

Characterization of Multicomponent Polyethylene Blends by Differential Scanning Calorimetry

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Synopsis

The melting behavior of physical blends prepared from low, medium, and high density polyethylene was examined by differential scanning calorimetry. Binary low/high and ternary low/medium/high density polyethylene blends showed two endothermic peaks which were attributed to the melting of the lower and higher density components. The percent crystallinity of the blends was calculated according to an additivity relationship using the crystallinity of the pure components. These results compared favorably with an experimental crystallinity measured from the area under the melting curves.

INTRODUCTION

Differential thermal analysis (DTA) techniques are widely used for studying the melting behavior of single¹⁻⁶ and multicomponent⁷⁻¹² crystalline polymer systems. This type of analysis is useful for determining properties and structure of polymeric materials such as melting temperature and range,¹⁻¹² heat of fusion,^{13,14} degree of crystallinity,^{15,16} and rate of crystallization.¹⁷⁻¹⁹

Previous investigations have examined two-component heterogeneous crystalline polymer systems in the form of either blends or copolymers.⁷⁻¹² On a DTA scan, two peaks were observed and were associated with the melting or fusion of the crystalline portion of each component.

In this work, differential scanning calorimetry has been used to characterize physical mixtures prepared from commercial grades of low, medium, and high density polyethylene. It will be shown that both binary low/high and ternary low/medium/high density polyethylene blends have two melting peaks which can be related to the melting of the lower and higher density components. Also, using an additivity relationship, it will be shown that the percent crystallinity of the blends can be calculated with good accuracy from the weight fraction and crystallinity of the pure components.

EXPERIMENTAL

The blends were prepared by melting and mixing the polyethylenes listed in Table I on a two-roll mill at a temperature of 435 K. After fluxing for 20 min, the molten mixture was removed from the mill and formed into sheets. Samples from the sheets were analyzed by a Perkin-Elmer differential scanning calorimeter, Model 1B, at a scanning rate of 10 K/min. The percent crystallinity was measured from the area under the melting curves.

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TABLE I
Commercial Grades of Polyethylene and DSC Analysis of Physical Properties

Supplier and trade name	Density (g/cc)	Melting point (K)	% Crystallinity
Gulf 1115 Low Density	0.920	383	27.1
USI Na 271 Medium Density	0.929	391	44.7
Phillips Marlex 6006 High Density	0.960	408	74.7

RESULTS AND DISCUSSION

Characterization by DSC

Figure 1 shows the DSC scans for the polyethylene homopolymers. As expected, the melting temperature and area under the endotherm increased with density and crystallinity. The experimental melting-point temperatures, which were determined at the location of the endothermic peaks, are listed in Table I.

The DSC scans for the binary low/high density polyethylene blends are shown in Figure 2. Two peaks are observed and are produced by the separate melting of the low and high density crystalline regions because the two types of polyethylene do not form isomorphous crystals.¹⁰ The respective melting points are listed in Table II under T_{m1} and T_{m2} . The melting point for the low and high

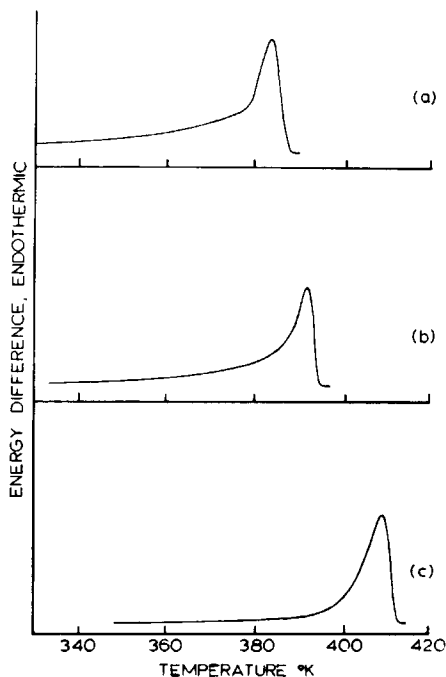


Fig. 1. DSC scans of polyethylene homopolymers: (a) Gulf 1115 low density PE; (b) USI Na 271 medium density PE; (c) Phillips Marlex 6006 high density PE.

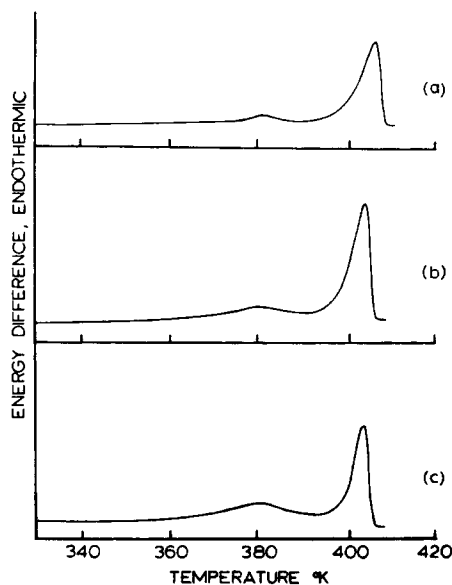


Fig. 2. DSC scans of binary polyethylene blends: (a) Sample 1, 33% low and 67% high density PE; (b) sample 2, 50% low and 50% high density PE; (c) sample 3, 67% low and 33% high density PE.

