

Application of Differential Thermal Analysis to Polyethylene Blends*

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Synopsis

The analytical application of differential thermal analysis (DTA) for the identification and evaluation of a number of polyethylene blends is described. New DTA data are presented for homopolymer blends of low and intermediate density polyethylenes and low and high density polyethylenes whose degrees of branching are sufficiently different. The concentration by weight of each of the crystalline components in the blend is determined from DTA thermograms by the peak area method and the melting point-density method. The density of polyethylenes and polyethylene blends is determined with the use of density gradient columns.

Introduction

The physical properties of fabricated polyethylene blends, as well as fabricated polyethylenes, are heavily dependent on their crystalline content. Crystalline content or degree of crystallinity of both low and high density polyethylene has been studied by differential thermal analysis (DTA).¹ DTA has been used to detect a polymer blend of high density polyethylene and isotactic polypropylene.¹ The compatibility of high density polyethylene-isotactic polypropylene blends has been studied by the use of DTA.² DTA has been used to study nylon 66-nylon 610 blends³ and nylon 6-nylon 11 blends.⁴ Excellent resolution has been shown by the use of DTA of a blend of seven polymers, including low density polyethylene, high density polyethylene, polypropylene, polyoxymethylene, nylon 6, nylon 66, and polytetrafluoroethylene.⁵ However, studies of low and high density polyethylene blends by DTA have been reported only recently.⁶

New DTA data are presented in this paper for homopolymer blends of low and intermediate density polyethylenes and low and high density polyethylenes.

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Experimental

The DTA apparatus and process used in this laboratory is similar to the one described by Ke;⁷ however, the temperature of the sample has been recorded instead of the temperature of the reference material. Iron-constantan thermocouples were used in this study, aluminum oxide being used as the reference material. Melting points were estimated to a tenth of a degree by the direct reading of a millivolt potentiometer. The temperature of the DTA system was programmed at linear cooling and heating rates of 2°C./min. The temperature programmer was a proportioning temperature controller driven by a clock motor. A Houston Instrument Model HR-92-4 X-Y recorder was used for recording the thermograms. The pre-amplifier was a Leeds and Northrup Model 9835-B.

First, experimental blends were made by solution blending. A 1.1% by weight solution was prepared by dissolving 1 g. of the blend components in 100 ml. of *p*-xylene at 130°C. and stirring for 30 min. with oxidation inhibitors. The oxidation inhibitors were 10 mg. of 2,6-di-*tert*-butyl-4-methylphenol in 100 ml. of *p*-xylene and a nitrogen atmosphere. The average dry weight per cent of the blends recovered from solution was 99.0%. Samples for DTA were obtained by melting and pressing 50 mg. of the powdery precipitate into a solid. Before testing, the samples were annealed in DTA sample cells by programming their temperatures from 150 to 25°C. at a linear cooling rate of 8°C./hr. It should be pointed out, however, that a cooling rate of 8°C./hr. is not a prerequisite condition. A faster cooling rate, e.g., 1°C./min., could be just as useful.

The density of the samples was determined by means of density gradient columns. Annealed samples for density determinations were prepared by programming their temperatures from 150 to 25°C. at a linear cooling rate of 8°C./hr.

Polyethylenes PE-1 and PE-2 have densities of 0.9165 and 0.9368 g./cc. at 23°C. and melt indices of 20 and 0.9 g./10 min., respectively. Polyethylenes PE-3 and PE-4 have densities of 0.9683 and 0.9209 g./cc. at 23°C. and melt indices of 5.5 and 2.0 g./10 min., respectively.

Results and Discussion

Figure 1 shows thermograms of an experimental homopolymer blend of equal amounts by weight of low and intermediate density polyethylenes PE-1 and PE-2 melting at 106.5 and 121.8°C., respectively. The weight concentration of each of the crystalline components in a polyethylene blend can be determined from DTA thermograms in different ways. We have used two methods.

