

STUDIES ON STRUCTURE, MORPHOLOGY AND FIBRILLATION BEHAVIOUR OF HIGH-DENSITY POLYETHYLENE AND BLENDED TAPES

by
S. MAHAJAN

*THESIS SUBMITTED
IN FULFILMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY*



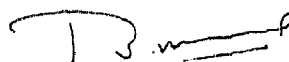
Department of Textile Technology
INDIAN INSTITUTE OF TECHNOLOGY, DELHI
APRIL 1994

.....to my beloved parents

CERTIFICATE

This is to certify that the thesis entitled "**STUDIES ON STRUCTURE, MORPHOLOGY AND FIBRILLATION BEHAVIOUR OF HIGH-DENSITY POLYETHYLENE AND BLENDED TAPES**" being submitted by **Mr. S. Mahajan**, 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. Mahajan has worked under my 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 in 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-110016.

ACKNOWLEDGEMENTS

I express my deep sense of gratitude to Prof. B.L. Deopura for his excellent guidance throughout the course of this research work. In these formative years of my research career, I have immensely benefited from his vast experience and knowledge, and it was indeed a great privilege and pleasure for me to have been associated with him. And, the importance of his role in moulding my career can not be expressed in words.

During the course of my research work, I have drawn help from a number of people; all of them deserve my sincere gratitude.

I wish to thank Dr. Yimin Wang of Chemical Fibre Research Institute, China Textile University, Shanghai, China, Dr. Sanjay Rastogi of Technical University of Eindhoven, Eindhoven, The Netherlands, Dr. Pankaj Joshi of University of Washington, Seattle, U.S.A., Dr. A. Venkataraman of BTRA, Bombay, India and Mr. S.S. Raje of MANTRA, Surat, India, for the assistance in X-ray diffraction work and for some useful discussions.

I also wish to thank Mr. Dheer of Paharpur Plastics Ltd. for providing necessary samples and technical information.

I am thankful to Dr. K.N. Bhoumik of Sanghi Polyesters, Hyderabad, Dr. D. Rama Rao of NAARM, Hyderabad and Dr. Anand Kumar of Mysore University, Mysore for their help and cooperation.

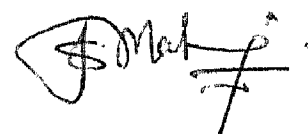
I wish to express my gratitude to Prof. M.L. Gulrajani, Prof. Bhaskar Dutta, Prof. P.K. Hari, Prof. V.B. Gupta, Prof. P. Bajaj, Prof. A.K. Mukherjee, Prof. R.B. Chavan, Dr. S.M. Ishiaque and Dr. Kushal Sen of Textile Technology Department for their help and encouragement.

I wish to thank Mr. V.K. Kala, Mr. R. Khattar, Mr. Ashok, Mr. Shiv Charan, Mr. Patilal, Mr. Amarjeet, Mr. Prakash of Fibre Science & Fibre Production Lab. Mr. D.C. Sharma of SEM lab. and Mr. Rajesh Arora of Textile Office deserve my special thanks for the excellent work of SEM and for the preparation of this manuscript.

Dr. J. Radhakrishnan, Mr. Rakesh Koul and Dr. R. Meenakshi deserve my special gratitude. My thanks are due to all my past and present colleagues; Dr. S.K. Rana, Mr. Y.C. Bhuvanesh, Dr. Ashish Bhowmik, Dr. Ratnam, Mr. G. Nalankilli, Dr. Pant, Dr. Sushil and Dr. Satish Balachandra, Dr. M. Patnaik, Mr. D.K. Paliwal, Dr. A.K. Roopanwal, Dr. S. Mehta, Mr. H. Bahrami and Mr. Preveen Arora. .

Mention must be made of my brothers and sister who have always been a source of encouragement to me.

Finally, I express my gratitude towards my parents who always stood by me in my venture and to them I solemnly dedicate this thesis.


(S. Mahajan)

ABSTRACT

The studies reported in this thesis have been made on uniaxially oriented tapes produced from high-density polyethylene (HDPE), polypropylene (PP), and blends of HDPE with various types of ethylene copolymers. These include high molecular weight polyethylene (HMWPE), linear low-density polyethylene (LLDPE), low-density polyethylene (LDPE), ethylene-vinylacetate (EVA), ethylene-propylene-diene terpolymer (EPDM), and ethylene-propylene block copolymers (EP₂C). The study of drawn tapes is mainly concerned with the inter-relationships between structure, morphology and properties with special emphasis on fibrillation behaviour. The tapes used for these studies were produced on a single stage extrusion-stretching-winding unit at 10 m/min. These tapes were uniaxially stretched to various draw ratios and at different temperatures. Structure and morphology of these tapes are studied, which include (i) characterization of crystalline and amorphous phase morphology, (ii) thermal shrinkage behaviour of tapes at elevated temperatures, (iii) static mechanical and dynamic mechanical behaviour, and (iv) tearing strength and fibrillation tendency.

