

CHARACTERIZING BLENDS OF LINEAR LOW-DENSITY AND LOW-DENSITY POLYETHYLENE BY DSC

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A two-step isothermal annealing (TSIA) procedure is described that enables the endothermic peaks of low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE) and their blends, to be satisfactorily resolved during analysis by differential scanning calorimetry. A modified form of multistep isothermal annealing, the TSIA procedure produces a highly characteristic profile of the blend components by facilitating the segregation of the phases based on branch density. It is proposed that the TSIA procedure may have significant merit in the identification and quantification of the components in an unknown blend as well as increasing the sensitivity in analytical procedures aimed at blend component quantification.

Keywords: DSC, LDPE, LLDPE, polyethylene blends, thermal fractionation

Introduction

Certain types of linear low-density polyethylene (LLDPE) show two or more distinct melting temperatures when examined using differential scanning calorimetry (DSC) [1–4]. The presence of multiple peaks in DSC curves has been explained by the presence of polymer fractions that possess different degrees of short-chain branching (SCB) [2, 5–7]. The highest melting temperature observed in a typical DSC curve of LLDPE is due to the ethylene rich or relatively linear molecules crystallizing from the melt first, whilst the peaks occurring at lower temperatures are due to the more branched species, such as octene rich fractions, which crystallize at later stages [2, 7–9].

The crystallinity of LLDPE is dependent upon its degree of branching where a lower proportion of side chains produce a greater degree of crystallinity [2, 10]. The melting temperature of a crystallite of LLDPE is determined, in part, by the lamellar thickness and so the broad endotherm typically seen in DSC traces of LLDPE is attributable to the distribution of lamellar thicknesses [4, 10, 11]. Moreover, the temperature at any point on the DSC trace is indicative of the proportion of lamellae in the sample with that melting temperature. Thus, it is expected that the melting temperature of the polymer will be affected by the extent to which side chains are incorporated in its crystalline structure and the resultant crystalline imperfections caused by these [3, 6, 10, 12].

Blends of conventional LLDPE with LDPE have been widely reported in the literature [13–18] and it has been suggested that the addition of LLDPE significantly improves various properties of LDPE. For instance, Siegmann and Nir [14] showed that the addition of LLDPE to LDPE to form a binary blend enhances the crystallization rate and improves properties such as impact strength, optical clarity, environmental stress cracking resistance and resistance to thermal embrittlement. The elongational viscosity of blends of LLDPE/LDPE is shown to vary in proportion to the LDPE content and this is an important factor when modeling processes such as blow moulding and film blowing [19]. The toughness of LDPE during tubular extrusion blowing [15, 20] and its bubble stability [16] are also improved through the addition of LLDPE. Furthermore, the addition of LLDPE to LDPE can result in significant improvements in film qualities including toughness, mechanical properties and optical properties as well as increasing the melt strength [13].

The melting behaviour of LLDPE and its blends with LDPE has been widely studied [21, 22] and such blends have been found to be miscible in the melt and do not segregate into separate phases provided they are cooled quickly from the melt [23]. The slow cooling of molten blends of LLDPE/LDPE, however, can result in the formation of independent crystalline phases that can be associated with the two constituent polymers [13, 24]. In most cases the melting endotherms show two or more distinct melting peaks corresponding to constituent polymers [25]. It has been suggested that the

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blend is volume filled by LLDPE and that LDPE crystallizes separately within the crystalline domains of the LLDPE component [25]. Prasad [26] used endotherm peak height changes to identify blends of LDPE/LLDPE and found the melting temperature of LDPE varies with density and is usually in the range of 106 to 112°C for film grade resins. The DSC curve of LLDPE is characterized by a broad range of melting peaks with a lower melting peak around 106 to 110°C and a higher one in the range of 120 to 124°C [26]. In a blend with LDPE, the ratio of the two endothermic peak heights changes such that at a given mass percent of LDPE, the ratio depends on the type of comonomer in the LLDPE (e.g. but-1-ene, hex-1-ene, oct-1-ene, etc.) [26].

