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Study of blends based on recycled polyethylene wastes

Part I *Variation of mechanical properties with composition*

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Data covering the physical properties of molten and solid samples of two binary blends of recycled polyethylene wastes, in a wide range of compositions, are reported. While some properties (density, fusion enthalpy) show a linear behaviour with composition other properties (microhardness, yield stress) show a deviation from linearity. Deviation of microhardness additivity of the single components has been interpreted, after analysis of the DSC thermograms, as being due to segregation and recombination of molecular species from both components during crystallization. It is also suggested that the presence of a high oxidation in one low-density polyethylene component, detected by infrared spectroscopy, influences the very low values observed for the melt flow index and melt elongation at break.

1. Introduction

Recycled grades of high-density polyethylene (PE) are recently becoming incorporated as new materials for packaging in the plastics industry [1, 2]. Extrusion blow-moulding is one of the techniques commonly used to produce recycled PE films and bottles [3]. Blends based on waste PE with different molecular weight grades may be employed for the preparation of extruded blown films for different applications [1, 3]. Despite the great amount of injection-moulding grade PE annually recovered (35×10^6 lb or some 16 000 tonnes), basic information on the microstructure and properties of these materials is missing in the literature. In the extrusion blow-moulding method it is important to know not only the mechanical properties of the solid material before extrusion but also those of the molten material (melt flow index, melt elongation at break).

In the present two papers a microstructural study of blends based on recycled polyethylene wastes is presented. In this first paper we report a detailed characterization of two particular recycled PE blends using the microhardness method, though results from Fourier transform infrared spectroscopy (FTIR), and differential scanning calorimetry (DSC) and additional mechanical data such as yield stress, melt flow index and melt elongation at break are also included. Blends of different PE grades show, depending on composition, complex DSC thermograms [4, 5]. This is a consequence of the specific morphology of the blends which, in turn, controls the mechanical behaviour of the single PE components. During the last few years studies carried out in our laboratory have demonstrated that the microhardness of semicrystalline polymers can be related to their microstructure (degree of crystallinity, thickness of crystalline lamellae, etc.) [6–10]. In particular, the microhardness of polymer blends has been shown to be affected by the composition and by the changes occurring in morphology as result of blending the single components [11–13]. Thus we believe that microhardness measurements could be advantageously applied to blends of recycled PE to provide some relevant information on the structure–property relationship of these materials. Since the method can be used on small sample sizes and is non-destructive, it represents an interesting research tool to investigate the mechanical properties of samples which are made on a small scale in a laboratory.

The second paper [14] will be concerned with a more detailed calorimetric study of blends with two different compositions to elucidate the level of mixed material after blending the two recycled PE components.

2. Experimental procedure

2.1. Materials

Two low-density polyethylene wastes (agricultural and packaging films) with number-average molecular weights M_n, of 15 500 (A1) and 22 700 (A2) and a higher-density polyethylene waste (industrial scrap) of $M_n = 38\,600$ (B) were selected to prepare blends A1/B and A2/B in a wide range of compositions. Blends were prepared by mixing the two components on a two-roll mill at 145–150 °C for 10 min. The milled material was hot-pressed at 140 °C for 3 min to prepare films of about 0.3 mm thickness.

2.2. Techniques

The melt flow index (MFI) was measured as the weight of molten material (190 °C) which flows through a 2.08 mm capillary under a load of 21.1 N after 10 min. The elongation at break of molten materials was measured in a chamber of 900 mm length at 150 °C using a speed of 200 mm min^{-1}. The percentage of gelation was measured in terms of the insoluble fraction of polyethylene treated in p-xylene for 48 h.

The microhardness of the samples was measured using a Leitz tester provided with a Vickers square-based diamond tip. The hardness value was calculated according to the expression $H = kP/d^2$ where P is the load applied, d the indentation diagonal and k a geometrical constant ($k = 1854.4$). A load of 0.15 N and a loading cycle of 0.1 min were used. The yield stress and elongation at break of the samples were measured using a tensile-testing machine and a deformation speed of 50 mm min^{-1}.

