Dynamic Mechanical Properties of Binary Blends of Different Polyethylenes. II. Isothermal Treatment

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SYNOPSIS

The relaxation processes and thermal properties of a series of blends of a highly linear high-density polyethylene (HDPE) with several branched high-density, linear low-density (LLDPE), and low-density polyethylenes (LDPE) have been measured as a function of crystallization temperature, T_c, and content of branched polyethylene (BPE). The influence of composition on the dynamic mechanical spectrum of the HDPE has been rationalized taking into account the dilution with increasing content of BPE of those crystals formed during the isothermal crystallization. The influence of the type of second constituent (HDPE, LLDPE or LDPE) on the relaxation process of the HDPE has been explained in terms of segregation material data.

INTRODUCTION

The miscibility between two polyethylene (PE) fractions is not apparent. In principle, accounting for their behaviour in the molten state, these blends should be considered as miscible.[1,2] However, on cooling from the molten state, molecular fractionation occurs.[3-7] Thus, conventional linear low-density PE (LLDPE) and linear PE (LPE) were found to be largely incompatible in the solid state.[8,9] Blends of broad molecular weight LPE and branched PE (BPE) were shown to be incompatible by Norton and Keller.[10] Cocrystallization of the two constituent PE samples were reported by some authors[9,11,12] when both components had similar branch content. Three types of crystallization were shown in LPE blends[1] depending on the crystallization temperature T: (i) at high undercoolings, partial cocrystallization is recognized based upon data from transmission electron microscopy (TEM) and differential

scanning calorimetry (DSC); (ii) at intermediate undercoolings, parallel but separate crystallization of the constituent components was suggested; and (iii) at low undercoolings, clear molecular segregation of the low molecular weight LPE species was found. Cocrystallization was shown to take place at high undercoolings in 50/50 (w/w) blends of LPE and BPE.[13,14] Finally, in an earlier report,[15] the dynamic mechanical behaviour associated with blends of high-density PE (HDPE) with fractions of HDPE, LLDPE, and low-density PE (LDPE) subjected to a nonisothermal treatment, viz. airquenching of the samples from the molten state, was reported.[15] In this study, cocrystallization was found to produce greater changes in the dynamic mechanical properties of the constituent PE than the existence of separate crystallization paths. If this information is technically interesting, since it provides a sound basis for simple modification by blending of existing PE, the understanding of the mechanical relaxation mechanism in PE to picture the entire range of possible variables that affect it also represents an important research task.

In this article, it is our intention to describe the influence of composition and crystallization temperature on the dynamic mechanical relaxation spectra of blends of HDPE with HDPE, LLDPE, and LDPE fractions. The components of the blends have been chosen accounting for their crystallization

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kinetic behaviour,[16,17] i.e., the blending of a highly linear HDPE with BPE fractions displaying different crystallization ranges must be associated with a wide variety of dynamic mechanical responses.

EXPERIMENTAL

Materials

The molecular features of the single components, as well as those of the blends, have been summarized in Table I. The headings in this table refer to the number- and weight-average molecular weights (M_n and M_w, respectively) (provided by the manufacturing company), and the number of CH_3 groups per 1000 CH_2 units (determined by infrared spectroscopy[16,17]). The nomenclature used for the single components and the blends was built by employing the following rules: H, LL, and LD denote high-density, linear low-density, and low-density polyethylene, respectively; H8065, H4255, and H4005 are, then, three different types of high-density polyethylenes; LL2049 and LLXZ07 are two different linear low-density polyethylenes that have hexyl branches; and LD585 is a low-density polyethylene characterized by branches bigger than six (long branches)[17]; a blend will be expressed as H8 corresponding to the highly linear HDPE plus H42, H40, LL2, LLX, or LD5 corresponding to the second component.

The preparation of the blends was carried out by dissolution of known weights of each single polymer in hot p-xylene, precipitation with an excess of methanol, centrifugation, and intensive drying in a vacuum oven. Each sample was compression moulded in a laboratory press at 423°K for 5 min and cooled in ice water.

Differential Thermal Analysis (DTA)

The DTA instrument, a Mettler TA-2000, was calibrated according to standard procedures. The melting endotherms were recorded at a scan rate of 10°K/min. All crystallinity determinations are based on a value of 293 kJ/kg as the heat of fusion of 100% crystalline polyethylene.[18] The calculation of the weight fraction of segregated material has been carried out following the criterion given in refs. 6 and 7.

Dynamic Mechanical Thermal Analysis (DMTA)

The mechanical analysis was performed in a Polymer Laboratories DMTA apparatus interfaced to a Hewlett Packard computer. The mechanical mode used was the bending one, sharp knife-like supported.[19] All samples were run according to the following instrumental conditions: a scan rate of 3°K/min, a frequency of 1 Hz, and a temperature range from 133–403°K (a point was recorded each half degree). The samples for this analysis were prepared as aforementioned. The mean dimensions for the samples between the clamps were 10 × 40 × 0.65 mm.

