CRYSTALLIZATION BEHAVIOUR AND STRUCTURE PROPERTY CORRELATION OF HIGH-DENSITY POLYETHYLENE/LINEAR LOW-DENSITY POLYETHYLENE BLEND

by

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Certified that the dissertation entitled "Crystallization Behaviour and Structure Property Correlation of High-density Polyethylene and Linear Low-density Polyethylene" which is being submitted to the Indian Institute of Technology Delhi by Suryya Kanta Rana in fulfillment for the Degree of Doctor of Philosophy is a record of his own work carried under our joint supervision and guidance. The matter embodied in this dissertation has not been submitted for the award of any other degree or diploma.

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„ „ „ „ „ „ „ „ „ „dedicated to my parents„

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ABSTRACT

The studies on crystallization behaviour and structure property correlation of the binary melt blend of high-density polyethylene (HDPE) and linear low-density polyethylene (LLDPE) are presented in this thesis. The aspects of these blends which are dealt in adequate detail are :

(a) Cocrystallization of HDPE/LLDPE

(b) Morphological modification of HDPE on blending with LLDPE

(c) Effect of blending on various mechanical properties

(d) Variation in the melt rheological properties of the blend.

The thesis is divided into a total of seven chapters. Findings are presented sequentially from Chapters 3 to 6, while the first two chapters (i.e. Chapter 1 and 2) delve upon the information of the blend terminology and elaboration of some of the non-conventional experimental techniques. The Chapter 7 summarizes the major findings of this work and project the overall behaviour of this HDPE/LLDPE blend.

The First Chapter enumerates the general introduction of the polymer blends, their historical background, conveniences and economics involved in

manufacturing along with some information presented on the structural differences on the varieties of polyethylenes available. The review on the studies conducted on melt and solution blended polyethylene are discussed. This chapter also defines the scope and objectives of the work.

The Second Chapter deals with the experimental details and characterization of polyethylene to provide necessary information on the properties of the material used. Some non-conventional experiments presented are described in greater detail and elaborated. Sample preparation, analysis procedure, calculation involved are outlined in this chapter.

The Third Chapter describes the crystallization behaviour of the HDPE/LLDPE blend studied through the DSC and x-ray techniques. In the DSC, studies the parameters related to the crystallization exotherm,viz. onset temperature, crystallization peak temperature, area under the crystallization peak and peak width are studied as a function of blend composition. The X-ray crystallization parameters are correlated with the data obtained from DSC crystallization exotherm. The singlet nature of the crystallization exotherm, the linear variation in the d-spacing and the crystallite size are attributed to crystallization of the constituting components (i.e. HDPE and LLDPE).

The study on the crystallization kinetics are presented in the Fourth Chapter. The kinetic parameters

i.e., Avrami exponent and activation energy, vary uniquely with blend composition. The gradual decrease of Avrami exponent from 3 to 2(i.e.,the values for HDPE and LLDPE, respectively) with increase in %LLDPE content has been interpreted to vary in two parts : (i) the blend composition invariant part and (ii) the blend composition variant part. The invariant part of the Avrami exponent (which is equal to 2) describes the sheaf-like growth of the crystallites for both the pure polymers and the blend, however, the variant part systematically changes from 1 for HDPE to 0 for LLDPE which is spread all over the composition range. This change in Avrami exponent interpreted as the systematic changes over of the types of the inception of nucleus from sporadic to instantaneous one from HDPE to LLDPE respectively. The combination of these two types of inception made up the fractional value of Avrami exponents for blends.

The Fifth Chapter discusses the effect of blends on various mechanical properties such as tensile properties, flexural behaviour, thermomechanical characteristics and dynamic mechanical thermal behaviour against blend composition. The tensile properties at yield varies linearly, whereas, modulus and tensile properties at break varies non-linearly as functions of the blend composition. On the basis of response towards the strain rate in flexural testing, the amorphous phase

is divided in two parts, i.e., the mobile part and the entangled part. Correlation has been established with the x-ray diffraction measurement data to the contributions of these two parts of the amorphous phase, hence supports the existence of mobile and entangled parts.

The Sixth Chapter deals with the capillary flow behaviour of HDPE/LLDPE melt at four extrusion temperatures. The melt compatibility of the blend is presented at different shear rates. The normal stress variation in the two regions of shear rate and their corresponding die-swell behaviour are discernible.

The Seventh Chapter sums up the important conclusions. This chapter projects the complete picture in terms of crystallization behaviour and structure property correlation of HDPE/LLDPE blend. Some possible extensions of the work are also given at the end of this Chapter.

SYMBOLS USED

Absolute Temperature	T
Activation Energy	E
α-Peak Temperature	T_α
Apparent Shear Rate	$\dot{\gamma}_{app}$
Apparent Shear Stress	τ_{app}
Area Under the Crystallization Exotherm	$A/m(A_T, A_P)$
Avrami Exponent	n
Bragg's Angle	2θ
Capillary Dia	d
Capillary Length	L
Coefficient of Thermal Expansion at 50°C	α_{50}
Complex Modulus	E^*
Concentration	c
Crystallization Peak Width at Half-height	ΔW
Crystallization Peak Temperature	T_p
Crystallite Size	$t_{(hkl)}$
Degree of Crystallinity	X_c
Density	ρ
Enthalpy	H
Entropy	S
Extension Coefficient	k
Film Thickness	l
Frequency Factor	A
Frequency of Reciprocation	f
γ-Peak Temperature	T_γ

Gas Constant	R ,k
Gibb's Free Energy	G
Intensity,transmitant light	I
Intensity,incident light	I_o
Length,initial	l_o
Length,reference	l_r
Intrinsic Viscosity	$[\eta]$
Lattice Constant	a,b,c and α,β,γ
Lattice Spacing Corresponding to 110 and 200 Plane	d_{110} and d_{200}
Loss Modulus	E"
Loss Tangent	tan δ
Melt Viscosity	η
Melting Temperature	T_m , $T^m{}_m$
Normal Stress	N
Onset Temperature	T_{onset}, T_o, $T^m{}_{(onset)}$
Partial Crystallinity	α
Piston Face Area	A
Piston Face Radius	R
Powerlaw Exponent	n
Pressure Drop	ΔP
Pre-exponent Factor	A
Relative Viscosity	η_r
Rate of Crystallization	tan S_i
Rate constant	k
Reference Temperature	T_r
Scanning Rate	β

Shear Stress	σ
Shear Rate	$\dot{\gamma}$
Solubility Parameter	δ
Specific Viscosity	η_{sp}
Strain Rate	$\dot{\epsilon}$
Storage Modulus	E'
Ultimate Length	l_u
Time	t
Volume	V
Volume Flow Rate	dV/dt
Volume Fraction	ϕ
X-ray Peak Width at Half-height	$\beta_{1/2}$
X-ray Wave Length	λ

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