It has been found that LLDPE samples having similar densities and melt flow indices can show significant differences in their molecular structure, particularly in regard to the distribution of SCB [11, 27–29]. The technique of DSC is particularly useful for identifying differences in the SCB content that exists between LLDPE samples since it enables the polymer to be fractionated on this basis [9, 12, 17, 30–32]. A limitation of the conventional DSC technique, however, is that the standard cooling procedure (i.e. from 180°C to room temperature at the rate of 10°C min⁻¹) yields curves that may have insufficient detail to enable the identification of an unknown LLDPE material [33]. Furthermore, curves produced using the standard DSC cooling procedure may demonstrate poor resolution of the LDPE and LLDPE components in a given blend [34, 35]. Any accurate determination of the areas under the peaks of the curve and the subsequent quantitative analysis of the components is therefore made difficult. One method of overcoming this problem is to measure the total area under the set of unresolved peaks and to obtain the individual areas by assuming a certain distribution curve for each component [32, 36]. Temperature rising elution fractionation (TREF) is often employed to fractionate polyethylenes and polyethylene blends based on the level of SCB of the polymer chains, however this technique can be time-consuming and relatively expensive [37–39]. Successive self-nucleation and annealing (SSA) is another technique that is widely used to promote molecular seg-

regation in copolymers and blends [5, 8–11, 37, 40, 41] whereby components in LLDPE and LDPE/LLDPE blends are segregated based on branch distribution and branch density [4, 39, 42, 43]. In a typical SSA procedure, however, it can take up to 20 h to perform the annealing step [39].

In this paper the use of DSC in the characterization of blends of LLDPE and LDPE is investigated. In particular, a relatively quick and simplified form of multi-step crystallization–fractionation, namely a two-step isothermal annealing (TSIA) procedure, is described which enables the LLDPE and LDPE exothermic peaks to be resolved satisfactorily and which produces a highly characteristic profile of the LLDPE component of the blend. It is proposed that the technique has significant merit in the quick identification and quantification of the components in an unknown blend.

Experimental

Materials and sample preparation

One LDPE resin and five LLDPE resins were used in the blend systems studied. The LLDPE resins were produced using conventional Ziegler–Natta catalysts. The characteristics of the resins are given in Table 1. The density and the melt flow index (MFI) of each resin were determined in accordance with ASTM method D-1505 and ASTM method D-1238 (Condition E), respectively. A mass of 2.16 kg was used in the determination of the MFI values. Blends of LLDPE1 through LLDPE5 with LDPE were prepared by melt mixing the polymers in a Brabender Plasticorder mixer at a temperature of 160°C for 5 min using a mixing speed of 60 rpm.

Plaques (400 µm thickness) of the blends were prepared by compression moulding at 180°C and 150 MPa and were immediately quench-cooled by immersion in cold water. Samples (ca. 5 mg) were punched from the plaques and sealed in aluminium pans in preparation for heat treatment and/or thermal analysis. Prior to the determination of its crystalline melting temperature, each sample was annealed

Table 1 Characteristics of the LDPE and LLDPE resins

Resin	Co-monomer	MFI/deg min ⁻¹	T_m /°C	Density/g cm ⁻³	T_1 /°C*	T_2 /°C*
LDPE1**		0.7	111.4	0.921	–	–
LLDPE1	butene (C4)	1.0	121.3	0.918	117	112
LLDPE2	hexene (C6)	0.8	126.2	0.926	121	116
LLDPE3	hexene (C6)	0.8	125.5	0.921	119	113
LLDPE4	hexene (C6)	0.9	123.8	0.918	122	116
LLDPE5	octene (C8)	1.0	120.5	0.920	119	113

* T_1 and T_2 are the temperatures used for the TSIA treatment;

**in each case, the 100 mass% LDPE reference materials were subjected to the same thermal treatment as the blended materials.

for 1 min at 180°C and cooled to room temperature at 10°C min⁻¹ on a Mettler FP2 hot stage.

