

Dynamic Mechanical Properties of Binary Blends of Different Polyethylenes. I. Nonisothermal 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. For the sake of comparison, all the samples were subjected to the same thermal treatment, that is, a rapid quenching from the molten state. The mechanical properties have been analyzed, taking into consideration the crystallization behavior of each sample. The existence of cocrystallization provides a bigger change in the dynamic mechanical properties than when segregation takes place. The observed changes in the end-corrected storage modulus supports this conclusion as well as those associated with the α , β , and γ relaxation temperatures.

INTRODUCTION

Polyethylene (linear and branched) displays three well-known relaxations in isochronal dynamic mechanical experiments: the α , β , and γ relaxations, which have been explained in terms of deformation movements within the crystalline or the amorphous phases.¹⁻⁷

In two recent papers the authors have described the study of the dynamic mechanical properties of a set of high-density polyethylenes (HDPE)⁸ and a set of linear low-density (LLDPE) and low-density polyethylenes (LDPE),⁹ relating these mechanical properties with structural features and crystallization conditions, evidencing the kinetic differences between all the samples and emphasizing the influence of molecular segregation on the mechanical spectra of these samples. The term *molecular segregation* describes a well-known phenomenon found in semicrystalline polymers during crystallization:

the rejection by the crystallizing chains of those molecules less favored from a thermodynamic standpoint.¹⁰⁻¹³ On blending two polymers, it is of importance to ascertain the degree of miscibility of both materials in the molten state because many other properties depend on the phase behavior of the system.¹⁴ This degree of miscibility is related to the interaction parameter χ . This magnitude was estimated to be -0.008 ^{15,16} by using a modified Flory-Huggins equation for these types of blends.

This article aims at determining the dynamic mechanical behavior of blends of a highly linear high-density polyethylene with other types of polyethylenes that exhibit different types and different concentrations of branches. As our primary concern is to determine the influence of composition, all the samples have been subjected to the same thermal treatment: a rapid quenching from the melting state that will be named *air quenched* hereafter.

EXPERIMENTAL

Materials

The molecular features of the single components as well as those of the blends are summarized in Table I. The headings in this table refer to the number-

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Table I Molecular Characteristics of the Single Polymers and Blends

Code	M_w^a (g/mol)	M_n^a (g/mol)	Number of CH ₃ /1000 CH ₂ ^b
H8065	63,000	15,000	< 1
H4255	72,000	21,000	5
H4005	40,000	11,500	16
LL2049	107,000	27,000	11
LLXZ07	128,000	31,500	26
LD585	70,000	12,500	21
H8H42-50	67,800	18,000	3
H8H40-50	54,000	13,300	9
H8LL2-75	78,900	18,000	4
H8LL2-50	90,700	21,000	7
H8LL2-25	99,800	24,000	9
H8LLZ-75	89,300	19,100	7
H8LLZ-50	106,600	23,300	13
H8LLZ-25	118,800	27,400	20
H8LD5-75	64,900	14,400	6
H8LD5-50	66,700	13,800	11
H8LD5-25	68,400	13,100	16

^a Provided by the supplier.^b Determined by means of infrared spectroscopy.^{8,9}

and weight-averaged molecular weights (M_n and M_w , respectively) and the number of CH₃ groups per 1000 CH₂ units. 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. Then, H8065, H4255, and H4005 are 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 and plus two digits that denote the weight fraction of component H8 in the blend.

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 molded 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

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 knifelike supported.¹⁹ All of the 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 to 403 K (a point was recorded each half degree). The samples for this analysis were prepared as indicated in the preceding. 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 program based on the five-point parabola method.

