

**Studies on high modulus high tenacity
polypropylene fibers
and single polymer composites**

by

Samrat Mukhopadhyay
Department of Textile Technology

*Submitted
In fulfillment of the degree of
Doctor of Philosophy*

to the

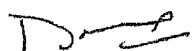


**Indian Institute of Technology, Delhi
February, 2004**

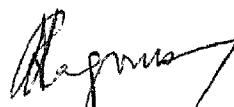
Certificate

This is to certify that the thesis entitled “**Studies on high modulus high tenacity polypropylene fibers and single polymer composites**” being submitted by Mr. **Samrat Mukhopadhyay**, 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. Mr. Mukhopadhyay has worked under our guidance and supervision and fulfilled the requirements for the submission of the thesis.

The results contained in the thesis have not been submitted, in part or full, to any other University or Institute for the award of any degree or Diploma.



(B.L. Deopura)
Professor,
Department of Textile Technology,
Indian Institute of Technology, Delhi
New Delhi – 110 016
India



(R. Alagirusamy)
Asst. Professor,
Department of Textile Technology,
Indian Institute of Technology, Delhi
New Delhi – 110 016
India

ACKNOWLEDGEMENT

I would like to profoundly thank **Prof. B.L. Deopura** who was not only my guide but also my source of inspiration. He gave me the freedom of thought and action and never imposed his ways. I found him always there to assist me when I went wrong. Thanks are also due to Ms. Deopura who also encouraged me with my work.

I would sincerely acknowledge the help of **Dr. R. Alagirusamy** who was my other guide and whose energetic approach along with his peaceful disposition assisted me to look at problems from a different angle. He taught me how to walk calmly in a tunnel even if the end doesn't seem visible.

I would sincerely thank Prof. Arumugam, Correspondent, Prof. Padmanabhan, Principal, Kumaraguru College and Prof. Natarajan, Head, Department of Textile Technology who always encouraged me and sanctioned leave at the proper time.

My sincere thanks are due to Prof. Charef Harrats, K.U.Leuven, Belgium, Prof. Gillespie, University of Delaware, Dr. Bhubanesh Gupta, Dr.A.K. Ghosh, Prof. S.N. Maiti, Dr. Manjeet Jassal, IIT Delhi, Ben Hsiao and Raj Somani, Dept. of Chemistry at Stony Brook, USA, Erik Andreassen, SINTEF, Norway, J.Loos, Netherlands and Prof. Gajanan Bhat, University of Tennessee, USA for useful discussions. Sincere thanks are due to Prof. V. B. Gupta, Ex-professor, IIT Delhi who always had time to discuss about my work. My sincere thanks to Prof. Kap Jin Kim, Kyung Hee University, South Korea, for his discussions and sending important papers in time.

Without the cooperation of the lab staff the work would have been impossible. Mr. Ashok, Mr. Khattar, Mr. Amarjeet, Mr. Omprakash, Mr. Kala, Mr. Patilal, Mr. D.C. Sharma, Mr. Rajender Prasad - I acknowledge their help with thanks.

My colleagues, A. Chatterjee, B.S. Butola, Vinayak Ogale, Anirban Guha, Naveen, Nilesh, Harinder, Anindya, Senthil (for his autocad drawings and formatting) - all helped me a lot. Thanks are due to Prakash, Rakesh Chawla - for his multi-faceted support, Rajkumar for their help. People like Arindam - burning midnight oil, Manabda and Preetidi was of perpetual help during times of adversity.

My sincere gratitude to my parents for their emotional support - especially my mother who always wanted to see me in this position and my in-laws for their encouragement.

My heartfelt thanks to my wife Mili who patiently shared the troubles of a research scholar. It would have been impossible to complete this task without her consistent support.

Samrat Mukhopadhyay

Samrat Mukhopadhyay
Research Scholar,
Department of Textile Technology.
IIT Delhi

Abstract

High modulus and high tenacity polypropylene (PP) filaments have been produced by subjecting as-spun filaments to a two stage drawing on a conventional mode and subsequently drawing on a heater having a gradient of temperatures. A three element gradient heater is developed for the drawing process. PP of 35 and 17 MFI are studied. Results show that filament properties are significantly affected by gradient heater settings i.e. nature and extent of gradient and end temperatures. It has been demonstrated that very high draw ratios could be obtained through gradient drawing process.

Gradient heater could be considered to consist of a series of a large number of heaters one after the other with increasing temperature. At each heater point the filament is drawn due to higher temperature than the previous point. This allows an increase in the level of orientation with low relaxation of molecules. Thus an incremental drawing over the heater plate is achieved. The process allows drawing to be carried out in the melting range. PP filaments are drawn in the gradient of temperatures in the range of (160-160-168)°C over the heater plate. On a constant temperature heater plate, maximum temperatures attainable are limited to much below the melting point. Alternately a very large number of heater plates will be required in a typical multistage drawing process.

The gradient drawn PP samples showed high crystal perfection and crystallinity. A sample with x-ray crystallinity values of 73%, crystalline orientation function of 0.96, amorphous orientation value of 0.83 has been obtained. The melting half widths are typically in the range of 4°C, indicating very narrow crystal size distribution and high

degree of crystal perfection. Fibers having initial modulus of 17.5 GPa and tenacity of 730MPa have been prepared. A very low thermal shrinkage of 7% at 150°C indicates excellent dimensional stability. Dynamic mechanical studies showed high storage modulus retention at high temperatures and shallow and delayed $\tan\delta$ peak indicating high amorphous orientation. The gradient drawing process has the advantage of being continuous in nature as compared to others, which are mainly batch processes.

