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THERMAL CHARACTERISATION OF LDPE AND LLDPE BLENDS

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ABSTRACT

The thermal behaviour of physical blends prepared from low density polyethylene (LDPE) and linear low density polyethylene (LLDPE) was examined by differential scanning calorimetry and thermogravimetry Single melting peak endotherms were obtained for the compositions 90, 80, 20 and 10% LLDPE Kinetic data were acquired by least-squares analyses of experimental points obtained by differentiating primary thermograms Degradation was found to be first order for LDPE and second order for LLDPE

INTRODUCTION

Blending of polymers leads to new materials which exhibit useful mechanical, electrical or thermal properties The potential technical importance of polymer blends is currently commanding considerable scientific interest The preparation of polymer blends is connected with various processing techniques in which the components are subjected to high temperature For this reason the knowledge of their thermal stability is of fundamental importance Differential thermo-analytical techniques are widely used for studying the melting behaviour of single- [1–6] and multi-component [7–9] polymer systems Thermal analysis is useful for determining properties and structure of polymeric materials, such as melting temperature and its range, heat of fusion [10], degree of crystallinity [11] and rate of crystallisation [12,13]

The key processing and end-use properties of linear low density polyethylenes (LLDPE) depend upon three basic parameters (a) the type of co-monomer used, (b) the co-monomer content, and (c) the distribution of co-monomer along the polymer molecules The heterogeneous character of the distribution of co-monomer elements [14] in LLDPE is a remarkable phenomenon This heterogeneity can be evaluated, for instance, from crystallisation and melting behaviour Differential scanning calorimetry (DSC) shows that crystallisation and melting cover large temperature ranges, and the DSC curves show several peaks [15,16]. Ethylene co-polymers, with a homogeneous distribution of co-monomer elements [17], produce single-peak

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DSC curves, the shapes of which depend on the ethylene sequence length distribution Low density polyethylene (LDPE), the sequence length of which is primarily determined by the distribution of short chain branching, also gives a single-peak DSC curve

The processing problems (power consumption and melt viscosity) of LLDPE are partly solved by blending with LDPE These dry blends produce films, whose properties are influenced by the mixing efficiency of the extruder Blends directly from polymerisation have been made by some producers The structure of such blends is not the same as that of the dry blends The long chain branching produced by free radical mechanisms with particular Ziegler catalysts is uniformly distributed over the whole polymer [18] In this work, differential scanning calorimetry and thermogravimetry have been used to characterise the blends prepared from LDPE and LLDPE

EXPERIMENTAL

The blends were prepared by melting and mixing LDPE and LLDPE on a two roll mill at a temperature of 165 ° C After fluxing for 20 min the molten mixture was removed from the mill and formed into sheets Samples from the sheets were analysed by a Dupont differential scanning calorimeter (model 910) attached to a Dupont 1090 thermal analyser at a heating rate of 10 ° C min^{-1} in a nitrogen atmosphere The thermogravimetric analyses (TGA) were carried out with a Dupont 950 thermobalance attached to a Dupont 1090 thermal analyser at a heating rate of 20 ° C min^{-1} in a nitrogen atmosphere

RESULTS AND DISCUSSION

Thermal techniques, particularly DSC, have been widely used to study diverse features of blend compatibility Figure 1 shows the DSC scans of LDPE and LLDPE and their blends The peak melting temperatures for LDPE and LLDPE and their blends were assessed The peak melting points and their respective enthalpy values for the various percentage compositions, obtained from the DSC curves, are listed in Table 1

The pure polymers give a single melting peak, whereas partially compatible polymer blends give more than one melting peak The number of peaks correspond to the number of components present in the composite material The 100% LDPE and 100% LLDPE, which are pure polymers yield single melting peak endotherms For the compositions 90, 80, 20 and 10% LLDPE, single melting peak endotherms were obtained This shows that at these compositions a homogeneous mixture may have formed resulting in a co-crystalline phase which yields a single melting temperature

