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

by

A. K. ROOPANWAL
Department of Textile Technology

Thesis submitted
in fulfilment of the requirements
of the degree of

DOCTOR OF PHILOSOPHY

to the

INDIAN INSTITUTE OF TECHNOLOGY, DELHI

NEW DELHI-110 016

DECEMBER, 1993

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.

Prof. (Miss) P. Bajaj
Department of Textile Technology
Indian Institute of Technology
New Delhi-110016.

Dr. (Mrs) G.R. Phalgumani
Director,
Central Testing Laboratory
Textiles Committee
79, Dr. A.B. Road
Worli, Bombay-400 018.

ACKNOWLEDGEMENTS

I wish to place on record my sincere thanks to prof. (Miss) P.Bajaj and Dr. G.R. Phalgumani for their valuable guidance, constant encouragement and unflinching help throughout the course of this research work. I wish to acknowledge my deep sense of gratitude to prof. (Miss) P. Bajaj for her personal attention and painstaking efforts to complete this thesis. Her advice and encouragement throughout the course of this study has been instrumental in shaping this study.

I express my sincere thanks to Prof. P.K. Hari, Head, Department of Textile Technology for allowing me to use the facilities of the Department and for his co-operation and encouragement.

I am thankful to Secretary, Textile Committee for granting permission for carrying out this research work.

I am thankful to the staff members of various laboratories in the Textile Department for their help and co-operation.

My warmest thanks are due to all my friends in Textile Department. My special thanks are due to Hazir Baharami, Sumesh Sharma, Ashish Bhargawa, Dr.J.Radhakrishnan, Dr. Sanjay Mehta, Meenakshi Goyal, S.J.Mahajan, Praveen kumar, Rakesh Koul, D.K.Paliwal, Dr.S.K.Rana, Y.C.Bhuvanesh, Dr. Reena and Srikumar.

Words are inadequate to express my gratitude to my parents for doing everything for me selflessly. I remain indebted to them. I wish to record my gratitude to my better half, Abha, who is my constant inspiration and reservoirs of limitless love and patience, who stands by me through all my joys and despairs and makes my dreams come true. I express my boundless love and gratitude to my daughter Swati and son Amit for their love and mental support throughout my thesis work. I acknowledge my heartfelt feelings.

I would like to thank Mr. R.K.Arora for typing this thesis and Mr. K.G. Padam for tracing the figures.

(A.K.Roopanwal)

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) nitrle 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^{-1}) with a multistep exothermic reaction as compared to precursor C(a terpolymer) with an Ea value of 20-22 kCal mol^{-1}. Also, precursor M showed lower weight loss in air at 500^{o}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., $KMnO_4$, cobaltous chloride, diammonium hydrogen phosphate, ammonium polyphosphate and hydrazine hydrate has been studied. Amongst the various treatments, $KMnO_4$ 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.

CONTENTS