The transition temperatures were more accurately determined by calculation of the first derivative of the mechanical spectra using a computer programme based on the five-points parabole method.

The determination for each sample of the end-corrected bending storage modulus at 298°K was carried out by means of a computer programme that, moreover, corrects the shear effect.

RESULTS AND DISCUSSION

The crystallization kinetic behaviour (variation of the semicrystallization time as a function of crystallization temperature) of the single components studied here is given in Figure 1. As can be seen from this figure, the samples used show different ranges of crystallization, mainly depending on branch content and branch type. Hence, the blending of the highly linear PE fraction H8065 with the

Table I Structural Characteristics of the Single Components

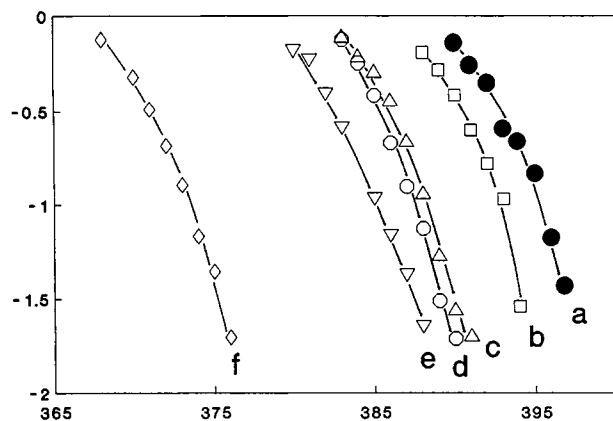| Code	M_w (g/mol)	M_n (g/mol)	Number of CH_3 per 1000 CH_2	Type of Branch
H8605	63,000	15,000	< 1	Short
H4255	72,000	21,000	5	Short
H4005	40,000	11,500	16	Short
LL2049	107,000	27,000	11	Hexyl
LLXZ07	128,000	31,500	26	Hexyl
LD585	70,000	12,500	21	Long

Figure 1 Inverse of the logarithm of the semicrystallization time against crystallization temperature for: (a), H8605; (b), H4255; (c), H4005; (d), LL2049; (e), LLXZ07; (f), LD585.

branched samples H4255, H4005, LL2049, LLXZ07, and LD585 is expected to produce different modification levels on the dynamic mechanical properties of the former. In the next sections, the changes observed on the relaxation features of H8065 will be related to data of segregated material levels as a function of temperature.

Influence of Composition

Prior to a comparison of the overall changes in the dynamic mechanical properties of H8065 brought about by blending this material with the different BPE samples mentioned above, the influence of composition will be analyzed. For this analysis, the blend H8LD5 (H8065 + LD585) has been selected, accounting for the fact that the two constituent components of the blend display the greatest difference of crystallization temperature ranges among all possible binary combinations and therefore LD585 is expected to greatly affect the dynamic mechanical properties of H8065. This will provide unequivocal experimental data since the changes produced will be big compared to the experimental error.

Figure 2 shows the variation of the α relaxation temperature (T_α) with crystallization temperature (T_c) for the single components H8065 and LD585 and three blends of them having different contents of both components (the composition is expressed in weight fractions; H8LD5-75 is therefore a blend containing 75 wt % of the component H8065). As shown in the previous paper,[15] the overall mechanical relaxation spectrum of the linear component H8065 changes as a function of composition. These changes are also detected when the blends are sub-

jected to isothermal treatment, as can be observed in Figure 2. Although the crystallization region suits that of the linear component, T_α experiences a variable decrease depending on the BPE concentration. On the other hand, the crystallization temperature appears to be irrelevant, viz. T_α is fairly constant, for each given composition, throughout the entire crystallization range for these blends. However, the airquenched samples[15] and the isothermally treated ones display a differentiate dynamic mechanical spectra since T_α for the former are lower than those of the latter. Recalling that the T_α values for the airquenched samples were: 314.2 K for H8LD5-75; 306 K for H8LD5-50, and 297 K for H8LD5-25, it is apparent that these values are ca. 4° lower than obtained for the isothermally crystallized materials given in Figure 2. This difference should be assigned to the existence of a bigger overall lamellar thickness within the isothermally treated samples than within the airquenched ones, as was pointed out by Popli et al.[18]

In principle, these changes could be considered to be due to two feasible changes within the linear polyethylene H8065 microstructure: (i) if total segregation of the component LD585 occurs, T_α may decrease as a consequence of the dilution of the relaxation of the dominant lamellae (those formed during the isothermal crystallization) since the concentration of the latter is decreasing with increasing BPE content; (ii) if partial cocrystallization takes place, the existence of mixed crystals (chains of both components are crystallizing together) is associated with a further increase of defective crystals.