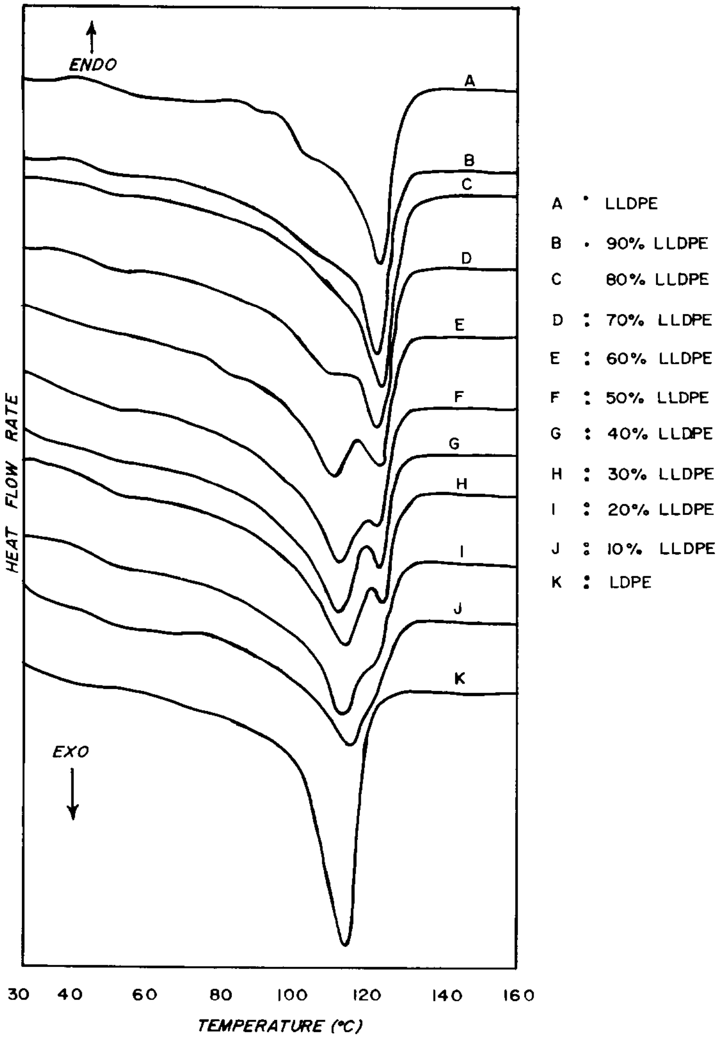

Fig 1 DSC curves of LLDPE, LDPE and their blends

The compositions 70, 60, 50, 40 and 30% LLDPE give two melting peaks The appearance of two peaks reveals that the two components yield a non-homogeneous mixture resulting in a phase separation They are not completely miscible at these concentrations The relative intensity of the melting peaks is proportional to the ratio of the two components in the blends Thus, it can be observed that the intensity of the melting peak corresponding to LLDPE increases, in increments, with an increase in the percentage of LLDPE The melting points of the blends lie between those of the individual polymers LLDPE and LDPE This may not necessarily be so in all cases as examples are cited in which the magnitude of the melting point is less or more than that of the individual polymers due to some

TABLE 1

DSC analysis of LDPE, LLDPE and their blends

Sample	Percentage composition		Melting point (° C)		Energy absorbed (J g^{-1})
	LDPE	LLDPE	LDPE	LLDPE	
1	0	100	–	124 8	12 0
2	10	90	–	124 0	14 3
3	20	80	–	124 7	14 0
4	30	70	111 6	123 7	14 3
5	40	60	112 3	124 6	14 8
6	50	50	113 2	123 6	15 1
7	60	40	112 9	124 8	15 7
8	70	30	114 7	124 7	15 7
9	80	20	113 9	–	15 0
10	90	10	116 2	–	12 4
11	100	0	115 2	–	13 2

secondary effects The melting point of pure LLDPE is approximately 124 3 ± 0 8 ° C and that of LDPE is approximately 113 5 ± 2 5 ° C