A Perkin-Elmer DSC-4 calorimeter provided with a cooling system was used to obtain the DSC traces from 10 °C up to 155 °C. A heating rate of 10 K min^{-1} and about 5 mg of sample were used. Transmission FTIR spectra of thin films (50–70 µm thick) were obtained with an instrument resolution of 2 cm^{-1} after eight accumulated scans. A density gradient column filled with a mixture of CCl_4 and toluene was used to measure the macroscopic density of the samples.

3. Results

Table I shows the values of M_n, MFI, elongation at break of molten (ε_m) and of solid (ε_s) samples, percentage of gelation G, density ρ, melting temperature T_m and integrated infrared absorbance A (1800–1670 cm^{-1}) for the three recycled PE samples used. Sample B refers to the recycled PE of higher molecular weight with a density value of 0.954 g cm^{-3}. Samples A1 and A2 are PE recycled materials from typical low-density polyethylene showing very different values for properties in the molten state (MFI, ε_m and G) but similar values for the solid-state properties (including tensile strength: 11.7 and 11.0 MPa). The infrared spectra revealed a substantial oxidation in the case of sample A1.

In Tables II and III data for MFI, ε_m, density, enthalpy of fusion (δH), yield stress (Y) and microhardness (MH) for the two series of A1/B and A2/B blends are respectively collected. While the density and enthalpy of fusion show a linear increase with increasing weight percentage of B (ϕ_B), a deviation from linear behaviour for the other properties investigated was observed. The variation of melt flow index values with increasing weight percentage of the B component is represented in Fig. 1. While the A2/B samples show a linear variation of MFI with increasing B content, the A1/B samples show a large deviation from linear behaviour and their MFI values are much smaller.

Fig. 2 shows the linear relationship found between the microhardness and the yield stress for the two series of blends A1/B and A2/B. However, as we will discuss later, the slope of this plot differs from that found for other PE samples [7] and predicted by the Tabor relation [15].

Fig. 3 illustrates the variation of MH for the A1/B blends with increasing ϕ_B values, indicating a deviation from an additive behaviour of MH for the two independent components. In the case of A2/B blends an even smaller deviation of MH from the additivity of MH values was found.

Fig. 4a and b show the DSC endotherms observed for A1/B and A2/B series of samples, respectively. The similarity of the thermograms for each particular composition between both series of samples is remarkable. Although the shape of the endotherms for the two low-density components is not the same, they show the same melting temperature (see Table I). DSC traces of blends with composition $\phi_B \leqslant 0.7$ are not

TABLE I Number-average molecular weight M_n, melt flow index (MFI), elongation at break of the molten (ε_m) and of the solid (ε_s) state, percentage of gelation G, density ρ, melting temperature T_m and integrated absorbance A (1800–1670 cm^{-1}) for the individual recycled polyethylene grades used in the preparation of the two blends

Sample	$M_n \times 10^3$	MFI	ε_m (%)	ε_s (%)	G (%)	ρ (g cm^{-3})	T_m (°C)	A (cm g^{-1})
A1	15.5	0.01	100	330	12.3	0.932	110.1	1470
A2	22.7	1.13	> 900	378	2.5	0.925	110.0	68
B	38.6	3.97	> 900	969	0.0	0.954	131.0	195

TABLE II Melt flow index (MFI), melt elongation at break ε_m, density ρ, enthalpy of fusion δH, yield stress Y, measured (MH) and calculated (MH_{cal}) microhardness for A1/B samples with different compositions

A1/B	MFI	ε_m	ρ (g cm^{-3})	δH (cal g^{-1})	Y (MPa)	MH (MPa)	MH_{cal} (MPa)
100/0	0.01	100	0.932	28.0	10.1	19.0	–
95/5	0.08	–	0.935	29.0	11.3	21.4	20.5
90/10	0.1	416	0.937	29.4	11.0	21.6	21.7
70/30	0.3	470	0.938	32.9	12.6	24.4	25.8
50/50	0.9	500	0.943	36.6	15.8	30.8	31.1
10/90	2.1	726	0.950	42.7	20.5	40.4	–
0/100	3.9	> 900	0.954	45.9	24.1	49.0	–