Measurement of thermal properties

Standard thermal analysis

Curves of the polymer blends were obtained using DSC on a Perkin-Elmer DSC-7 instrument. Nitrogen was used as the purge gas and an empty aluminium pan was used as a reference. Temperature calibration of the instrument was performed using indium as a standard (*m.p.* 156.6°C). During each run the samples were heated from 50 to 150°C at the rate of 10°C min⁻¹. The crystalline melting temperature of each pure polymer was determined from the temperature axis on its curve. These temperatures (T_1 and T_2) were used in programming the optimum TSIA processes for the blends on the basis that maximum segregation and crystallization would occur at these temperatures.

Two-step isothermal annealing

The optimized TSIA process for blends of LLDPE1 through LLDPE5 with LDPE involved heating each blend to 180°C on the hot stage, maintaining this temperature for approximately 1 min, and then cooling at the rate of 2°C min⁻¹ to the temperature of the first crystallization minimum (T_1). The sample was held at this temperature for 2 h, after which it was cooled at the rate of 2°C min⁻¹ to the second minimum (T_2) where it was held for 4 h. The sample was then cooled to 20°C at the rate of 10°C min⁻¹.

Results and discussion

Thermal analysis before and after TSIA treatment

Figure 1 shows DSC curves for blends of ethyl-branched (C4 butene comonomer) LLDPE1 with LDPE over the composition range of 0, 5, 25, 30, 60 and 100 mass% of LLDPE1, prior to the TSIA treatment. For the 100 mass% LDPE and the blend containing 5 mass% LLDPE1, each DSC trace is comprised of a single, broad peak with a melting temperature of ca. 110°C. The DSC traces of the remaining blends comprise two main peaks with the peak at the lower melting temperature due to the LDPE component whilst the peak at the higher melting temperature is associated with LLDPE1. Blends containing 25 and 30 mass% show the presence of a shoulder on the LLDPE1 peak that suggests the presence of a third crystalline phase [1, 35, 44]. The position of the LLDPE peak on the temperature axis increases with increasing LLDPE content in the blend whereas the position of the LDPE peak re-

mains relatively constant for each blend. This increase in the peak melting temperature of LLDPE1 may be due to increased disruption of the LLDPE crystalline structure caused by the presence of the LDPE component [17, 25]. The peak melting temperature for 100 mass% LLDPE1 was found to be 121.5°C which is in good agreement with the literature value of 121°C obtained by Haghghat and Birley [35].

DSC curves for blends of LLDPE1 with LDPE after TSIA treatment and over the same composition range as in Fig. 1 are shown in Fig. 2. The curve of the 100 mass% LDPE is comprised of a single peak, as expected, with a peak melting temperature of ca. 110°C while the blend containing 5 mass% LLDPE1 shows an additional small peak. The curves of the remaining

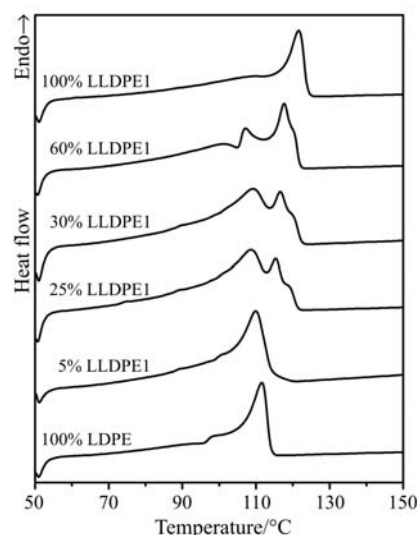


Fig. 1 DSC curves of LDPE, LLDPE1 and LDPE/LLDPE1 blends prior to the TSIA procedure

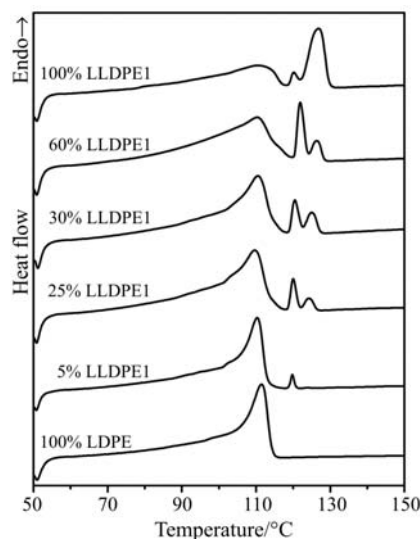


Fig. 2 DSC curves of LDPE, LLDPE1 and LDPE/LLDPE1 blends after the TSIA procedure