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

RESULTS AND DISCUSSION

Prior to the discussion of the dynamic mechanical results for these blends, it is interesting to show the thermal behavior associated with the air-quenched samples provided that this behavior is related to the final mechanical conduct as has been pointed out in previous works.^{8,9}

Thermal Behavior

The thermal results obtained by means of differential calorimetry are summarized in Table II. As expected, the inclusion of chain defects brings about a decrease of both degree of crystallinity and melting temperature as long as the fraction of the branched components increases. Apart from this behavior associated with the blending of linear and branched materials, another interesting characteristic to be pointed out is the absence of any molecular segregation for all the samples in the entire range of composition except for the case of the blend H8LD5. Even in this case, however, the amount of segregated material does not equal the weight fraction of the branched component within the system, the former

Table II Thermal Characteristics of Single Polymers and Their Blends

Code	W_{crys}^a (%)	Melting Point (K)	W_{seg}^b (%)
H8065	75.5	405.8	—
H4255	63.3	402.5	—
H4005	60	394	—
LL2049	45	390	—
LLXZ07	28	389	—
LD585	42	378	—
H8H42-50	75.5	404	—
H8H40-50	70	401	—
H8LL2-75	65	405.6	—
H8LL2-50	64	404	—
H8LL2-25	55	398	—
H8LLZ-75	65	404.7	—
H8LLZ-50	54	403.5	—
H8LLZ-25	41	400	—
H8LD5-75	65	404	—
H8LD5-50	53	403	33
H8LD5-25	42	399.5	53

^a Weight fraction of crystalline material obtained by using a value of 293 kJ/kg as the heat of fusion of 100% crystalline polyethylene.¹⁵

^b Weight fraction of segregated material obtained as the ratio between the area under the peak corresponding to the segregated material and the total area.

being always smaller than the latter. These results indicate that a certain degree of cocrystallization and colamellar formation (this meaning that the resulting crystals are formed by chains of both components) is taking place in all the blends regardless of the type of branched sample that has been used, though the presence of a single melting peak in a sample should be interpreted as a necessary but not sufficient condition for the existence of cocrystals. This colamellar formation, however, has been proved by Stein and co-workers²⁰ by means of small-angle X-ray scattering and longitudinal acoustic Raman spectroscopy on blends of HDPE and LLDPE. The cocrystallization can be explained by considering that the crystallization of the linear polyethylene in a first stage of the process becomes the driving force for the crystallization of those segments within branched chains that are long enough to deposit in the growing substrate. This means that although short segments between branches are rejected, they are bound to already crystallized segments and complete segregation is therefore not possible. This is not the case for the blend HDPE-LDPE where segregation takes place for weight fractions of linear polymer of 50 and 25%. In discussing this behavior,

we must bear in mind that we are dealing with a nonisothermal-type crystallization, and therefore, this takes place within few seconds.

Returning to the change of the melting temperature as a function of composition, it is important to highlight that while for the blends HDPE-HDPE and HDPE-LLDPE the decrease of this magnitude must be related to a decrease of the mean lamellar thickness, for the blend HDPE-LDPE it must be due to a dilution effect from segregation.

Dynamic Mechanical Properties

Examples of the influence of the addition of branched chains to the highly linear polyethylene H8065 on the mechanical spectra of this polymer is shown in Figure 1. Figure 1(a) corresponds to the blend H8LL2 and Figure 1(b) to the blend H8LD5. The other systems HDPE-LLDPE display similar mechanical spectra to these two, while the systems HDPE-HDPE show the same mechanical spectra as the component H8065. This representation enables us to state that the general appearance of the spectra is not influenced by the existence or not of molecular segregation. It is also interesting to point out the similarity between these spectra and those obtained by Clas et al.^{21,22} on copolymers of ethylene and 1-alkanes, indicating that the blending at different compositions of a linear and a branched polyethylene is as efficient in the modification of the mechanical properties as to change the fraction of 1-alkanes in LLDPE copolymers.

Before focusing this discussion on each separate relaxation, it is important to analyze the results concerning the variation of the end-corrected storage modulus at 298 K (E'_{298}) as a function of composition for all the blends (Fig. 2). It is apparent from this figure that (i) the storage modulus decreases as long as the fraction of branched chains is bigger; (ii) E'_{298} is a function of the type of branching. In blends HDPE-HDPE, E'_{298} is constant (H8H42) or decreases slightly (H8H40), while in blends HDPE-LLDPE and HDPE-LDPE this change is more pronounced; (iii) an increase of the concentration of hexyl branches in the HDPE-LLDPE blends implies a decrease in the modulus values; and (iv) an increase of the length of the branches (the branch concentration being approximately constant) on passing from the blend H8LLX to the blend H8LD5 does not mean a decrease of the modulus but rather the other way round.