TABLE II
DSC Analysis of Polyethylene Blends

Sample	Weight % Polyethylene			Melting points (K)		% Crystallinity		
	Low density	Medium density	High density			Exp.	Eq. (1)	% Difference
				T_{m1}	T_{m2}			
1	33	—	67	381	406	62.5	59.0	5.6
2	50	—	50	380	404	54.1	50.9	5.9
3	67	—	33	380	403	50.5	42.8	15.3
4	25	50	25	389	402	51.2	47.8	7.2
5	33.3	33.3	33.3	386	403	52.9	48.8	7.8
6	37.5	25	37.5	386	403	54.5	49.4	9.4
7	40	40	20	387	401	47.4	43.7	7.8
8	20	40	40	390	403	55.3	53.2	3.8

density crystalline regions was slightly lower than for the pure homopolymers. This type of behavior has been detected for binary blends and has been attributed to a possible interplasticizing action caused by some molecules of one component acting as a diluent within the crystalline regions of the other component.^{7,10,20} Also, the relative intensity of the melting peaks was proportional to the ratio of the two components, as observed for other heterogeneous blends.^{7,10}

Figure 3 contains the DSC curves for the ternary low/medium/high density polyethylene blends. Again, only two melting peaks are observed, and the melting points associated with them are listed in Table II. In all cases, the lower melting temperature, T_{m1} , occurred between the melting points of the low and medium density polyethylene homopolymers. To account for this behavior, if the low and medium density polyethylenes were sufficiently compatible, a homogeneous mixture could be formed resulting in a co-crystalline phase which

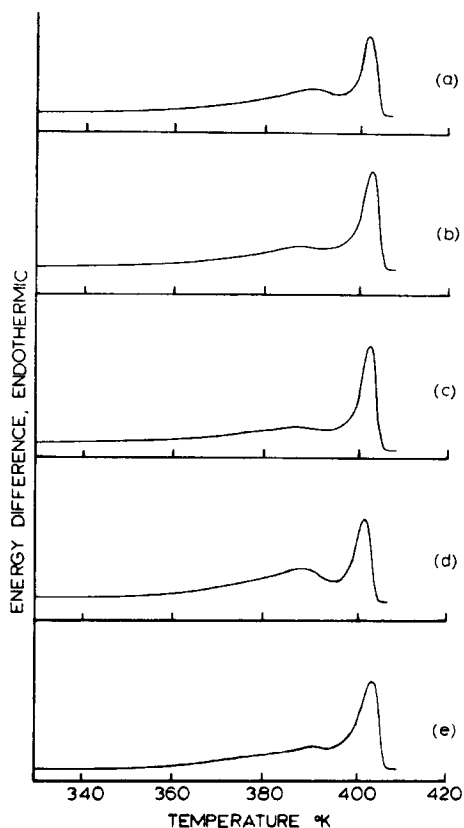


Fig. 3. DSC scans of ternary polyethylene blends: (a) Sample 4, 25% low, 50% medium, and 25% high density PE; (b) sample 5, 33.3% low, 33.3% medium, and 33.3% high density PE; (c) sample 6, 37.5% low, 25% medium, and 37.5% high density PE; (d) sample 7, 40% low, 40% medium, and 20% high density PE; (e) sample 8, 20% low, 40% medium, and 40% high density PE.

would yield a single melting temperature. This may be possible since the density difference between these particular low and medium density polyethylenes is not very large. Consequently, structural differences on a molecular level may be at a minimum, allowing the molecules of these two components to mix together and to pack into the same crystals. In further support of this hypothesis, the intensity of the lower temperature melting peak was directly proportional to the combined low and medium density polyethylene content in the blend, indicating that both components simultaneously were passing through a melting stage as part of a homogeneous co-crystalline phase. Also, the location of the melting temperature T_{m1} is affected by the low to medium density ratio in addition to the overall blend composition. The higher melting temperature T_{m2} which is due to high density polyethylene, was slightly lower than that of the pure high density homopolymer as was observed for the binary systems. Again, this behavior could be attributed to a plasticizing action of some of the low and medium density polyethylene molecules acting as a diluent within the high density crystalline regions.²⁰ Finally, the intensity of the higher temperature peak, as expected, was proportional to the high density polyethylene content in the blend.

Determination of Crystallinity

The crystallinity of the pure and blended polyethylenes was determined by measuring the area under the melting curves from the DSC scans,²¹ and the results are listed in Tables I and II. The percent crystallinity of the blends can be calculated with good accuracy by an additivity relationship defined by eq. (1):

$$\% \text{ Crystallinity} = \sum_i w_i X_i \quad (1)$$

where w_i is the weight fraction of component i and X_i is the percent crystallinity of component i . Using the experimental data for the homopolymers, the percent crystallinity of the blends was calculated by eq. (1) and is reported in column 8 of Table II. The accuracy of eq. (1) was very good as evidenced by the difference between experimental and calculated results, column 9 of Table II, which were less than 10% except for sample 3.

Since the total crystallinity of the blends appears to follow an additivity principle, it seems that, within a mixture of the various types of polyethylene, the ability of one component to crystallize is not prevented by the other components. Apparently, the various polymer species either mix or phase separate and then form crystals either in concert with another component or alone, depending upon differences in molecular structure.

CONCLUSIONS

It has been shown that both binary low/high and ternary low/medium/high density polyethylene blends exhibit two melting peaks during a DSC scan. For the binary systems, the peaks were associated with the separate melting of the low and high density crystalline regions. However, for the ternary systems, the low-temperature peak may be due to the melting of co-crystals of the low and medium density polyethylene while the high temperature peak is associated with the melting of the high density component.

The percent crystallinity of the blends was calculated according to an additivity relationship using the weight fraction and crystallinity of the homopolymers. In general, calculated results deviated by less than 10% from experimentally measured values.

Further work is being planned to explore the effect of a variety of medium density polyethylenes on the melting behavior, compatibility, and morphology of ternary blends.

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