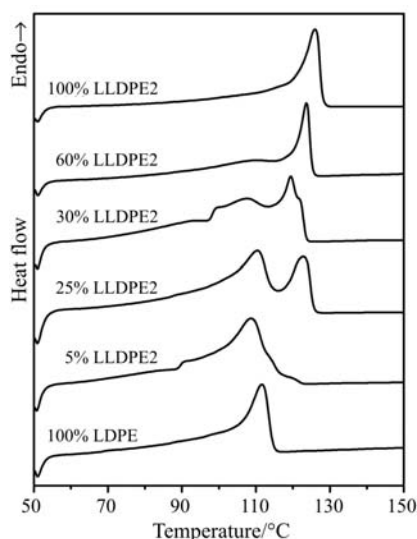


Fig. 3 DSC curves of LDPE, LLDPE2 and LDPE/LLDPE2 blends prior to the TSIA procedure

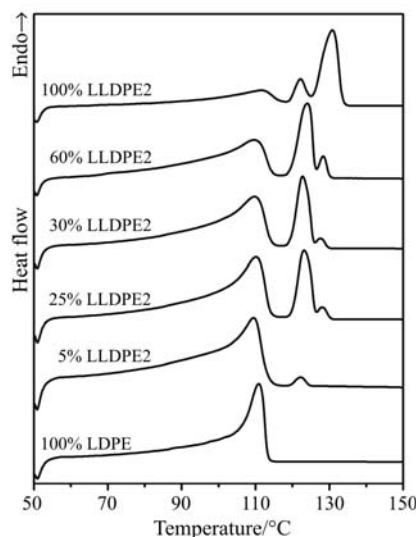


Fig. 4 DSC curves of LDPE, LLDPE2 and LDPE/LLDPE2 blends after the TSIA procedure

blends and the 100 mass% LLDPE1 are each comprised of three main peaks. In each case, the peaks associated with the LDPE and LLDPE1 components are better resolved than the corresponding peaks in Fig. 1. The higher melting peak in Fig. 2 occurs at ca. 127°C which is about 5°C higher than the peak melting temperature of 100 mass% LLDPE1 prior to the TSIA treatment. This temperature is also ca. 10°C less than a typical unbranched HDPE suggesting that the TSIA treatment results in the segregation of a phase that has a lower branch density than the corresponding material in Fig. 1 that produced the highest melting range peak [3, 11].

DSC curves for blends of butyl-branched (C6 hexene comonomer) LLDPE2 with LDPE over the composition range of 0, 5, 25, 30, 60 and

100 mass% of LLDPE2, prior to the TSIA treatment, are shown in Fig. 3. The curves for the blends containing 25 and 30 mass% LLDPE2 are comprised of two peaks whereas each of the other curves is comprised of a single peak. Figure 4 shows the DSC curves for the same blends after the TSIA treatment at the same compositions that are shown in Fig. 3. The curve of the 100 mass% LDPE is comprised of a single peak whilst that of the blend containing 5 mass% LLDPE2 is comprised of two peaks. The curves of the remaining blends and the 100 mass% LLDPE2 are also comprised of three peaks. The lower melting peak corresponds to the 100 mass% LDPE component with a relatively consistent peak temperature of ca. 110°C. The second melting peak corresponds to the 100 mass% LLDPE2 component with a peak temperature ranging between 122 and 124°C. The higher melting peak ranges between 128 and 131°C, which is ca. 5°C higher than that of the 100 mass% LLDPE2 after standard annealing. This may be attributed to an enhanced crystalline perfection at the lamellar surface resulting from a lower branch density [2, 8, 11]. Curves before and after the TSIA procedure for the remaining C6 LLDPE3 and C6 LLDPE4 blends (data not shown) behave similarly to the blend system shown in Figs 3 and 4.