TABLE III Melt flow index (MFI), melt elongation at break ε_m, density ρ, enthalpy of fusion δH, yield stress Y, measured (MH) and calculated (MH_{cal}) microhardness for A2/B samples with different compositions

A2/B	MFI	ε_m	ρ (g cm^{-3})	δH(cal g^{-1})	Y (MPa)	MH(MPa)	MH_{cal} (MPa)
100/0	1.1	> 900	0.925	25.1	8.7	16.5	–
95/5	1.4	> 900	0.926	26.0	9.5	18.8	17.8
90/10	1.6	> 900	0.928	27.6	9.8	19.3	18.6
70/30	1.8	810	0.935	31.1	11.3	23.3	25.5
30/70	3.0	–	0.944	40.0	–	37.0	–
5/95	3.5	> 900	0.954	43.8	21.5	46.0	–
0/100	3.9	> 900	0.954	45.9	24.1	49.0	–

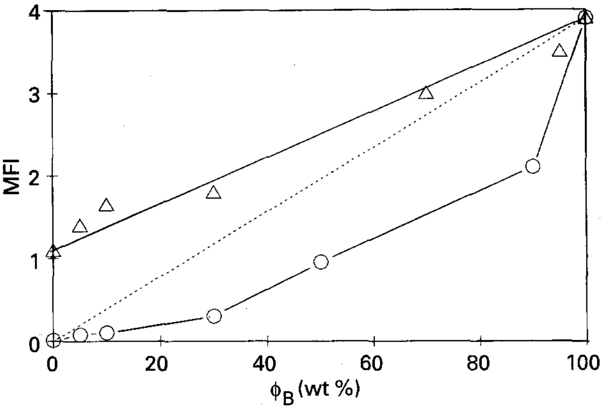

Figure 1 Variation with composition ϕ_B of melt flow index values (given in g/10 min) for the blends (○) A1/B and (△) A2/B.

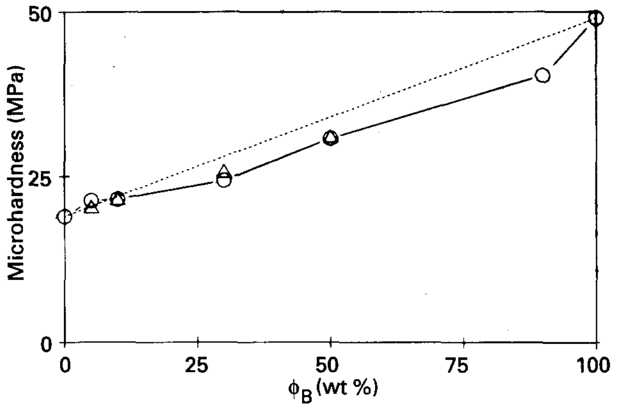

Figure 3 (○) Variation of the hardness measured for A1/B samples with composition. The calculated values (△) for some samples are also drawn.

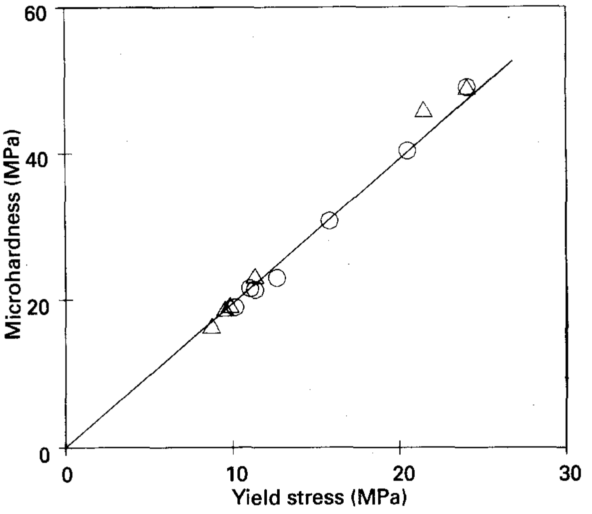

Figure 2 Correlation between microhardness and yield stress observed for (○) A1/B and (△) A2/B blends based on recycled polyethylene wastes.

simple and show, in between the two endothermic peaks associated with the single (A and B) components, an intermediate endothermic region which shows up an important reorganization of the crystallizable material after blending [16]. This intermediate region is clearly resolved for $0 < \phi_B \leqslant 0.5$. A second DSC run of the samples revealed a further crystal reorganization of the material (to be reported in the Part II [14]).