Segregation material data (Fig. 3) shows that mixed crystals are formed during the isothermal crystallization. As can be observed in Figure 3, the
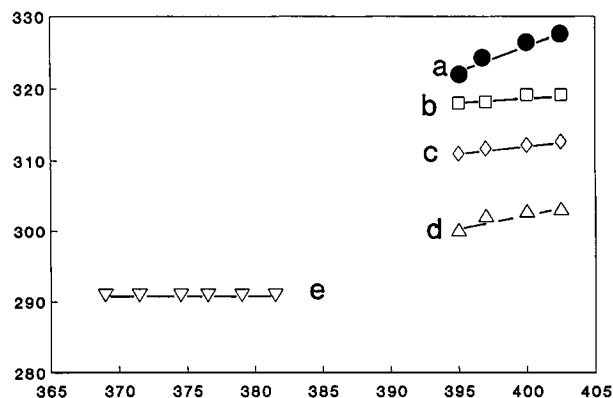

Figure 2 Change of T_α with crystallization temperature for: (a), H8605; (b), H8LD5 (25 wt % in LD585); (c), H8LD5 (50 wt % in LD585); (d), H8LD5 (75 wt % in LD585); (e), LD585.
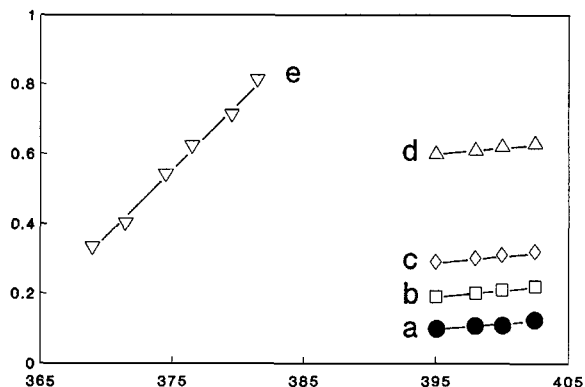
Figure 3 Variation of the weight percent of segregated material as a function of crystallization material for: (a), H8605; (b), H8LD5 (25 wt % in LD585); (c), H8LD5 (50 wt % in LD585); (d), H8LD5 (75 wt % in LD585); (e), LD585.

weight percentage of segregated material is always smaller than the weight fraction of BPE component within the blends, e.g., H8LD5-25 (75 wt % of LD585) presents an average segregation of 60 wt %. This mixed crystal formation takes place even though both constituent polyethylenes display very different crystallization ranges. Therefore, some chains of the LD585 fraction, presumably those having the greatest distance between branches, co-crystallize with chains of the linear H8065, thus distorting the lamellar thickness of the latter.

According to Boyd,[19] the α relaxation involves deformation movements into the amorphous region due to reorientations within the crystallites. The thicker the lamella, the greater energy is necessary to achieve a complete reorientation movement and therefore the temperature for which the α relaxation is observed is higher. On the other hand, the existence of a lamellar size distribution is associated with existence of a distribution of relaxation temperatures. Thus, T_α represents only a mean value. A theoretical approach that will relate these two distributions, lamellar thickness and relaxation temperatures, is currently being developed. Thus, the results given in Figure 2 must be understood as a consequence of changes in the lamellar distribution when the PE fractions considered here are blended. This implies that, although not perceptible, the crystals formed isothermally (H8065 and mixed crystals) show their relaxation temperature at higher values than those given in Figure 2, which correspond to the mean value.

The stability of T_α with crystallization temperature T for the blends and the branched single component LD585 must also be assigned to the dilution
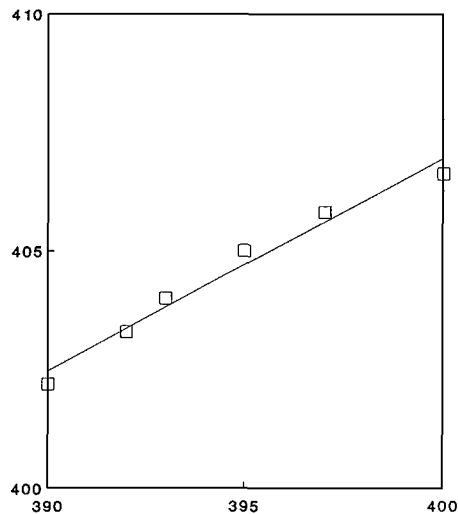

Figure 4 Melting point against crystallization temperature for the blend H8LD5 (50 wt % in LD585).

of the isothermally formed crystals. Even though these latter crystals increase their thickness with increasing T_c, as suggested by the melting point temperature T_m-crystallization temperature T_c plot given in Figure 4 and the relationship melting point-fold period,[20] these changes cannot be observed in the mechanical spectrum due to the aforementioned statistical character of the dynamic mechanical relaxation.