Figure 5 shows DSC curves for blends of hexyl-branched (C8 octene comonomer) LLDPE5 with LDPE over the composition range of 0, 5, 25, 30, 60 and 100 mass% of LLDPE5, prior to the TSIA treatment. Other than the 100 mass% LDPE and the blend containing 5 mass% LLDPE5, the curve of each blend is broad and is comprised of two or more peaks that are poorly resolved. The curves of the same blends after the TSIA treatment are shown in Fig. 6. It appears that the LDPE component is effectively segregated from the LLDPE component as a result of the TSIA process. The peak melting temperature for 100 mass% LLDPE5 was found to be 121.8°C before TSIA, and 122.6 and 124.6°C after TSIA, which is in good agreement with the literature value of 124.3°C obtained by Starck [4].

Melting temperatures

The peak melting temperature as a function of composition for the C6 LLDPE2 blends before and after the TSIA treatment is shown in Fig. 7. Similar plots for the remaining blends were obtained (data not shown). In all cases, only two melting peaks are evident before the TSIA treatment, whereas three peaks are observed after the TSIA treatment. This suggests that the TSIA procedure can be used to deconvolute the peaks of LDPE and LLDPE in blends where there is a significant peak overlap or a single peak is present. The trend

in the peak melting temperatures for the C6 LLDPE blends reflects the trend in the densities of these resins with the resin of highest density (and concomitantly the highest crystallinity) having the highest peak melting temperature in the composition range (Table 1).

The peak melting temperatures of the C8 LLDPE and C4 LLDPE resins and blends are consistently lower than those of the C6 LLDPE resins and blends studied (Table 1). These observations suggest that the peak melting temperature of LLDPE is a maximum when the polymer contains butyl branching which is consistent with the notion that the C6 LLDPE blends contain thicker lamellae [8, 32, 40].

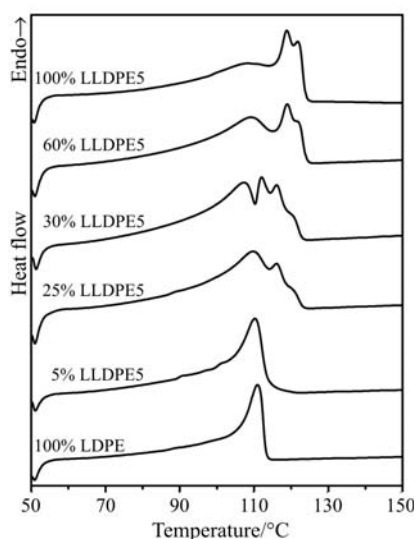


Fig. 5 DSC curves of LDPE, LLDPE5 and LDPE/LLDPE5 blends prior to the TSIA procedure

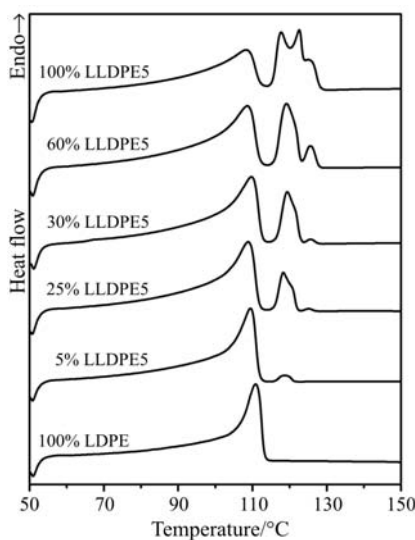


Fig. 6 DSC curves of LDPE, LLDPE5 and LDPE/LLDPE5 blends after the TSIA procedure

Integrated area analysis

Figure 8 shows the integrated area of the LLDPE component vs. blend composition for the C4 LLDPE1 blends before and after the TSIA treatment. Plots of the integrated area vs. blend composition before and after the TSIA treatment for the C6 LLDPE2 and C8 LLDPE5 blends are shown in Figs 9 and 10, respectively. Similar plots were obtained for the remaining C6 LLDPE3 and C6 LLDPE4 blends (data not shown).