The preceding point (iv) can be associated with the molecular segregation found for this particular blend. While in all the other blends, the lamellar

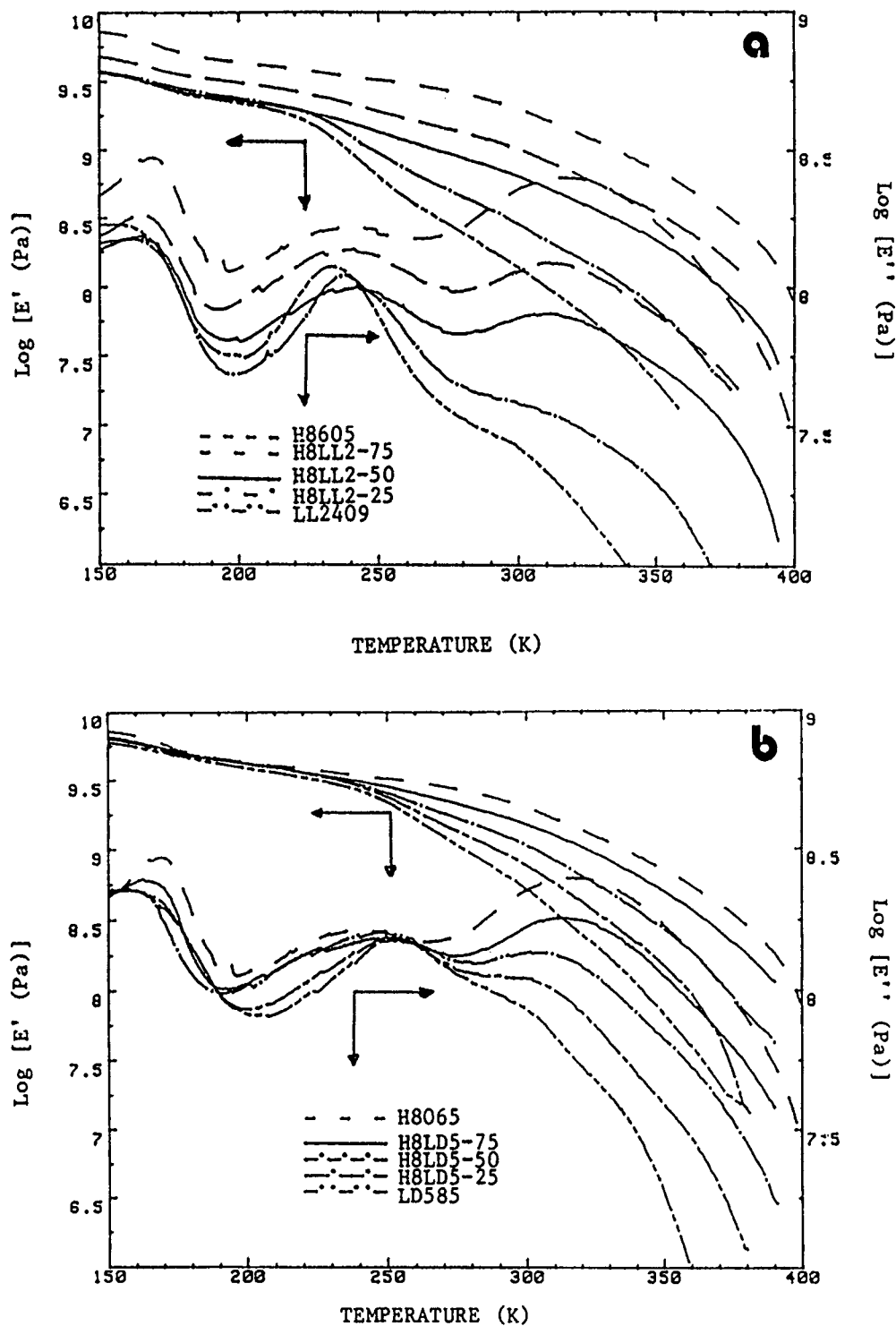


Figure 1 Isochronal spectra of the blends (a) H8LL2 and (b) H8LD5.

thickness is being modified due to the presence of cocrystallization, in this blend, the growing crystals of the linear compound reject the branched chains, thus giving rise to the presence of two clear lamellar

distributions. The final effect of this segregation is the dilution of the relaxations of the linear compound, having a less dramatic influence on the mechanical properties than the colamellar formation.