The study led to some interesting insights into the interaction between fibrillation behaviour and structure of amorphous phase particularly the strong dependence of fibrillation tendency on molecular orientation and fraction of amorphous phase. To gain an understanding of this phenomenon at gross morphological level, the structure and morphology of both crystalline and amorphous phases were characterized in terms of fine structure of crystallites, crystallite orientation, amorphous phase orientation and fraction of amorphous phase with the help of small-angle X-ray scattering (SAXS), polarizing microscopy, and wide-angle X-ray diffraction (WAXD). Some additional aspects relating to gross fibrillar structure of oriented tapes were also studied. These include,

determination of void parameters such as, void dimensions in equatorial and meridional directions, volume fraction of voids and void number density per unit volume of tape with the help of combination of SAXS, density, and differential scanning calorimetry (DSC) analyses. The fibrillation process and fracture surface morphology of drawn tapes were also studied with the help of scanning electron microscopy (SEM). Combining results of these studies with the morphology of crystalline and amorphous phases of oriented tapes, an effort has been made to understand the nature of crack initiation, crack propagation and final fracture of oriented tapes in tearing, as well as, in combined tension-twist mode.

A summary of the principal features of the investigations made and the main findings are given below.

The influence of molecular structure of ethylene copolymers on crystallization behaviour, structure- morphology and mechanical properties of HDPE/ethylene copolymer blends of 90:10 blend composition have been investigated. The tensile drawing study of undrawn tapes show an enhanced strain hardening and a consistent reduction in natural, as well as, maximum draw ratio with increase in molecular irregularity of different ethylene copolymers. It is observed that blends are partially miscible in amorphous phase. Ethylene components of copolymer form cocrystalline phase with HDPE. The lateral crystallite thicknesses, crystallinity and amorphous phase orientation of blends consistently decreases with increase in molecular irregularity of ethylene copolymers. This relates to large scale change in crystallization and drawing behaviour of HDPE in the blends. It is stipulated that molecular network exerts an important influence on physical and mechanical properties of undrawn and drawn tapes.

The oriented tapes prepared from HDPE/PP and HDPE/EP₆C are incompatible at higher blend composition range. This is supported by the presence of two δ -relaxation

peaks each of PE and PP in the dynamic mechanical spectra of these blends. The two peaks however, merge into a very broad, single relaxation peak at low blend compositions (9 and 18% blends), indicating partial miscibility and compatibility of blend components. Variation of blend composition significantly affects the melting and crystallization temperature, crystallinity, crystallite dimensions, crystallite and amorphous phase orientation of blend components, which in turn, affects the mechanical properties of undrawn and drawn tapes. A relatively simple method to estimate the amorphous phase orientation of blends is also proposed.

The tear energy (G_c) required to propagate a tear along the direction of molecular orientation show a direct relation with amorphous phase orientation, fraction of amorphous phase, void size in meridional direction and volume fraction of voids. The decrease in G_c with increase in molecular orientation and crystallinity of tapes is due to the formation of large number of axially elongated voids at interfibrillar regions and decrease of viscous flow occurring in the vicinity of propagating crack tip. Large increase (15 to 45%) in G_c , was obtained for HDPE blended tapes containing about 10% EVA, EPDM and EP₆C. This is related to the extensive interfibrillar molecular network, improved interfibrillar adhesion and an increase in fraction of amorphous phase.

The fibrillation behaviour (axial splitting tendency) of drawn tapes was characterized by combined tension-twist fibrillation test. This is a new test proposed for determination of fibrillation strength. It was found that increase in amorphous phase orientation and crystallinity of tapes systematically decrease the fibrillation strength and fibrillation toughness as a consequence of deterioration in interfibrillar adhesion and formation of large number of axially elongated voids at interfibrillar regions. General models to explain this phenomenon via microcrack formation, interfibrillar shearing process and failure are proposed.

CONTENTS

		Page No.
CHAPTER I	INTRODUCTION	1
CHAPTER II	REVIEW OF LITERATURE	
2.1	Some Co-relations Between Processing Parameters, Fibrillation Behaviour of Drawn Tapes	6
2.1.1	Introduction	6
2.1.2	Effects of Various Types of Deformation Modes on Fibrillation Behaviour	6
2.1.3	Effects of Heat-setting Parameters on Fibrillation Behaviour	8
2.2	Structure-morphology and Fibrillation Behaviour of Drawn Blended Tapes	9
2.2.1	Introduction	9
2.2.2	Polymer Blends which Reduce Fibrillation Tendency	9
2.2.3	Polymer Blends which Enhance Fibrillation Tendency	12
2.3	Crystallization Behaviour, Structure-Morphology and Properties of Linear Polyethylene and Ethylene Copolymers	13
2.3.1	Introduction	13
2.3.2	Crystal Structure	14
2.3.3	Crystallinity and Crystal Size	15
2.3.4	Amorphous Region and Crystal Amorphous Interphase	18
2.4	Crystallization Behaviour, Phase Morphology and Properties of Polyolefin Blends	21

2.4.1	Introduction	21
2.4.2	Crystallization Behaviour in Polymer Blends	21
2.4.3	Selected Examples of Polyolefin Blend	24