(1) In the peak area method, the peak areas of the blend components are measured and compared to the measured peak areas of the pure substances or other similar substances. This method is similar to the ones reported by Clampitt⁶ and Inoue.⁴ Clampitt's method provides for the estimation of the linear or high density polyethylene content in low and high

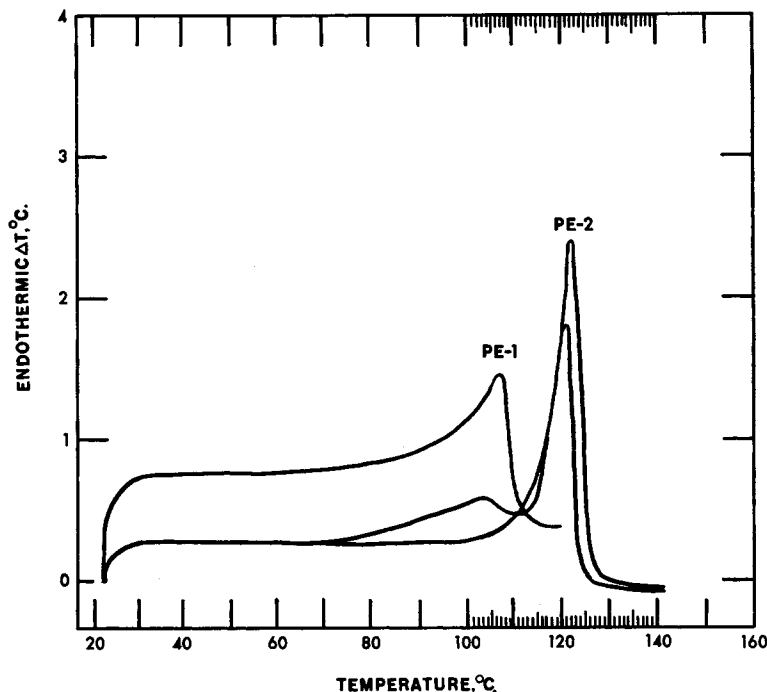


Fig. 1. Thermograms of a blend of low and intermediate density polyethylenes, PE-1 and PE-2.

density polyethylene blends. Inoue's method provides for the estimation of the concentration of both components in nylon 6-nylon 11 blends.

(2) In the melting point-density method, DTA melting point data and density data are used. The density can be determined with the use of density gradient columns. This method is also similar to the one reported by Inoue.⁴ Inoue's method offers DTA melting point data and density data on nylon 6-nylon 11 blends and nylon 66-nylon 6 blends.

The two methods are quite often used concurrently.

In the peak area method, each component of the blend produces a peak on the thermogram which has a shape and melting point similar to the peak of the pure substance. The enclosed areas under the peaks are proportional to the amount by weight of each component present when compared to the peak areas of the pure substances. In this study, a straight-line extension of the base line was the graphical means of closing the open end of the DTA peak in order to planimeter the peak area.

To study the peak area-weight concentration relationship in more detail, experimental homopolymer blends of low and high density polyethylenes PE-3 and PE-4 were made with weight concentrations varying by 5% of each component. These polyethylenes were selected as representative types, and because they are free of additives. More of the recent commercial polyethylene blends appear to consist of low and high density poly-

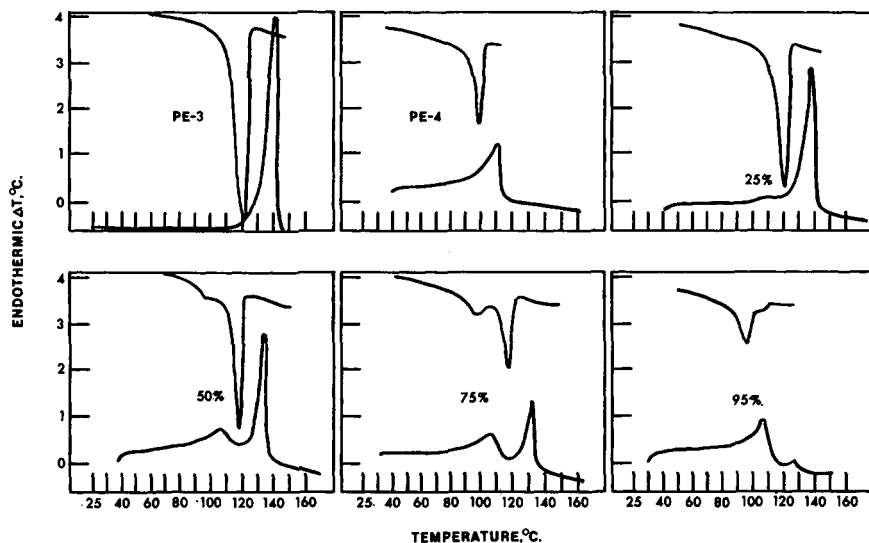


Fig. 2. Thermograms of blends of high and low density polyethylenes, PE-3 and PE-4, with increasing PE-4 content.

ethylenes. Figure 2 shows thermograms of some of these experimental blends of high and low density polyethylenes with increasing PE-4 content (25, 50, 75, and 95%). The cooling and heating curves are at the top and the bottom of these thermograms, respectively.