4. Discussion

4.1. Properties of the single recycled materials

Concerning the physical properties of the two starting low-density recycled PE samples (Tables I–III), material A1 shows slightly higher density, fusion enthalpy, yield stress and microhardness values than sample A2. However, the values of the melt flow index and the melt elongation at break for sample A1 are considerably smaller than for A2. The low values of MFI and ε_m are the main reason why the A1 material is not useful for the preparation of films by blown extrusion because the molten material would break during the deformation process.

In order to understand the different behaviour in the molten state of these PE recycled materials, transmission infrared spectra of thin films were obtained (Fig. 5). In addition to the three main absorption regions (725, 1470 and 2900 cm^{-1}) typical for the i.r. spectrum of polyethylene, the spectrum for A1 in particular shows additional bands of significant intensity. These bands, appearing at about 1700–1800 and 1000–1200 cm^{-1}, can be assigned to the presence of carboxylic groups. Keto-aldehyde groups cannot be discarded although the broad absorption observed at 1000–1200 cm^{-1} and a weaker broad absorption at about 3400 cm^{-1} support the presence of carboxylic groups [17]. A much smaller oxidation is also present in A2 and B samples (Table I). Consequently, it can be concluded that an important oxidation involving carboxylic group formation is present in the A1 sample. The measured integrated absorbance

A (1800–1670 cm^{-1}) represents 40% of the integrated absorbance A (765–686 cm^{-1}). Comparison of absorbance and MFI values in Table I reveals the apparent influence of carboxylic groups on the rheological properties of these materials. To explain this result one may suggest that the interaction between oxidized groups could be connected with the low values of melt elongation at break and MFI observed for sample A1. On the other hand, the higher amount of insoluble fraction observed for A1 ($G = 12.3\%$, Table I) would also contribute to a decrease of the MFI and ε_m values for this component.

Melting-point data and particularly the mechanical properties (MH and Y) corresponding to the B component, with a medium density value, are considerably higher than those observed for the low-density A1 and A2 components. The hardness values observed for the A and B recycled materials are close to those measured in commercial branched polyethylene samples with similar density values [18].

