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Study of blends based on recycled polyethylene wastes

Part II *Thermal behaviour and degree of molecular mixing*

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A calorimetric study of binary blends based on recycled, low and high density polyethylene, wastes is presented. The physical properties of these blends were reported previously [1]. A comparison between the first and second differential scanning calorimetry (DSC) traces of blended samples reveals the presence of an intermediate endothermic peak which can be associated to the melting of crystals from mixed molecular species of the single components. Further thermal treatments after the second DSC run at temperatures just below and above the intermediate peak for two compositions ($\phi_B = 10$ and 30% of high density component) highlight the dependence of the various crystal populations upon annealing. A quantitative analysis of a series of consecutive thermograms for each sample has allowed us an estimation of the relative amount of material associated to the three main endothermic peaks.

1. Introduction

In the first part of this series the dependence of physical properties upon composition of binary blends based on recycled polyethylene (PE) wastes was presented [1]. These materials are gaining recently in importance as new industrial products in the packaging industry [2, 3]. While some of the properties (density, fusion enthalpy) were shown to vary linearly with composition, others (microhardness and yield stress) deviated from the additivity of the single components [1]. The deviation of the additivity behaviour of microhardness as a function of composition was explained by a chain rearrangement which occurs during the blending process. This molecular rearrangement results in a new lamellar distribution, as revealed in differential scanning calorimetry (DSC) thermograms [1]. It is well known that endothermic peaks are related to the melting of crystalline lamellae [4]. Both, the melting temperature and the shape of the peak offer information about the crystal size and the crystal size distribution, respectively [4]. The crystal perfection, which is related to chain linearity, affects notably the melting temperature [5].

In the case of polymer binary blends their thermograms become rather complex, depending on the compatibility degree of the components [6, 7]. The compatibility of two components, at molecular level, results in a thermogram showing just a single endothermic peak. On the contrary, the incompatibility of the two molecular species leads to a thermogram showing the corresponding two peaks of the isolated components. In the case of PE blends with two different grades, multiple peak thermograms have been observed [8, 9].

In the present paper (the second of this series) a detailed calorimetric study of blends with different compositions is presented. The aim of this work is to study the nature and thermal behaviour of the microstructure developed upon blending low and high density recycled PE grades by means of differential scanning calorimetry.

2. Experimental procedure

2.1. Materials

In Table I the molecular weight, the density, the melting temperature and the fusion enthalpy of the blend components are shown. Samples A1 and A2 are two low density PE components and sample B is the higher density one. Experimental details about the blend preparation of recycled PE wastes and the properties of their individual components were described in Part I. Films 0.3 mm thick were processed by compression moulding of the milled material at 140 °C for 3 min.

2.2. Techniques

A Perkin-Elmer DSC-4 calorimeter provided with a cooling system was used to obtain the DSC traces in

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TABLE I Number-average molecular weight M_n, density ρ, melting temperature T_m and fusion enthalpy δH for the individual recycled polyethylene grades used in the preparation of the two blends

Sample	$M_n \times 10^3$	ρ (g cm^{-3})	T_m (°C)	δH (cal g^{-1})
A1	15.5	0.932	110.1	28.0
A2	22.7	0.925	110.0	25.1
B	38.6	0.954	131.0	45.9

the 10–155 °C range. A heating rate of 10 K min^{-1} followed by a rapid cooling (320 K min^{-1}) to 10 °C were used. A second DSC run was performed in all samples.

In case of some selected samples, an additional thermal treatment at a given temperature for 10 min, after the second DSC run, was performed using a Mettler hot stage under N_2 flow. Thereafter, the sample was quenched on a metal plate and a new DSC run was obtained.

The thermal treatment was as follows:

(a) The samples were brought to a temperature T_1 corresponding to the minimum observed below the intermediate peak (peak 2) in the second DSC run.
(b) A third DSC run was then performed.
(c) The sample was brought to a temperature T_2 corresponding to the minimum observed above peak 2 after the third DSC run (the choice of temperatures T_1 and T_2 is illustrated in Fig. 3(a)).
(d) A fourth DSC run was performed and, immediately after, the fifth DSC run was carried out.

The endothermic areas associated to the three main peaks were measured as described in the Appendix.