The peak area data of the blend components examined are listed in Table I. PE-4 is not detectable in concentrations of less than 20% from the thermograms. Plots of the peak area-weight per cent data of the blend components examined give nearly straight lines. To determine the weight concentrations of the blend components, their peak areas were compared by algebraic proportions to the peak areas of the pure substances. The DTA estimated weight per cents of these blend components are also listed in Table I.

Therefore, it is possible to determine by the peak area method the weight concentration of polyethylene blend components in the blend examined or another similar blend whose composition is unknown.

In the melting point-density method, DTA melting points of blend components are lower than those of the pure substances. This change in melting points may be explained by Flory's theory⁸ of the melting point depression of polymer-solvent and copolymer systems. The melting point-weight per cent data of the blend components examined show this effect in Figure 3. The melting points of PE-4 cannot be determined in concentrations of less than 30% from the thermograms. For simplicity, the assumption is made that the peaks in the thermograms are the end of melting, but this is not actually correct, according to Strella.⁹

In order to determine the true melting points of blend components from the thermogram, a melting point correction must be made for melting

TABLE I
Experimental Data for High and Low Density Polyethylene Blends

Calculated composition		DTA			
PE-3, wt.-%	PE-4, wt.-%	DTA peak areas, cm. ²		estimated composition	
		PE-3	PE-4	PE-3, wt.-%	PE-4, wt.-%
100	0	15.8	—	—	—
95	5	15.0	—	95	—
90	10	14.5	—	92	—
85	15	13.0	—	82	—
80	20	12.7	0.6	80	13
75	25	11.4	1.2	72	27
70	30	11.2	1.3	71	29
65	35	10.6	1.6	67	36
60	40	9.4	1.8	60	40
55	45	8.6	1.9	54	42
50	50	7.7	2.1	49	47
45	55	6.9	2.3	44	51
40	60	6.8	2.4	43	53
35	65	5.1	2.6	32	58
30	70	4.5	3.1	29	69
25	75	4.1	3.3	26	73
20	80	3.1	3.6	20	80
15	85	2.0	3.8	13	84
10	90	1.5	4.0	10	89
5	95	0.5	4.3	3	96
0	100	—	4.5	—	—

point depression. Figure 3 can be used to make the necessary melting point corrections for the blends examined. For example, the melting point correction for the components of the blend examined or another similar blend whose composition is unknown may be obtained by estimating visually or by the peak area method the weight concentration of the blend components from the thermogram and by the use of Figure 3.

If the true melting points of the components in the blend examined or another similar blend are known, then their densities can be determined from DTA melting point data and density data for low, intermediate, and high density polyethylenes as shown in Figure 4. These polyethylenes were selected because they are representative types and because they are free of additives.

Finally, the weight concentration of the components in the blend examined or another similar blend whose composition is unknown can be determined from density-weight per cent data as shown in Figure 5 and the density of the blend whose composition is unknown. The densities of these binary blends were determined with the use of density gradient columns and also calculated by the use of the general mixture law:

$$100/D = (C_1/D_1) + (C_2/D_2) + \dots \quad (1)$$

where C_1 , C_2 , etc. are the weight per cents of the components, and D_1 , D_2 , etc. are the corresponding densities. In ideal mixtures there is no association between molecules, and the density of the mixture follows the mixture law. To the extent that the blends in this experiment deviate from ideal mixtures, this deviation will appear in the total density D . The experimentally determined and the calculated densities of these blends agree well. Therefore, it is possible to determine by the melting point-density method the weight concentration of polyethylene components in the blend examined or another similar blend whose composition is unknown with the use of Figures 3, 4, and 5 or eq. (1).