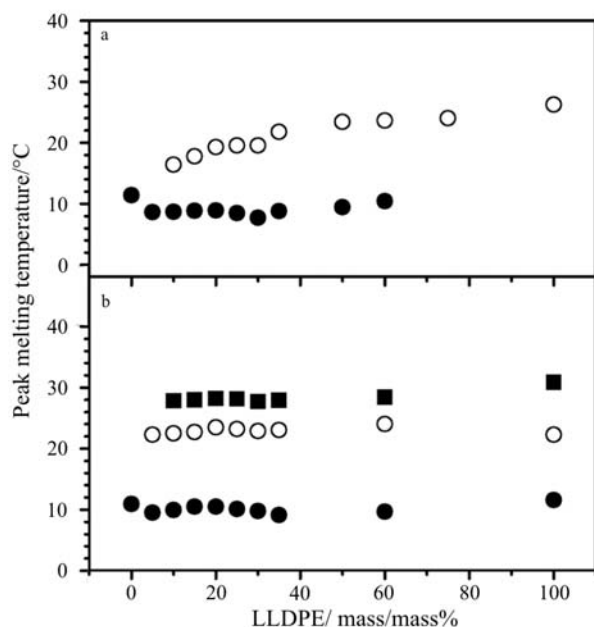


Fig. 7 Peak melting temperature vs. blend composition for the LDPE/LLDPE2 blends: a – before the TSIA treatment and b – after the TSIA treatment; ● – LDPE, ○ – LLDPE peak 1 and ■ – LLDPE peak 2

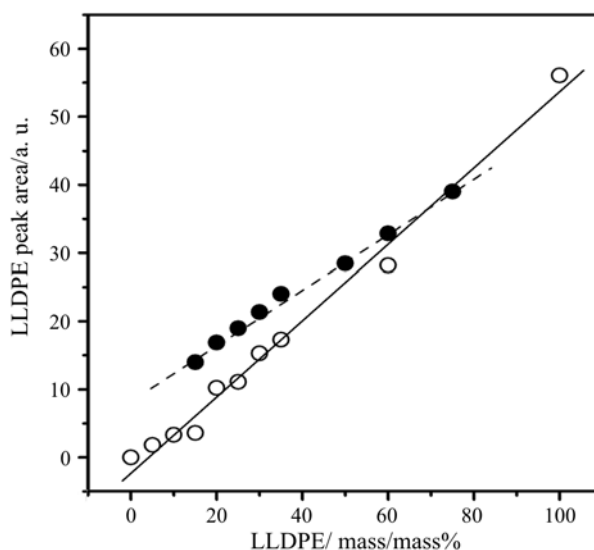


Fig. 8 Integrated area under the LLDPE peak vs. blend composition for the LDPE/LLDPE1 blends: ● – before the TSIA treatment and ○ – after the TSIA treatment

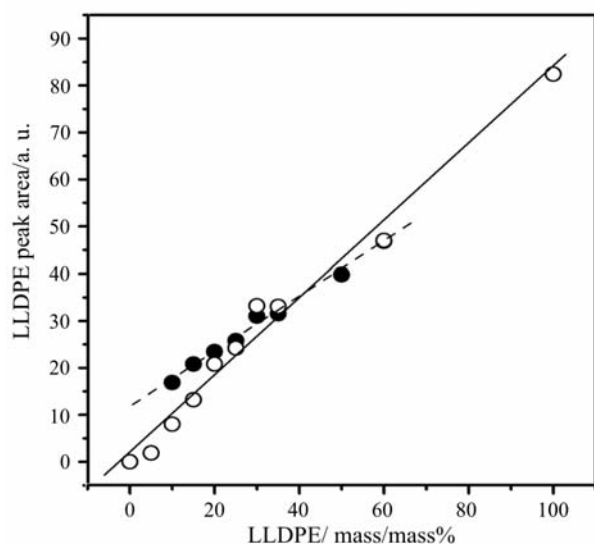


Fig. 9 Integrated area under the LLDPE peak vs. blend composition for the LDPE/LLDPE2 blends: ● – before the TSIA treatment and ○ – after the TSIA treatment