In relation to the β and γ relaxations, the most important changes have been observed to be associated with the composition rather than with the crystallization temperature, and these changes have already been reported in ref. 15.

Influence of the Type of BPE

The analysis of the different extents of modification produced by blending H8065 with PE fractions hav-
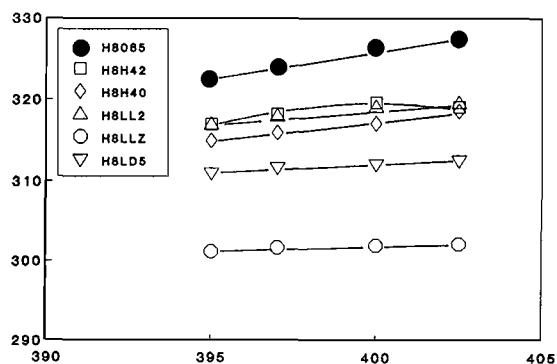

Figure 5 Change of T_α with crystallization temperature for the different 50/50 wt % blends.
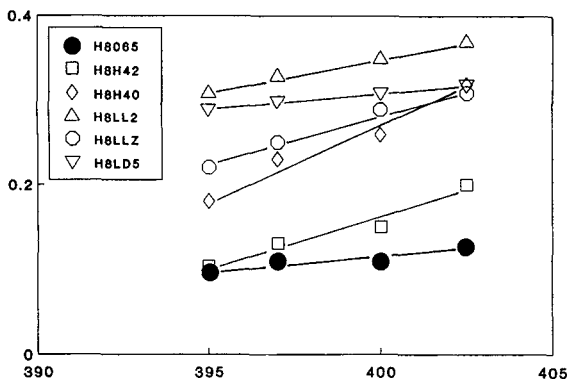
Figure 6 Change of the weight percent of segregated material with crystallization temperature for the different 50/50 wt % blends.

ing a wide range of structural features, i.e., molecular weight distribution, branch type, and branch concentration, has been carried out on 50/50 (wt %) blends of H8065 and the materials given in Table I. As in the previous section, only the α relaxation region will be analyzed since this relaxation is more amenable to changes due to blending than the β and γ relaxations.

The variation of T_α with T_c for the different blends is given in Figure 5. In principle, changes in this relaxation temperature in the sequence shown in Figure 1 were expected, i.e., a larger decrease in T_α as far as the crystallization temperature range for the single BPE component decreases. This expected trend is far from the observed one. The most remarkable observations arising from this Figure 5 are: (i) the blend H8LL2 shows T_α values comparable to those found for H8H42 and H8H40; (ii) H8LLZ shows the lowest T_α values in spite of the similar kinetic behaviour and structural features of LLXZ07 and LL2049 and the much higher crystallization range of the former compared to LD585; (iii) the influence of T_c on the location of the α peak is more pronounced for samples H8H42, H8H40, and H8LL2 than for H8LLZ and H8LD5.

It is apparent, therefore, that the changes observed in the dynamic mechanical spectrum of H8065 are influenced by factors other than the kinetic ones. The nature of these factors can be found on segregated material data obtained by DTA (Fig. 6). As can be observed from Figure 6, as before, all samples display weight percentages of segregated material that are lower than the content of BPE constituents within the blend. This result implies that formation of mixed crystals is taking place during the isothermal crystallization. This mixed crystal formation is more facile for the blends H8H42 and

H8H40 due to the structural similarities between high-density PE fractions (viz. type of branch). For these blends, a higher branch content is accompanied by bigger segregation. This trend, which coincides with that given by Figure 1, vanishes for the blends H8LL2, H8LLZ, and H8LD5. Thus, H8LL2 shows the highest segregation, followed by H8LD5 and finally H8LLZ. These results provide a guideline to understand the dynamic mechanical ones. Surprisingly enough, the higher segregation observed for H8LL2 than for H8LLZ is also associated, as aforementioned, with higher T_α for the former than for the latter. Higher segregation can be understood as lower concentration of mixed crystals due to the existence of cocrystallization of chains of both components during the isothermal treatment. The formation of mixed crystals implies an increase of defective lamellae during the isothermal crystallization and therefore a decrease of the concentration of the thicker crystals formed from H8605 alone. Consequently, cocrystallization produces bigger changes in the lamellar size distribution, which brings about a higher decrease of T_α.

Finally, the changes of T_α with T_c were also noticed for the single components and were rationalized[16,17] in terms of the capability of each sample to reorganize the crystallizable chains in lamellae of different size depending on T_c. The lower the branch content, the higher this capability and therefore the bigger T_α. According to the previous work,[16,17] the blends H8H42, H8H40, and H8LL2 behave like high-density PE (the slope of the plot T_α vs. T_c is slightly positive) whilst H8LLZ and H8LD5 show the same behaviour as the constituent BPE.

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