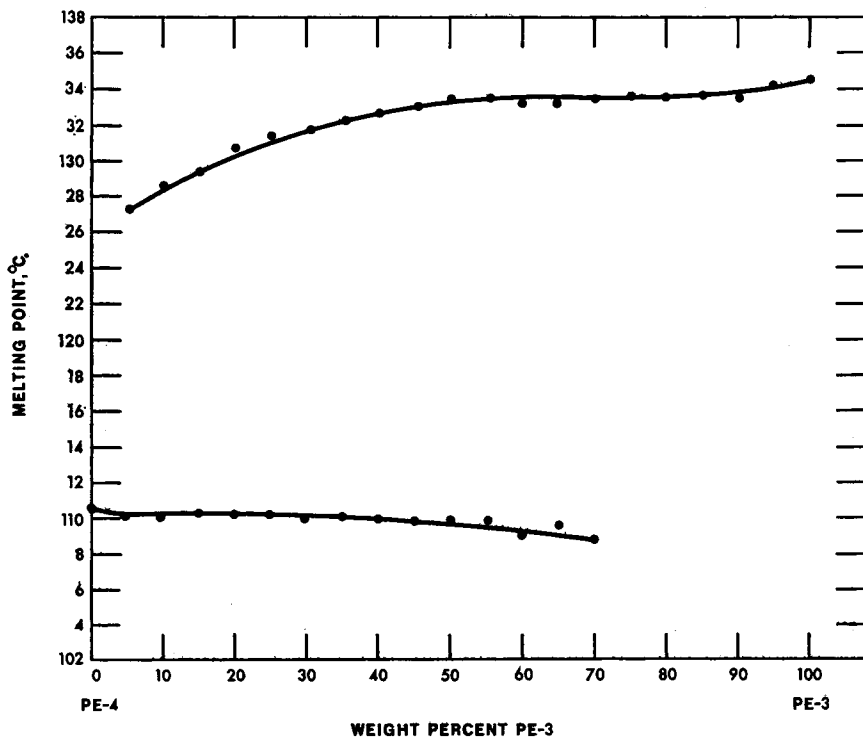


Fig. 3. Melting point-weight per cent data for PE-3 and PE-4.

Equal amounts by weight of PE-3 and PE-4 were solution-blended for 72 hr. instead of 30 min. with oxidation inhibitors. The purpose of this experiment was to determine if the two peaks produced by blending for 30 min. would change when given more time to blend. A thermogram of this sample nevertheless showed two peaks which did not change as the result of 72 hr. blending.

Blends of equal amounts by weight of PE-3 and PE-4 were prepared with the use of a roll mill, Banbury mill, and an extruder. A thermogram of each of these samples showed two peaks, and they were identical to those of solution-blended samples having the same composition.

Homopolymer blends of polyethylene have not been studied with the use of DTA until recently, because it was felt probably that the molecules of the components of a polyethylene blend were too similar in structure, and

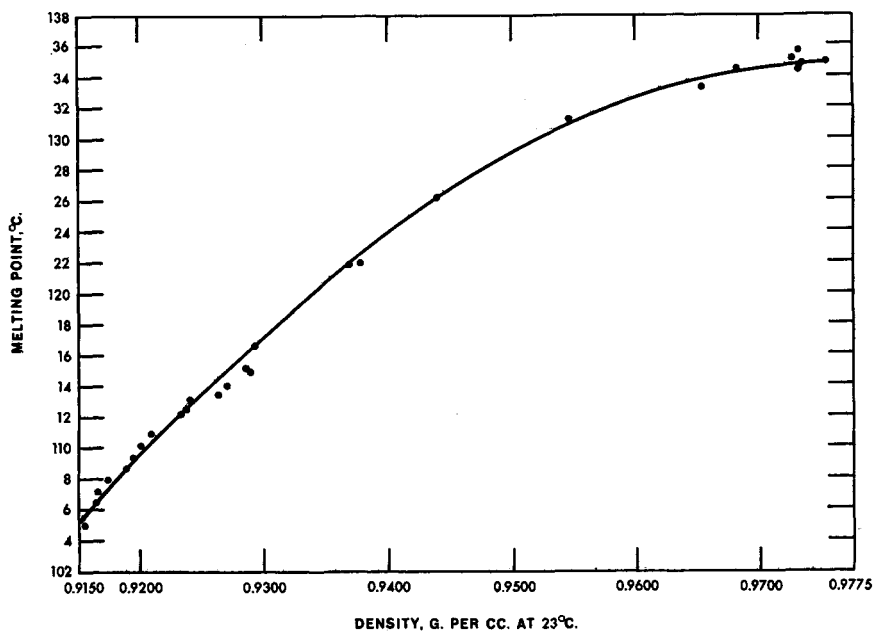


Fig. 4. Melting point-density data for low, intermediate, and high density polyethylenes.