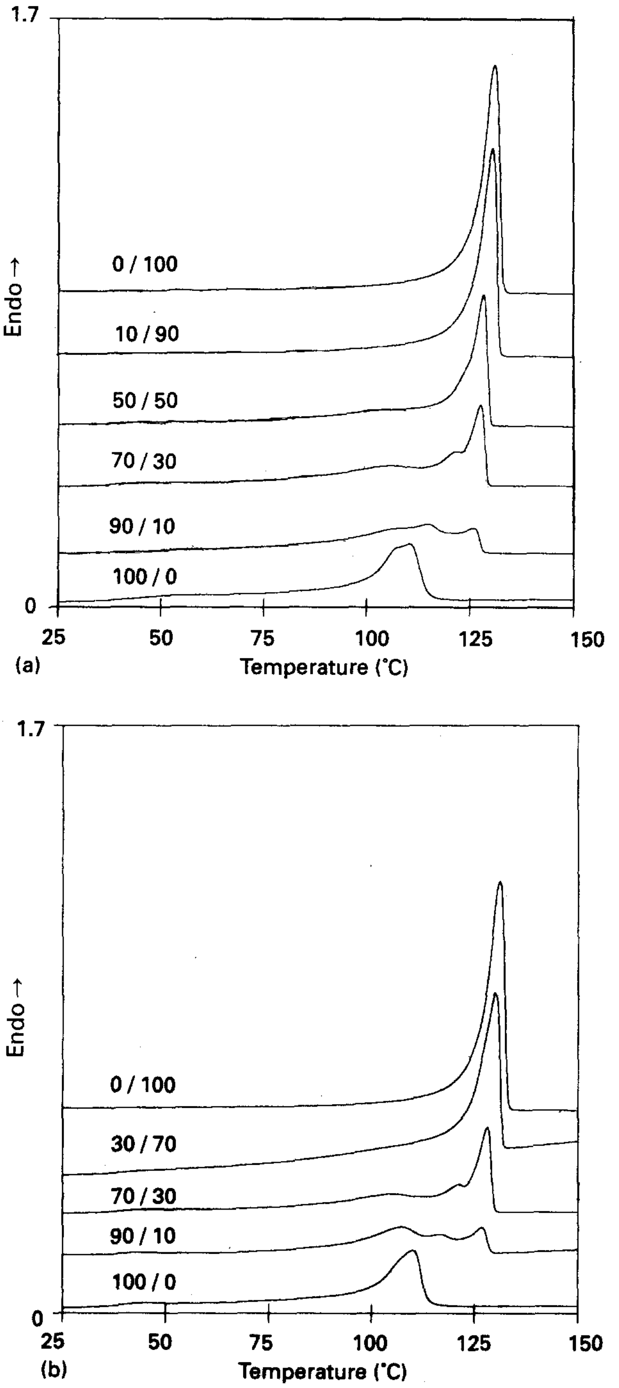

Figure 4 DSC traces for samples (a) A1/B and (b) A2/B with different compositions.

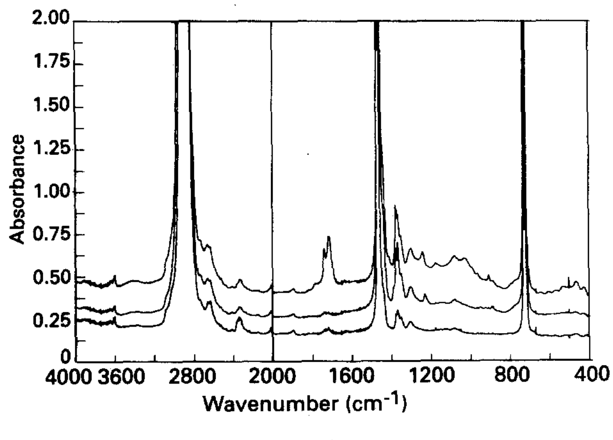

Figure 5 Transmission FTIR spectra from thin films of the polyethylene waste material used. From top to bottom: A1, A2 and B samples.

4.2. Mechanical study of the blends

The simultaneous increase of both MH and Y with composition ϕ_B for the two series of recycled samples gives rise to a linear correlation between these two mechanical properties with a ratio $MH/Y \simeq 2$ (Fig. 2). This ratio is notably smaller than that previously found for polyethylene [7] and predicted by the Tabor relation ($H = 3Y$) for an ideal plastic solid [16]. The smaller MH/Y ratio found for these materials can be related to the relatively high deformation speed (50 mm min^{-1}) used in the macroscopic measurement, which is about 40 times higher than that used in the microhardness test.

The linear variation of density and fusion enthalpy with composition are consistent with each other. In addition, the linear variation of δH with ϕ indicates that the crystallinity values of the individual A and B components remain constant for the whole range of compositions. A linear variation of δH with ϕ has been previously obtained in other PE blends [19].

In order to explain the deviation of hardness from a linear behaviour in an MH versus composition plot (Fig. 3) it is convenient to examine the thermograms of the blends in Fig. 4. It is known that the endothermic area of DSC thermograms represents the fraction of crystallized material in the sample. The presence in the thermograms of a high-temperature peak at ~ 130 °C and other low-temperature peaks in the range 110–120 °C suggests the coexistence of two types of lamellae: thick lamellae (15 nm) and thinner ones (7.0–9.5 nm). The former correspond essentially to the B component while the latter are a mixture of those from the A component plus additional intermediate thick ones arising from a new endothermic peak, or shoulder, appearing in the range 115–120 °C. The fraction of material (from B component) associated with the high-temperature peak (HTP) can be calculated using the expression.