These filaments are arranged in uniaxial direction and hot compacted under temperatures of approximately 154°C and pressure, to make a sheet like structure, using a constant loading device. Composites of 330 MPa strength and 25% elongation could be prepared. Morphology of the composites revealed excellent fiber-matrix adhesion. Initial experiments showed retention of filament properties to around 60% of those of the starting samples even at such high compaction temperatures, which gives the composite high strength. The matrix morphology undergoes a significant change in crystallinity upon compaction and is reflected in the thermo-mechanical properties.

CONTENTS

1 Introduction

1.1 Introduction	1
1.2 Scope of the work	2
1.3 About the thesis	3

2. Review of previous work

2.1 Introduction	5
2.2 Factors affecting properties of polypropylene fibers:	6
2.2.1 Feed Parameters	6
2.2.1.1 Molecular weight (MW) of the sample	6
2.2.1.2 Initial morphology	8
2.2.1.3 Polydispersity	8
2.2.1.4 Presence of entanglements	9
2.3 Processing parameters:	9
2.3.1 Spinning parameters	9
2.3.1.1 Spin line stress	9
2.3.1.2 Spinning temperature	10
2.3.1.3 Cooling procedure	10
2.3.1.4 Take up velocity	10
2.3.2 Post spinning parameters	12
2.3.2.1 Draw ratio, number of drawing stages and drawing speed	14
2.3.2.2 Drawing techniques	15
2.3.2.2.1 Tensile drawing	15
2.3.2.2.2 Zone drawing and zone annealing	15
2.3.2.2.3 Constant load oven drawing	17
2.3.2.2.4 Die drawing	17
2.3.2.2.5 Hot nip drawing	19
2.3.2.3 Temperature of drawing	19
2.3.2.4 Heat setting / annealing	21

2.4 Summary of Previous production of High Modulus Polypropylene Fibers	23
2.4.1 Crystallite and amorphous orientation	24
2.4.2 Amorphous modulus values	26
2.4.3 Degree of crystallinity	28
2.4.4 Presence of taut tie molecules	28
2.5 Fiber reinforced composite	29
2.5.1 Thermoplastic matrices and Polypropylene	30
2.5.2 Importance of the interphase	31
2.5.3 Processing conditions affecting the properties of the Composite	31
2.5.4 Single Polymer Composite	31
2.6 Conclusion and justification for present work	36
 3. Experimental	
3.1 Introduction	38
3.2 Materials	38
3.3 Monofilament preparation	38
3.4 Polymer MFI and Filament Characterisation	41
3.4.1 Melt Flow Index (MFI)	41
3.4.2 Sonic Modulus	41
3.4.3 Differential Scanning Calorimetry	41
3.4.4 Wide-Angle X-Ray Diffraction	42
3.4.4.1 Crystallinity and Crystallite Perfection	42
3.4.4.2 Crystalline Orientation Function	43
3.4.5 Birefringence and amorphous orientation function	44
3.4.6 Density and Density crystallinity	45
3.4.7 Volume fraction of Voids	45
3.5 Mechanical Properties	45
3.5.1 Quasi-Static Mechanical Properties	45
3.5.2 Dynamic mechanical properties	46
3.6 Thermal properties	46
3.6.1 Thermomechanical Analysis	46
3.6.2 Free Thermal Shrinkage	47
 4. Gradient heater - design, process analysis, and selection of samples	
4.1 Introduction	49
4.2 Initial experiments	49

4.3 Simulation of gradient profile	51
4.4 Fabrication and experiments on three element heater	53
4.5 Sample nomenclature and further selection	56
4.6 Conclusion	60

5. Structure, Morphology, Mechanical and Thermal properties

5.1 Introduction	62
5.2 Experimental	63
5.3 Results and discussion	65
5.3.1 DSC crystallinity, melting peak and peak half-width	65
5.3.2 Presence of multiple endotherms in DSC	69
5.3.3 Crystallite dimensions, crystallite and amorphous orientation and void fraction	70
5.3.4 Density and void fraction	73
5.3.5 Quasi-static tensile properties	75
5.3.6 Dynamic Mechanical Analysis	80
5.3.7 Free Thermal shrinkage studies	83
5.3.8 Thermomechanical analyses	85
5.3.9 Fracture morphology	88
5.3.10 Morphological changes during the gradient drawing process	90
5.4 Conclusions	91

6. Composites based on Gradient Drawn filaments

6.1 Introduction	93
6.2 Experimental	94
6.2.1 Materials	94
6.2.2 Characterisation of composites	96
6.2.2.1 Static Mechanical Properties	96
6.2.2.2 X-ray studies	97
6.2.2.3 Differential Scanning Calorimetry studies	97
6.2.2.4 Optical Microscopy	97
6.2.2.5 Morphology	98
6.2.3 Basis for preparation of single-polymer composites	98
6.2.4 Selection of material and process parameters	100
6.2.4.1 Consolidation Pressure	100
6.2.4.2 Consolidation Time and mode of transfer	101

6.2.4.3 The optimized temperature pressure cycle	102
6.3 Results and Discussion	103
6.3.1 Structure and Morphology	103
6.3.2 Tensile properties	108
6.4 Conclusion	113
 7. Conclusions	 115
References	117
Appendix	123