, FT-IR and ^{1}H-NMR spectroscopic techniques. In the FT-IR spectra of nadimides, characteristic bands due to imide groups appeared at 1784 and 1722 cm^{-1}. The presence of NH_2 groups in the mononadimides was indicated by NH stretching at 3230 cm^{-1} In samples containing BTDA, a broad absorption band at 1720 cm^{-1} with a shoulder at 1630 cm^{-1} was observed. The $\nu_{c=o}$ band for

amide groups in ABB based nadimides was observed at 1680 cm^{-1}. The absorption bands due to P-C_6H_5 and >P=0 for TAP based nadimides were observed at 1430 and 1185 cm^{-1} respectively. In the ^{1}H-NMR spectra of nadimides, aromatic protons were observed as a multiplet in the region δ = 7.2-8.2 ppm and the olefinic protons appeared as a singlet at δ = 6.2 ppm. The methylene protons appeared at δ = 1.5-1.8 ppm and the remaining aliphatic protons were observed around δ = 3.4 ppm. In nadimides containing free NH_2 groups, the NH protons were seen at δ = 2.0 ppm. The ratio of total aromatic to olefinic protons was used for structural characterisation of the nadimides.

Thermal characterisation of various nadimides was done by using differential scanning calorimetry and thermogravimetric analysis (chapter III). For the ABB/APF based nadimides having FMW less than 1100 (A-2, B-2, B-1 and A-1P), well defined melting endotherms in the range of 208-301°C were observed. An exotherm, indicative of curing (230-330°C) was observed in the DSC scan. For the TAP based nadimides, no melting endotherm was observed; only exothermic transition associated with curing was present (exothermic peak position in the range of 270-310°C). The DSC studies showed that TAP based nadimides cured at relatively lower temperatures than ABB or APF based nadimides. The weight loss during curing was monitored by dynamic TG as well as isothermal oven curing. In the TAP based nadimides, weight loss of 0.5-3% (temperature range: 50-110°C) was due to absorbed moisture. A 1.5-4% weight loss was observed in the temperature range of 125-215°C and has been attributed to volatilisation of cyclopentadiene. During exothermic curing reaction, a weight loss of 6-11.5% was seen.

For the ABB/APF containing nadimides, no moisture desorption step was observed. Softening/melting was associated with release of cyclopentadiene via endo-exo isomerisation or RDA reaction. Final breakdown of the polymer occured in the temperature range of 450-700°C.

An attempt was made to cure the resins by heating at 250°C for 1 h in air. However, solubility studies in DMF indicated only partial curing. Curing was therefore, done at 300°C for TAP based oligomers and at 325°C for ABB/APF based oligomers. Resins insoluble in DMF were obtained on such a treatment. In DSC scan of the cured samples, exothermic transition, indicative of residual cure was absent. The cured nadimides decomposed in a single step. The initial decomposition temperatures were in the range of 415 ± 60°C. The T_{max} values were in the range of 463-594°C. Char yields of cured resins were in the range of 63-77%.

Thermal behaviour of allyl nadicimides was investigated. Onset temperature of decomposition (T_1) was higher for allyl nadicimides than the nadimide resins. However, char yields were 2-3 times lower than nadimides. T_{max} values for allyl nadicimides were also lower. Phosphorus based nadimides were co-cured with three allyl nadicimides using three compositions viz. 1:1, 1:3 and 3:1 (w/w) of nadimide and allyl nadicimide. These co-cured resins were characterised by thermogravimetric analysis. The char yield at 800°C in these resins was significantly affected by the composition. Increase in phosphorus containing nadimides in the resin formulation resulted in an increase in char yield of allyl nadicimides. The observed char yields were much higher than the

calculated values (according to rule-of-mixtures) indicating thereby a synergistic effect on co-curing. A mechanism has been proposed to account for this synergism.

The details of fabrication and characterisation of glass fibre reinforced composites using TAP based nadimides and allyl nadicimide and their 1:1 blend (w/w) are described in chapter IV of the thesis. Resin content was in the range of 34-40% (by volume). ILSS and flexural strength was in the range of 33-70 MPa and 500-640 MPa respectively. A marginal decrease in ILSS was observed when these laminates were placed in boiling water for 100 h or on oven aging at 300°C for 200 h. The ILSS was maximum for composite based on PMDA. More polar nature of the matrix resin may be responsible for this behaviour.

General discussion and summary of the work are given in chapter V of the thesis. Suggestions for future work are also given. References are given at the end of the thesis.

CONTENTS