3. Results

3.1. Influence of blend composition

Fig. 1 illustrates the first (bottom) and second (top) DSC traces of three A1/B samples with different compositions. Specially, the second DSC traces show more clearly the presence of three endothermic peaks (which can be related to the melting of three different populations of lamellae). DSC traces from samples with $\phi_B = 50\%$ (not shown in Fig. 1) still show three endothermic peaks while for higher ϕ_B values the intermediate peak is not observed anymore. The lower temperature peak, which can be associated to the low density (A1) component (peak 1), is very broad in comparison to the intermediate and high temperature peaks. The latter two peaks are related to the "new mixed" material (peak 2) and to the high density (B) component (peak 3), respectively. A similar behaviour is observed in the case of A2/B samples. Fig. 2 shows the plot of the melting temperature measured at the peak maximum for both first and second DSC traces of A1/B samples as a function of composition.

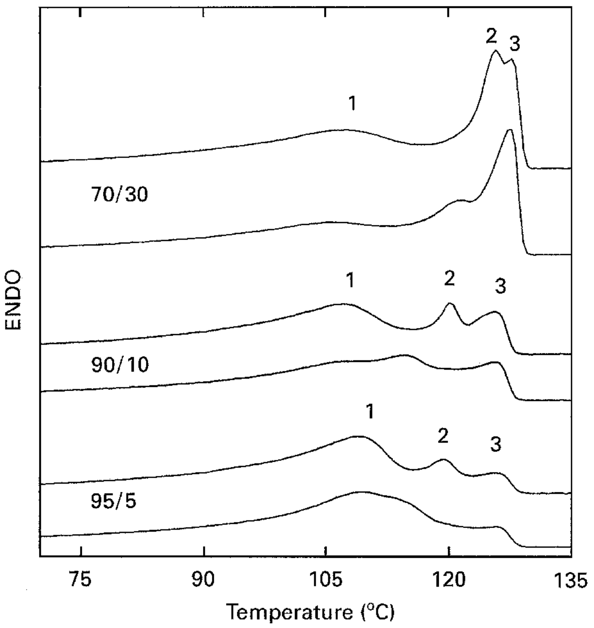

Figure 1 First (bottom) and second (top) DSC traces of samples A1/B with different compositions. The position of the three main endothermic peaks (1–3) is indicated.

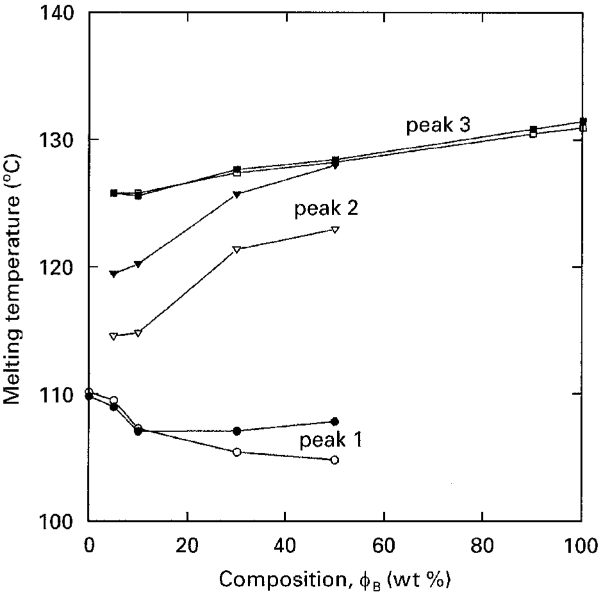

Figure 2 Variations of the melting peak temperatures of samples A1/B with composition. Open and filled symbols refer to data from the first and second DSC runs, respectively.

For the first DSC traces peak 3 increases linearly with ϕ_B while peak 1 decreases with ϕ_B showing a large decrease rate for low ϕ_B values (5–10%) and then a levelling off with composition. For the second DSC traces, very similar values are observed for peak 3. Peak 1 shows similar temperature values for $\phi_B \leq 10\%$ while for $\phi_B \geq 30$ the melting temperature is higher than that observed for the first DSC trace.

As far as peak 2 is concerned its position increases with composition as shown in Fig. 2. Peak 2 appears in the first run about 4 °C above the position of peak 1 for $\phi_B = 5\%$ and it shifts drastically towards higher temperatures with increasing ϕ_B. At $\phi_B = 50\%$ peak 2 appears as a shoulder of peak 3 and it is not anymore resolved for higher ϕ_B values. After a second DSC run a shift of about 5 °C is observed in the position of peak 2 for all the samples with ϕ_B up to 50% (see Fig. 2). At $\phi_B \geq 50\%$ peak 2 merges with peak 3.

3.2. Variation of DSC traces upon thermal treatments

In order to investigate the nature of the intermediate peak two thermal treatments were carried out, particularly on samples with composition $\phi_B = 10$ and 30%. These samples were previously used to obtain both the first and second DSC runs. Two specific temperatures T_1 and T_2 just below and above the intermediate peak were used (see experimental part).