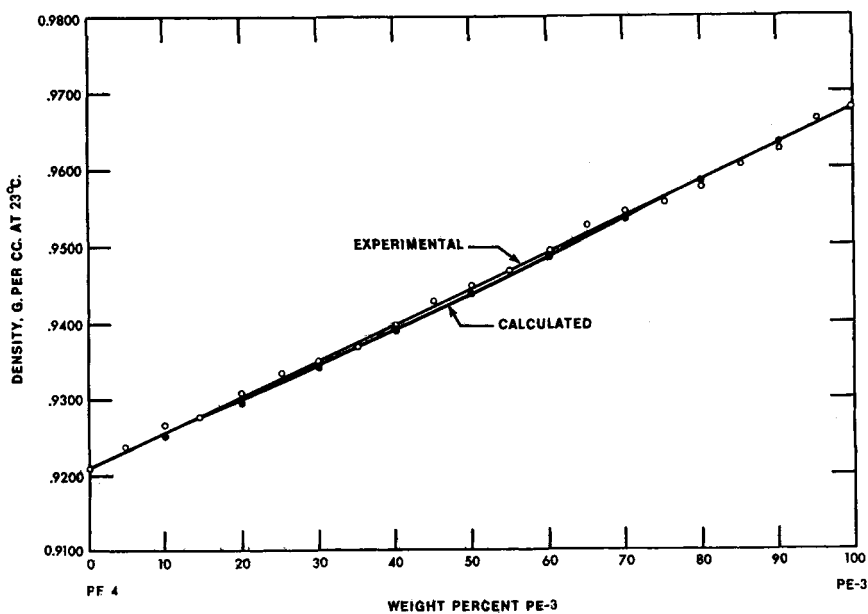


Fig. 5. Density-weight per cent data for PE-3 and PE-4 blends.

when melted and blended together, they would form a single broad melting material and give only one DTA peak.

Therefore, polymer fractions of a blend of equal amounts by weight of low and high density polyethylenes whose degrees of branching are 17.4 and 2.9 methyls per 1000 carbon atoms and melt indices are 6.5 and 2.7 g./10 min., respectively, were examined by DTA. The purpose of this experiment was to show that the molecules of the components of polyethylene blends are not too similar in structure, and this makes it possible to differentiate between the components of homopolymer blends. Thermograms of several of the fractions, except those of very low or high molecular weights, showed the presence of the two components. The fractionation process does not appear to have separated them. The fractions examined have very narrow molecular weight distributions, and so it does not appear that molecular weight, except for the very low or high molecular weights, has as great an effect on the segregation of the blend components as does branching. Thus, it appears in this particular case, as well as in the other cases reported in this paper, that the segregation of the blend components of polyethylene is the result of the components having sufficiently different degrees of branching.

Furthermore, Charlesby and Callaghan¹⁰ found, from their specific volume measurements on a low and high density polyethylene blend, that there is only a limited amount of crystalline interaction between the components of the polyethylene blend having widely differing degrees of branching.

The fact that DTA can be used to investigate polyethylene blends in the same way as other polymer blends has made it a valuable tool. A review of the literature has not revealed that the melting point-density method has ever been used to evaluate polyethylene blends, although the technique has been recognized by many workers in this field and has actually been used in some industrial control laboratories. The use of polyethylene blends is becoming more important in industry and, therefore, the DTA method should find considerable use.

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Résumé

On décrit l'application analytique de l'analyse thermique différentielle (DTA) pour l'identification et l'évaluation d'une série de mélanges de polyéthylène. Des données nouvelles sont présentées pour des mélanges d'homopolymères de polyéthylène de densités basse et intermédiaire et pour des polyéthylène de densités basse et élevée, dont les degrés de ramification diffèrent suffisamment. La concentration par pesée de chacun des composants cristallins dans le mélange est déterminée à partir des thermogrammes DTA par la méthode de la surface de pics et par la méthode de la densité au point de fusion. La densité des polyéthylènes et des mélanges de polyéthylènes est déterminée au moyen de colonnes à gradient de densité.

Zusammenfassung

Die analytische Anwendung der Differentialthermoanalyse (DTA) zur Identifizierung und Bewertung einer Anzahl von Polyäthylenmischungen wird beschrieben. Neue DTA-Daten werden für Homopolymermischungen aus Polyäthylen niedriger und mittlerer Dichte und niedriger und hoher Dichte, deren Verzweigungsgrade sich genügend unterscheiden, vorgelegt. Die Gewichtskonzentration jeder der kristallinen Komponenten in der Mischung wird aus DTA-Thermogrammen nach der Zackenflächenmethode und der Schmelzpunkt-Dichtemethode bestimmt. Die Dichte von Polyäthylenen und Polyäthylenmischungen wird mit Dichtegradientensäulen bestimmt.

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