STUDIES ON ARYLENE PYROMELLITIMIDE POLYMERS AND FIBRES

By

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Dedicated

to my

Parents

CERTIFICATE

This is to certify that the thesis entitled "Studies on arylene pyromellitiimide polymers and fibres" being submitted by Mr. Ravindra Nath Goel to the Indian Institute of Technology, Delhi, for the award of the degree of Doctor of Philosophy in Textile Technology, is a record of bonafide research work carried out by him. Mr. Ravindra Nath Goel has worked under our guidance and supervision and has fulfilled the requirement for the submission of this thesis which to our 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

In the present work, polyimides were synthesised by a two stage process from pyromellitic dianhydride and benzidine (B), hydrazine (H), m-phenylenediamine (M), p-phenylenediamine (P) and 4,4'-diaminodiphenylmethane (D). Several copolymers were prepared by taking different molar ratios of two diamines in the initial monomer feed . Low temperature solution polycondensation was carried out in DMF to get polyamic acids which were chemically cyclodehydrated by acetic anhydride, pyridine and benzene mixture (1:1:1) to polyimides. Polyamic acids were characterised by intrinsic viscosity measurements and estimation of nitrogen. Intrinsic viscosity of $(B)_a$ polymer was maximum which may be due to stiffness of the backbone and greater reactivity of B. In copolymers a decrease in $[\eta]$ was observed on increasing the ratio of M in the initial feed. The Huggin's constant (K') values, were also determined from viscosity data.

Structural studies were carried out by ir and density measurements. Characteristic imide bands were observed in the ir spectra of polyimides. The density of the polyimides having p-phenylene groups was higher than those with m-phenylene groups. The following order was observed : $(P)_i > (B)_i > (M)_i > (D)_i$.

Thermal and thermo oxidative behaviour of polyamic acids and polyimides was studied using dynamic thermogravimetric analysis (TGA). The relative thermal stability of the polymers was evaluated by integral procedural decomposition temperature; following stability order was observed : $(B)_i > (P)_i > (M)_i > (D)_i$. The activation energy of decomposition depended on the backbone structure and in air atmosphere was found to be in the range 293-101 KJ/mole. The ageing behaviour of polyamic acids in DMF was evaluated by measurement of η_{inh} as a function of storage time.

$(B)_a$, $(D)_a$ and $(M_1B_3)_a$ were spun into fibres with the help of a bench scale wet spinning unit. Parameters such as : (a) effect of molecular weight, (b) spinning solution concentration, (c) composition of coagulation bath, (d) jet stretch during coagulation, (e) hot drawing on mechanical properties were studied. Strong, lustrous monofilaments resulted on hot drawing at 300°C. $(M_1B_3)_i$ & $(D)_i$ fibres with a tenacity - 344 and 380 mN/tex, % extension - 10 and initial modulus - 11200 and 4060 mN/tex were obtained. Effect of heating at 300°C for 10 hrs. on mechanical properties of $(D)_i$ fibres was also investigated. The crystalline structure of $(D)_i$ fibre was studied by wide angle X-ray diffraction. Hot drawing increased the crystallization and resulted in orientation of molecules. A decreas in density of polyimide fibres was observed on hot drawing. Morphological studies by scanning electron microscopy revealed the presence of voids in undrawn fibres which may account for the observed density behaviour.

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