Fig. 3(a) shows the five consecutive DSC runs (from top to bottom) for the sample A1/B with $\phi_B = 10\%$. After the third and fourth runs a large variation in the DSC curves upon the thermal treatment of the samples is evident. However, it is noteworthy that the fifth DSC is similar to the second one. This indicates the reversibility, and consequently, the capability of the lamellar distribution to recover the original structure of run 2 after undergoing the two thermal treatments and DSC runs. The third DSC run shows a deep and large valley between the first peak and the other two peaks which appear now closer to each other. Furthermore, in this DSC curve peak 2 becomes dominant in relation with peak 3.

During the second thermal treatment at T_2 the intermediate size lamellae (peak 2) melt as evidenced by the fourth DSC trace. In this DSC trace, peak 3 appears now isolated and quite shifted towards higher temperatures because of annealing of the thicker (or less defective) lamellae [2]. A fifth DSC run

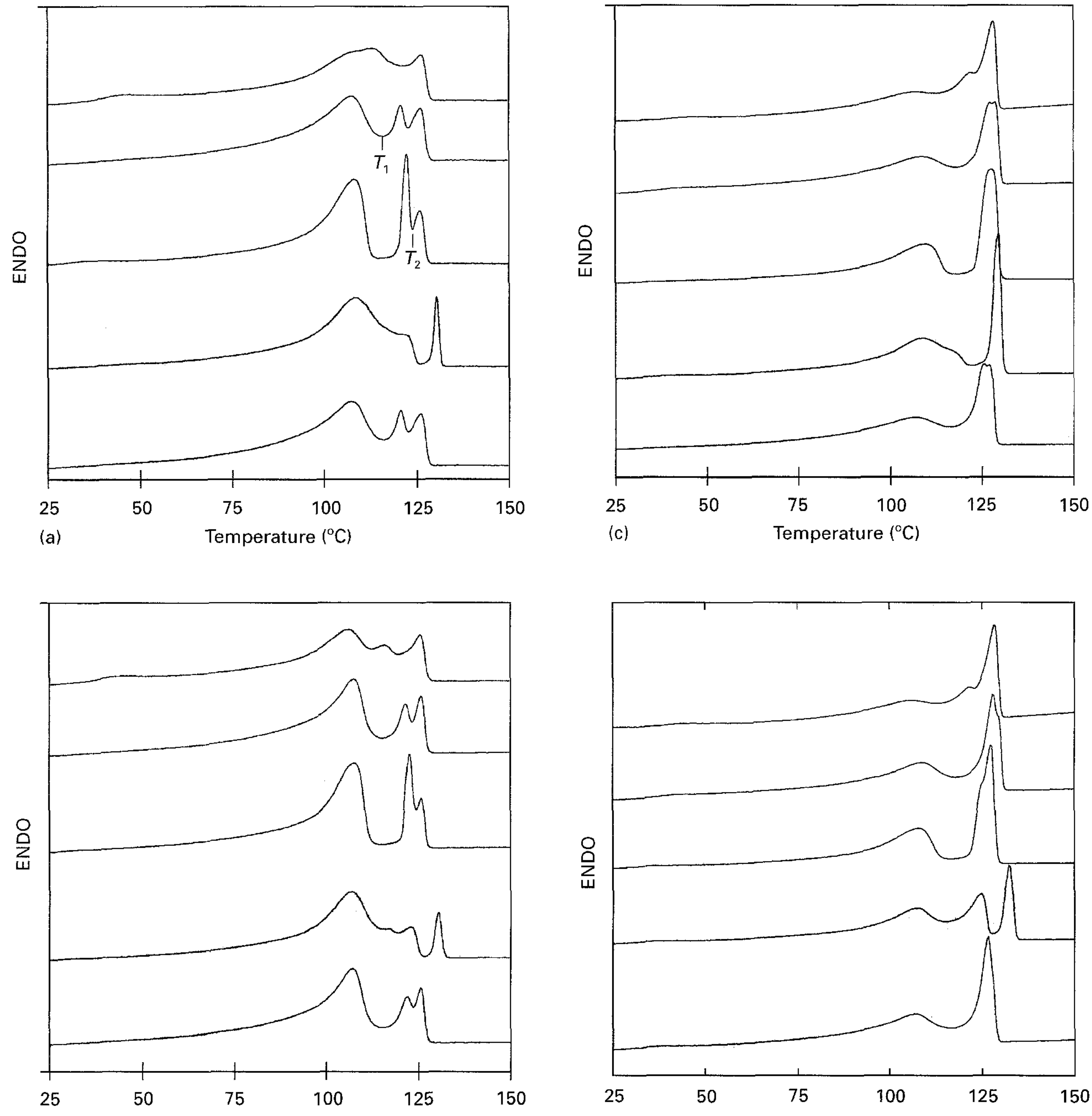

Figure 3 Consecutive DSC traces (from top to bottom) for samples: (a) A1/B (90/10); (b) A2/B (90/10); (c) A1/B (70/30); (d) A2/B (70/30). The annealing temperatures T_1 and T_2 are indicated in (a).

