DEVELOPMENT OF POLYIMIDE RESINS, ADHESIVES AND FIBRES

By

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CERTIFICATE

This is to certify that the thesis entitled "Development of Polyimide Resins Adhesives and Fibres" being submitted by Mr. B.S. Rao to the Indian Institute of Technology, Delhi, for the award of the degree of Doctor of Philosophy in Chemistry, is a record of bonafide research work carried out by him. Mr. B.S. Rao has worked under my guidance and supervision and has fulfilled the requirement 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.

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ABSTRACT

The thesis deals with the effect of Structure on the Properties of Polyimides which may be used as adhesives fibres and organic matrix resins for fibre reinforced composite materials. The aim was to improve the thermal and processing characteristics of the state-of-the-art resins. To achieve this objective several polyimide resins having different structures in the backbone were synthesized by reacting pyromellitic dianhydride (PMDA) or benzophenone tetracarboxylic acid dianhydride (BTDA) with suitable aromatic di and tri amines. Some of the amines employed were commercially available [p-phenylene diamine (P), m-phenylene diamine (m), 4,4'-diaminodiphenyl ether (E)] while others were synthesized in the laboratory by the reduction of nitro-compounds. These included 2,5-bis(p-aminophenyl) 1,3,4-oxadiazole (ODZ), 4,4'-diaminobenzanilide (DAB), bis(3-aminophenyl) methyl phosphine oxide (DAP), 4,2',4'-triaminobenzanilide (TAB) and tris (3-aminophenyl) phosphine oxide (TAP).

Polyamic acids were prepared by reacting a DMF solution of amines with PMDA or BTDA at low temperature. The characterization was done primarily by intrinsic viscosity

measurements, though ir and density of some of these polyamic acids was also recorded. The highest intrinsic viscosity was obtained with P-E and lowest with B-DAP. These results have been explained on the basis of reactivity of the amines and the flexibility of the polymer backbone.

Cyclodehydration of polyamic acids to polyimide was carried out chemically by acetic anhydride, pyridine and benzene mixture and in few cases thermal cyclisation at 200°C was also attempted. All of these polyimides, with the exception of B-DAP, were insoluble in DMF, NMP or DMSO. In the infrared spectra of these polyimides, characteristic absorption bands due to imide group were observed. Density of these polymers was determined by suspension method.

Thermal behaviour of polyimides was investigated by thermogravimetry. Effect of intrinsic viscosity of polyamic acid precursor, backbone structure and atmosphere of degradation, on thermal stability was evaluated. Thermal stability of B-E polyimides depended on the intrinsic viscosity of the polyamic acids. Better packing in P-phenylene structure may be the reason for the superior thermal stability of B-E-p copolyimides over B-E-m copolyimides. The polyimide B-DAP had reasonably good thermal stability. Incorporation of triamine TAP or TAB resulted

in an increase of temperature of decompositions. Formation of azomethine >C=N linkage by the reaction of carbonyl group of BTDA and free amino group of triamine may be the reason for the enhanced thermal stability. The char yield of the copolyimide B-DAP_4-TAP_1 was found to be 66%. The glass transition temperature of B-DAP polyimide as indicated by differential thermal analysis was 210°C.

Polyamic acids of P-DAB, P-ODZ, P-E and P-E_9-DAP_1 were spun into fibres with the help of bench scale wet spinning unit. Effect of heat and radiation on the mechanical properties of the fibres was investigated. The mechanical properties of fibres were deteriorated by such exposure. The polyimide film B-ODZ had tensile strength of 21,290 psi.

Lap shear strengths of 495, 510 and 695 psi were obtained for polyimides B-E, B-m, and B-DAP respectively. Introduction of m-phenylene groups in the backbone of B-E resulted in an increase of lap shear strength. The lap shear strength of B-DAP polyimide was increased with the incorporation of TAP and TAB. Good tensile strength (43×10^3 psi) was obtained for a glass fabric reinforced laminate based on B-DAP_9-TAB_1.

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