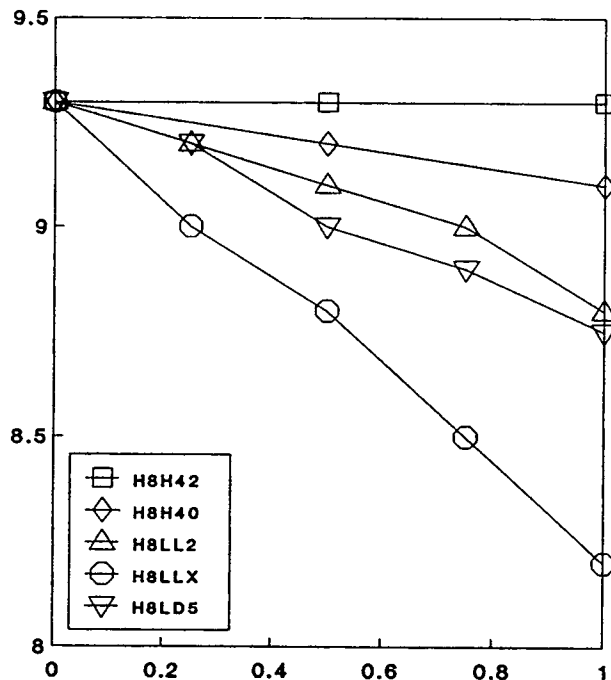


Figure 2 Corrected storage modulus at 298 K as a function of weight fraction of branched component.

α Relaxation

Figure 3 shows the variation of the α relaxation temperature (T_α) as a function of the weight fraction of the branched component. It is apparent from this

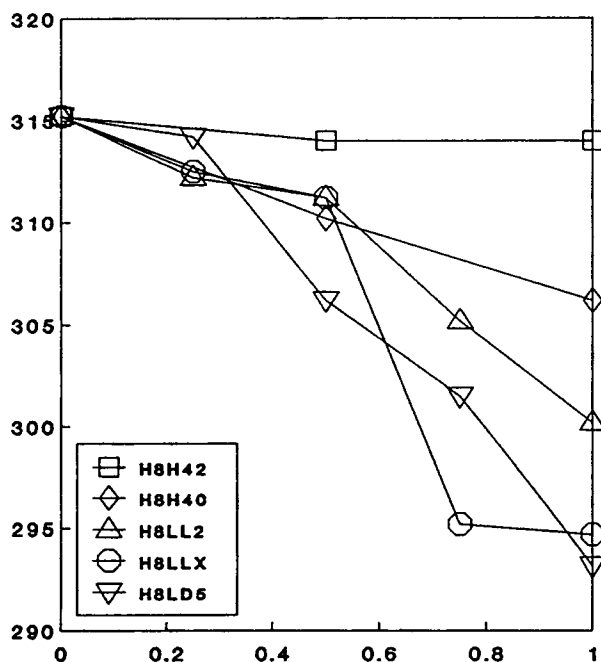


Figure 3 Variation of T_α (α relaxation temperature) as a function of weight fraction of branched component.

figure that the T_α decreases with increasing content of the branched compound. It is interesting to emphasize the sharp decrease observed for the systems H8LL2 and H8LLX from a composition of 50% in the branched component, while the blend H8LD5 decreases in a more uniform way. It is also of importance to point out that the relaxation temperature at a composition of 25% in the branch content is higher for the blend H8LD5 than for all the others (except the blend H8H42 for which the blending does not affect this property), indicating again a higher degree of mixing for the blends H8H40, H8LL2, and H8LLX than for the blend H8LD5.