$$\phi'_B(\%) = \left(\frac{\text{Area of HTP}}{\text{Total area}}\right)\left(\frac{\delta H_{\text{sample}}}{\delta H_B}\right) \times 100 \quad (1)$$

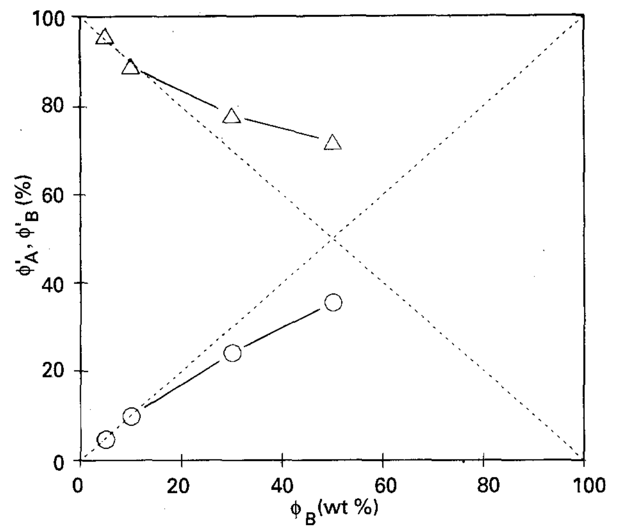

Figure 6 Comparison between nominal and evaluated composition for (○) A1 and (△) B components for samples A1/B with composition up to 50% of B.

From the remaining area of the thermogram associated with the fusion of crystals of low-density material, the fraction of A material (ϕ'_A) can be calculated. The fractions ϕ'_A and ϕ'_B are represented as a function of the nominal weight percentage of B for A1/B samples in Fig. 6. A clear deviation from the bisector line is observed for compositions $\phi_B > 10\%$. For all the samples investigated $\phi'_A + \phi'_B \simeq 1$.

We can now use the new composition values ϕ'_A and ϕ'_B to derive *MH* for blends of recycled PE in terms of a composite having two populations of crystals (the thick ones and the rest of the thinner ones). According to the additivity law

$$MH_{\text{cal}} = MH_B\phi'_B + MH_A\phi'_A \qquad (2)$$

where MH_B and MH_A are the microhardness values of the single B and A components.

The MH_{cal} values are given in Tables II and III for the A1/B and A2/B samples, respectively. In Fig. 3 the MH_{cal} data for A1/B samples are also represented. The good agreement obtained between calculated and experimental data (Tables II and III) confirms that the hardness of these blends, if one uses the new composition data derived from calorimetry, can be explained in terms of a simple additive system of the two single components MH_B and MH_A. The reason for the deviation of *MH* (and also *Y*) from a linear additive behaviour with nominal composition can be attributed to a great reorganization of molecules forming the microcrystals (hard elements) during the blending process. As pointed out above, new crystals are formed after blending as revealed by the presence of the intermediate endothermic peak in the DSC traces (Fig. 4). This intermediate peak arises most probably from a molecular segregation and recombination of both more defective (from B component) and less defective (from A component) molecules during crystallization. It is well established that the hardness of polyethylene crystals is very much dependent on crystal size and perfection [6–8], factors which also influence the melting temperature. Thus, we think that the reduction in intensity obtained for the high-temperature peak for a given composition (Fig. 6) is the main reason for the depression of *MH* values observed in the blends (Fig. 3).

5. Conclusions

Binary blends of recycled polyethylene wastes with low and medium density values in the whole range of composition show a linear additivity with composition of most physical properties (density, fusion enthalpy). However, a deviation from additivity is observed for the mechanical properties (yield stress, microhardness). The deviation of hardness values is related to a molecular reorganization during blending which originates crystalline material with intermediate melting temperatures.

The presence of high oxidation (including carboxylic groups) in the low-density component of blends A1/B mainly affects the properties in the molten state of the samples (very low values of MFI and melt elongation at break), but it does not appreciably affect the other physical and mechanical properties investigated here. Consequently, special attention must be paid to the chemical oxidation of some polyethylene wastes which could give samples with very small values of MFI and ε_m and therefore would not be useful for the preparation of films by the blown extrusion method.

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