

**Effect of Comonomers and Chemical Pretreatments  
on the Thermo-oxidative Stabilization of Acrylic  
precursors and Resulting Carbon Fibres**

*by*

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*Thesis submitted*

*in fulfilment of the requirements*

*of the degree of*

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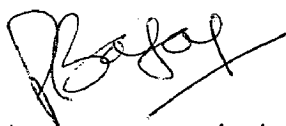
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Dedicated  
to  
my Parents

CERTIFICATE

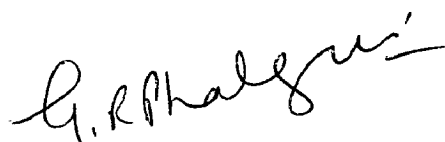
This is to certify that the thesis entitled "Effect of Comonomers and Chemical Pretreatments on the Thermo-oxidative Stabilization of Acrylic Precursors and Resulting Carbon Fibres" being submitted by Shri A.K. Roopanwal, to the Indian Institute of Technology, Delhi, for the award of the degree of Doctor of Philosophy in the Department of Textile Technology, is a record of bonafide research work carried out by him. Shri A.K. Roopanwal has worked under our guidance and supervision and fulfilled the requirements for the submission of the thesis.

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

Thermo-oxidative stabilization of acrylic precursors is the most important step in the manufacture of carbon fibres. A set of chemical reactions occur during this process accompanied by physical changes in the fibres. There are three primary groups of reactions, namely i) nitrile group cyclization, ii) dehydrogenation of saturated carbon-carbon bonds, and iii) oxidation. The present study deals with the thermal behaviour and structure development of two acrylic precursor fibres, which would control the structure-morphology of resulting carbon fibres after carbonization. Precursor M, P(AN/MAA) contains about 2% methacrylic acid as a comonomer, and precursor C consisted of 92% acrylonitrile and 6% methyl acrylate and 1% itaconic acid. Progression of thermal stabilization has been followed by differential scanning calorimetry (dynamic and isothermal mode), DSC-FTIR, TGA, mass spectroscopy etc. Kinetics of stabilization has been studied. The present examination has been focused on the specific difference in the thermal stabilization of two precursors having different comonomers. The study revealed that precursor M has a higher activation energy (28-38 kcal mol<sup>-1</sup>) with a multistep exothermic reaction as compared to precursor C (a terpolymer) with an E<sub>a</sub> value of 20-22 kcal mol<sup>-1</sup>. Also, precursor M showed lower weight loss in air at 500°C as compared to precursor C.

On the basis of online thermal analysis of precursors through DSC-FTIR, some insight into the complex reactions

occurring during stabilization has been provided. It appears in precursor M, the dehydrogenation reaction is dominant in the initial stages of stabilization, while cyclization reaction in precursor C.

Information gathered from heat flow calorimetry, both the precursor fibres were thermally stabilized in a tubular furnace at different temperatures for 1 to 4 hrs. Extent of stabilization has been followed by measuring the density, aromatization index and oxygen pickup.

In the second phase of the investigation, influence of various chemical treatments, viz.,  $\text{KMnO}_4$ , cobaltous chloride, diammonium hydrogen phosphate, ammonium polyphosphate and hydrazine hydrate has been studied. Amongst the various treatments,  $\text{KMnO}_4$  and cobaltous chloride seem to influence significantly the path of chemical transformations during heating of precursor M.

In the last phase, preliminary studies have been made on the carbonization of stabilized precursors in order to understand the role of comonomers and chemical pretreatments on the structure development of carbon fibres.

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