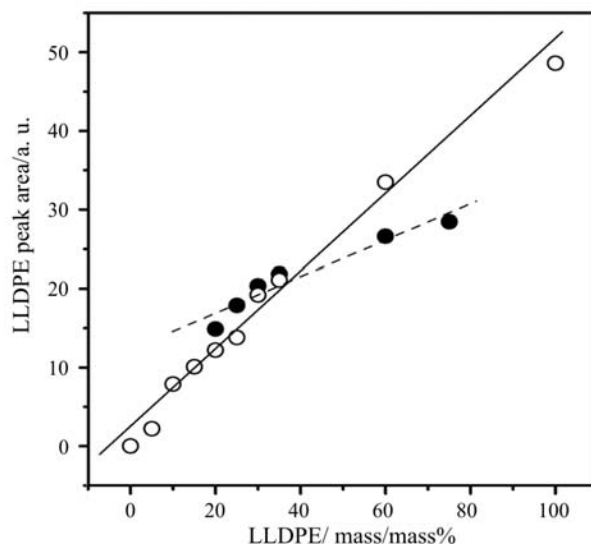


Fig. 10 Integrated area under the LLDPE peak vs. blend composition for the LDPE/LLDPE5 blends: ● – before the TSIA treatment and ○ – after the TSIA treatment

Table 2 Linear regression data for peak area vs. blend composition graphs before and after TSIA treatment

Blend	Before TSIA treatment*				After TSIA treatment*			
	c	m	$m_{\text{err}}/\%$	r^2	c	m	$m_{\text{err}}/\%$	r^2
LDPE1/LLDPE1	8.81	0.40	3	0.995	-2.12	0.56	4	0.988
LDPE1/LLDPE2	11.83	0.58	4	0.992	1.90	0.82	5	0.981
LDPE1/LLDPE3	9.21	0.56	4	0.991	6.36	0.77	5	0.978
LDPE1/LLDPE4	8.88	0.48	6	0.977	1.37	0.57	4	0.983
LDPE1/LLDPE5	12.36	0.23	14	0.930	2.20	0.49	4	0.984

* c is the intercept, m is the gradient, m_{err} is the error associated with gradient, and r^2 is the correlation coefficient.

Linear regression analyses were performed for all blend systems. The gradients, gradient errors, intercepts and correlation coefficients are reported in Table 2. Generally good linear relationships were obtained for each series of blends both before and after TSIA as revealed by the regression data obtained from these analyses.

It is evident from Figs 8 to 10 and the data in Table 2 that the TSIA procedure has the effect of increasing the gradient of the plot in each case and thereby increases the analytical sensitivity if such a plot were to be used as a calibration for an analytical method to determine the composition of a blend. The sensitivity, as reflected by the gradients, is increased by a factor of between 18 and 114%. Furthermore, it is interesting to note that the intercepts are reduced by a factor between 30 and 124% as a result of TSIA. This confirms that the thermal treatment is effective at segregating the components of the blend and further suggests that a time of annealing between 2 and 4 h is sufficient to obtain satisfactory resolution. This result contrasts with the longer times of annealing suggested by other workers [5, 10, 37, 39, 45].

Conclusions

A modified form of multistep isothermal annealing, the TSIA procedure, appears to segregate effectively the LDPE component from the LLDPE component in all blends regardless of the comonomer type with the LLDPE component possessing a higher peak melting temperature after the TSIA treatment presumably due to a decrease in branch density. Furthermore, the TSIA procedure results in the segregation of two or more phases of LLDPE of varying branch density. It has also been shown that the segregation method provides sufficient resolution to suggest that it may form a useful part of a quantitative analytical technique for the characterization of LDPE/LLDPE blends. In particular, this method may have applicability to blends containing low concentrations of the minor component (e.g. 5–10 mass%) admixed polymer where conventional treatment prior to DSC analysis often produces curves that lack resolution.

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