(bottom of Fig. 3(a)) reveals a great similarity with the second DSC trace. This indicates the occurrence of a similar lamellar distribution for this sample after the corresponding DSC runs and, consequently, a clear reversibility and recovery of the microstructure developed upon blending of PE components. A very similar behaviour was also observed in the case of sample A2/B with the same composition (Fig. 3(b)).

For A1/B and A2/B samples with $\phi_B = 30\%$, similar experiments were also carried out and the corresponding DSC traces are shown in Fig. 3(c) and (d), respectively. For this composition, the peak 2 appears relatively close to the peak 3. Therefore, special attention was paid to carry out the second treatment of the sample in the hot stage at the convenient temperature, T_2 i.e. temperature in between peaks 2 and 3. The fourth DSC trace in Fig. 3(c) and (d) shows an isolated high temperature peak (peak 3) which resembles the corresponding DSC trace of Fig. 3(a) and (b). Finally, the last DSC trace is also very similar to the second one for both blends A2/B 90/10 and 70/30 (Fig. 3(b) and (d)), as it was also observed for the blends A1/B (Fig. 3(a) and (c)).

3.3. Relative amount of the "new mixed" material

We have tentatively estimated the relative amount of material which can be associated to the three lamellae populations as revealed by DSC traces. To do this we carried out a measurement of the three main endothermic areas in which each DSC trace could be resolved (see Appendix).

As shown previously [1] the fraction of material associated with an endothermic peak (i) can be calculated using the expression

$$\phi_i(\%) = \frac{S_i}{S}\frac{\delta H_{\text{sample}}}{\delta H_i} \times 100 \qquad (1)$$

where S is the total area of thermogram and S_i is the area of peak i measured from a thermogram hard copy (a planimeter was used). δH_{sample} is the fusion enthalpy measured for each DSC run and δH_i is the fusion enthalpy of each individual component (see Table I). In the case of peak 2 a value of 46 kcal g^{-1}, as for peak 3, was used for calculations.

The quantitative results so obtained for the blends A1/B and A2/B with ϕ_B values of 10 and 30% are shown in Table II. We can see that the sum of the calculated fractions of material ϕ_1, ϕ_2 and ϕ_3 is about 100 for all samples, as expected.

4. Discussion

The influence of the processing conditions on the physical properties of polymer materials is well known [10]. The results shown in Figs 1 and 2 are good

TABLE II Fusion enthalpy δH, total area (S) and individual areas S_2 and S_3, measured from thermograms and the fraction of molten material calculated from Equation 1 for the consecutive DSC runs of the blends A1/B and A2/B

DSC run	δH (cal g^{-1})	S (cm^2)	S_3 (cm^2)	$S_2 + S_3$ (cm^2)	ϕ_1%	ϕ_{2+3}%	ϕ_3%
A1/B (90/10)							
1	29.0	10.2	1.9	–	84.2	–	11.7
2	29.3	10.6	1.4	2.6	78.8	15.6	8.4
3	28.7	10.4	0.8	2.3	79.8	13.8	4.8
4	28.0	10.4	0.5	–	95.3^a	–	3.0
5	29.4	10.5	1.5	2.5	80.1	15.2	8.5
A1/B (70/30)							
1	33.0	10.3	3.9	5.1	73.2	35.5	27.1
2	34.6	10.8	–	3.7	82.6	26.0	–
3	32.9	10.6	–	3.8	76.6	25.7	–
4	33.4	10.4	2.9	–	88.1^a	–	20.0
5	33.5	10.4	–	3.9	76.0	27.3	–
A2/B (90/10)							
1	27.9	8.5	1.1	2.0	85.4	14.1	7.9
2	27.5	8.5	0.8	1.5	90.3	10.7	5.4
3	26.6	8.5	–	1.5	87.3	10.3	–
4	26.0	8.4	0.5	1.6	82.4	10.9	3.4
5	27.3	8.7	0.8	1.6	89.7	10.5	5.1
A2/B (70/30)							
1	31.0	10.0	3.6	4.8	64.5	32.8	24.3
2	32.0	10.5	–	3.5	85.1	23.3	–
3	31.5	10.6	–	3.9	79.1	25.4	–
4	31.4	10.6	1.6	4.5	72.3	29.0	10.3
5	31.1	10.1	–	3.6	80.4	23.9	–