CHAPTER III EXPERIMENTAL

3.1	Introduction	28
3.2	Materials	28
3.3	Sample Preparation	29
3.4	Characterization of Undrawn and Drawn Tapes	31
3.4.1	Density and Density Crystallinity	31
3.4.2	Differential Scanning Calorimetry	32
3.4.3	Birefringence	34
3.4.4	Wide-Angle X-ray Diffraction	34
3.4.4.1	Crystallite size and Interplanar Spacing	35
3.4.4.2	Crystallite Orientation Factor	36
3.4.4.3	Amorphous Orientation Factor	37
3.4.5	Small-Angle X-ray Scattering	39
3.4.5.1	Determination of Long Period	39
3.4.5.2	Determination of Void Dimensions	39
3.4.6	Volume Fraction of Voids and Void Number Density	42
3.4.7	Mechanical Properties	42
3.4.7.1	Static Mechanical Properties	42

3.4.7.2	Dynamic Mechanical Analysis	43
3.4.8	Thermal Shrinkage	43
3.4.9	Optical Microscopy	44
3.4.10	Scanning Electron Microscopy	44

CHAPTER IV THE STRUCTURE AND PROPERTIES OF DRAWN TAPES OF (HIGH-DENSITY POLYETHYLENE/ETHYLENE COPOLYMER) BLENDS

4.1	Introduction	45
4.2	Experimental	46
4.3	Results and Discussion	47
4.3.1	Undrawn Tapes	47
4.3.1.1	Crystallization and Drawing Behaviour	47
4.3.2	Drawn Tapes	51
4.3.2.1	Interplanar Spacing, Crystallite Thicknesses and Crystallinity	51
4.3.2.2	Melting Behaviour	54
4.3.2.3	Crystallite and Amorphous Phase Orientation	54
4.3.2.4	Mechanical Properties	55
4.3.2.5	Dynamic Mechanical Analysis	58
4.4	Concluding Remarks	600

CHAPTER V THE STRUCTURE AND PROPERTIES OF DRAWN TAPES OF (HIGH-DENSITY POLYETHYLENE/ETHYLENE-PROPYLENE COPOLYMER) BLENDS

5.1	Introduction	661
-----	--------------	-----

5.2	Experimental	62
5.3	Results and Discussion	63
5.3.1	Structure and Properties of Undrawn Tapes	63
5.3.1.1	Crystallization Behaviour and Morphology	63
5.3.1.2	Drawing Behaviour	64
5.3.2	Structure and Properties of Drawn Tapes	65
5.3.2.1	Melting and Crystallization Behaviour	65
5.3.2.2	Crystallinity and Crystal Size	70
5.3.2.3	Crystallite and Amorphous Phase Orientation	75
5.3.2.4	Shrinkage Behaviour	76
5.3.2.5	Mechanical Properties	78
5.3.2.6	Dynamic Mechanical Analysis	80
5.4	Concluding Remarks	81

**CHAPTER VI STRUCTURE-MORPHOLOGY AND TEAR
STRENGTH OF ORIENTED TAPES OF
POLYETHYLENE AND ITS BLENDS**

6.1	Introduction	83
6.2	Experimental	84
6.2.1	Structural Characterization of Oriented Tapes	84
6.2.2	Measurements of Tear Strength	84
6.3	Results and Discussion	86
6.3.1	Fibrillar Structure of Drawn Tapes	86

6.3.2	Effect of Amorphous Phase Orientation on G_c	91
6.3.3	Effect of Fraction of Amorphous Phase on G_c	93
6.3.4	Effect of Blending of Various Ethylene Copolymers to HDPE on G_c of Blended Tapes	94
6.3.5	Effect of Blend Composition on G_c of HDPE/PP and HDPE/EP _b C 3.5 Blends	96
6.3.6	Fracture Behaviour and Fracture Surface Morphology of Drawn Tapes	97
6.4	Concluding Remarks	101

CHAPTER VII FIBRILATION BEHAVIOUR OF ORIENTED TAPES OF POLYETHYLENE AND ITS BLENDS

7.1	Introduction	103
7.2	Experimental	104
7.2.1	Structural Characterization of Drawn Tapes	104
7.2.2	Fibrillation Analysis of Drawn Tapes Using Combined Tension-Twist Test	106
7.2.2.1	Fibrillar Morphology of Drawn Tapes	107
7.2.2.2	Stress Distribution Pattern and Fibrillation of Tape in a Combined Tension-Twist Test	108
7.2.2.3	Testing Procedure and Equipment	109
7.2.2.4	Test Analysis	110
7.3	Results and Discussion	112

7.3.1	Effect of Amorphous Phase Orientation on Fibrillation Strength of Drawn Tapes	112
7.3.2	Effect of Amorphous Phase Orientation and Fraction of Amorphous Phase on Fibrillation Toughness of Drawn Tapes	115
7.4	Concluding Remarks	120
CHAPTER VIII	SUMMARY AND CONCLUSIONS	121
	REFERENCE	125