Thermogravimetric analysis of LDPE, LLDPE and their blends was carried out to evaluate the effect of the composition of the blends on the thermal degradability of the polymers The thermograms of LDPE, LLDPE and their blends are given in Fig 2 The method used for the calculation of degradation reaction order and the energy of activation was a variation of the technique of Freeman and Carroll [19] as modified by Anderson and Freeman [20,21] The kinetic data were obtained by least-squares analyses of

TABLE 2

Thermogravimetry analysis of LDPE, LLDPE and their blends

Sample	Percentage composition		Temperature for initial decomposition (° C)	Temperature for half decomposition (° C)	Temperature for max decomposition (° C)	Order of reaction	Activation energy (kcal mol^{-1})
	LDPE	LLDPE					
1	0	100	310	435	430	2	90 20
2	10	90	425	500	505	1	73 98
3	20	80	420	505	510	1	70 01
4	30	70	330	455	460	2	61 85
5	40	60	335	450	450	2	102 11
6	50	50	380	480	480	1	61 04
7	60	40	405	485	490	1	79 89
8	70	30	440	510	510	1	83 22
9	90	10	440	500	510	1	62 27
10	100	0	285	415	415	1	32 38

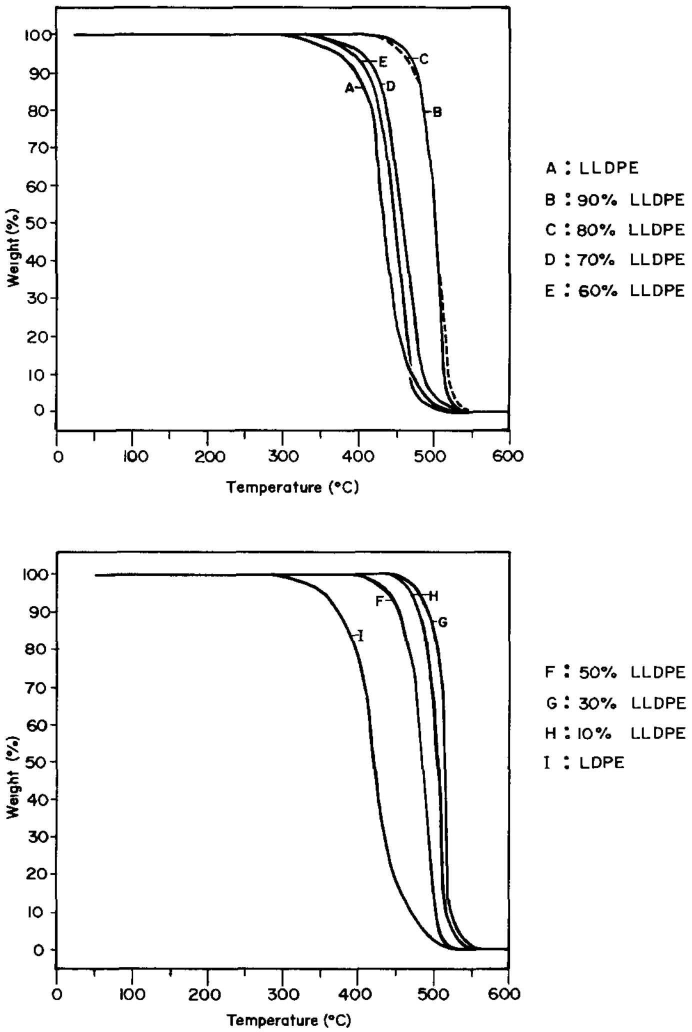

Fig 2 Thermogravimetric curves of LLDPE, LDPE and their blends

experimental points obtained by differentiating primary thermograms The thermogravimetric data are given in Table 2 Degradation of LDPE started at 285 °C The temperature at which half the initial sample weight was lost was 415 °C For LLDPE, the degradation started at 310 °C and 50% of the polymer had degraded and volatilised at 430 °C However, the degradation temperatures of the blends do not lie in between the temperatures of the individual polymers The reaction order was calculated to be unity for LDPE and two for LLDPE The activation energy for LDPE was 32 kcal mol^{-1} and that for LLDPE was 90 kcal mol^{-1} The maximum activation energy was obtained for the blend having the composition 40% LDPE and 60% LLDPE

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