^{a}Value for ϕ_{1+2}.

examples of the influence of film processing on the thermal properties of the blends. One also sees that the thermal history induced through processing is lost after the first DSC run. During preparation of the films by compression moulding from the melt, the material is subjected to stresses. These are partially released during storage of the film and are totally released upon melting. A second DSC run of the film sample reveals the appearance of a new microstructure of the blended material.

The linear increase of peak 3 with ϕ_B (Fig. 2) has been also observed for other polyethylene blends [8]. This has been attributed to a plasticizing effect of the low density component [11].

From the results of Table II it is apparent that a different chain reorganization upon blending, which depends on ϕ_B, is taking place. For the A1/B (90/10) blend the component B seems to retain its character because the material fraction given by ϕ_{2+3} is larger than 10%. On the contrary, for $\phi_B = 30\%$, particularly after the first run, the values of ϕ_{2+3} are smaller than those expected. This would indicate (for $\phi_B = 30\%$) a net exchange of material from the B component towards the A component. For $\phi_B = 10\%$ it seems that the intermediate melting peak has its origin in a contribution of material from both A and B components.

After the first DSC run the highest temperature peak (peak 3) is reduced considerably as shown by the low ϕ_3 values obtained. This would suggest a segregation of material in the B component. Thus, in the process of blending in the molten state, the more defective chains from the B component will probably mix with the less defective ones from A component originating material, which yields the intermediate endothermic peak.

In the case of A1/B blends, after the second thermal treatment at T_2 (fourth DSC run), the intermediate peak appears overlapped with peak 1. Thus, an accurate separation is difficult to make. Therefore, the contribution of peak 2 appears together with that of peak 1 in the fourth run of Table II, i.e. ϕ_1 is actually ϕ_{1+2}.

A comparison of the results obtained for the fourth run of A1/B and A2/B samples with $\phi_B = 30\%$ reveals a large difference between the ϕ_3 values (see data for both blends in Table II). However, this difference could be attributed to a small variation in the selected T_2 value used for the second thermal treatment. The great overlapping of peak 2 and peak 3 for samples with $\phi_B = 30\%$ makes difficult a proper choice of T_2 to perform the second thermal treatment. Consequently, changes of tenths of degree in the T_2 value would be responsible for dramatic changes in the area of the isolated peak 3 to be observed in the fourth thermogram.

Finally, it is worth highlighting the similarity of data corresponding to the second and fifth DSC runs. This finding clearly supports the recovery in the lamellae distribution, upon thermal treatment, of the samples. This could also indicate that an equilibrium situation for the chain rearrangement after the blending process is reached.

5. Conclusions

1. The thermal study of binary blends of recycled low and high density polyethylene wastes reveals an important chain reorganization in the blending process which yields an intermediate peak (associated to a "new mixed" component) in the thermograms of samples with a low density PE concentration larger than 50%.
2. An estimation of the relative amount of material associated to the three main endothermic peaks has been performed. Thus, the reduced intensity of the highest temperature peak shows that the high density PE component is contributing mainly to the "new mixed" material.
3. Despite the changes observed in the lamellar distribution upon the various thermal treatments, below and above the intermediate peak, it is shown that after melting and recrystallization of the blend the initial microstructure is recovered.

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Appendix

The method used for the separation of the endothermic areas attributed to the above mentioned peaks 1, 2 and 3 is as follows:

(a) In all cases a baseline was drawn between the DSC curve at 30 °C and temperatures just above peak 3. This line was used to measure the total area S which is proportional to the fusion enthalpy.

(b) In the case of the third and fourth DSC runs showing a deep, wide valley a vertical line throughout the mid-valley temperature was drawn to separate the two main areas of thermograms. We shall call these two areas S_1 and $(S_2 + S_3)$ for the third DSC run, and $(S_1 + S_2)$ and S_3 for the fourth DSC trace, respectively.

(c) In case of the first, second and fifth DSC traces the separation of peak 2 and/or peak 3 was carried out by drawing smoothly the left side of each peak till the baseline is reached. In this drawing procedure the usual peak asymmetry observed in DSC traces of the individual component B was taken into account [1]. It is to be noted that particularly, for the second and fifth DSC traces the use of a criterion equivalent to that described in (b) gives similar results.

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