The relationship between the melting points (T_m) of the systems and T_α is given in Figure 4, which shows that the dependence of T_m with T_α is linear for the systems H8H42 and H8H40 in the entire T_α range, while for the blends H8LL2, H8LLZ, and H8LD5 two different types of behavior can be observed: (i) for lower T_α values [relative to the lowest value, which is represented by the constituent linear low-density (LL2049, LLXZ07) and low-density (LD585) polyethylenes], these three systems experience on blending a sharp increase in T_m (this increase corresponds to the samples containing 25 wt % in the high-density polyethylene); (ii) for higher T_α values (which correspond to a weight percent of the high-density polyethylene of 50 and 75

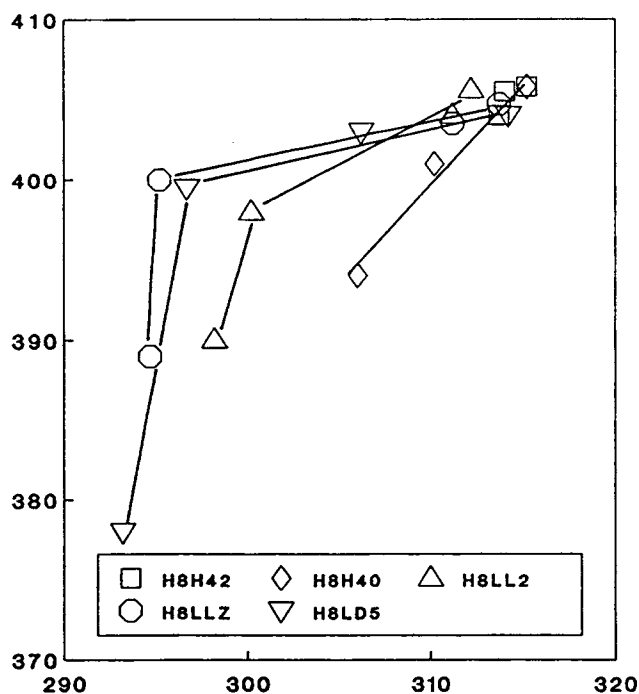


Figure 4 Melting temperatures (T_m) as a function of T_α .

wt %), the dependence is again linear, a large increase in T_α being only accompanied by a small change in the melting point. It is important to notice that in the T_α range where all the systems display linearity, the slope of the curves decrease in the sequence H8H42, H8H40, H8LL2, H8LLZ, and H8LD5. This behavior can be explained by the types of modification brought about by each parent component on the high-density polyethylene H8065: while the components H4225 and H4005 show cocrystallization with H8065, this cocrystallization decreases in the systems H8LL2 and H8LLZ (although no segregation is observed by thermal analysis), and the system H8LD5 displays clear molecular segregation.

The representation of T_α as a function of branch content (Fig. 5), moreover, enables us to state that this relaxation fits a fairly linear dependence with the branch content for these blends regardless of the kind of branches.

In considering the strength of the α relaxation (expressed hereafter as $\langle \sin \delta \rangle$), the influence of the neighboring β must be taken into account due to distortion brought about by the latter in the former, above all for high weight fractions of the branched component. This problem can be overcome by determining the ratio between the strengths of both relaxations. Figure 6 shows the variation of the ratio $\langle \sin \delta \rangle_\alpha / \langle \sin \delta \rangle_\beta$ as a function of the weight fraction of the branched component. It is apparent

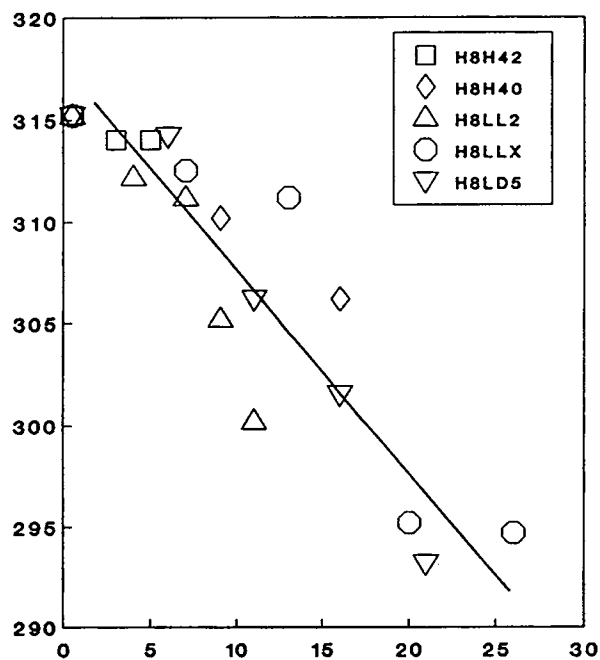


Figure 5 T_α as a function of branch concentration.

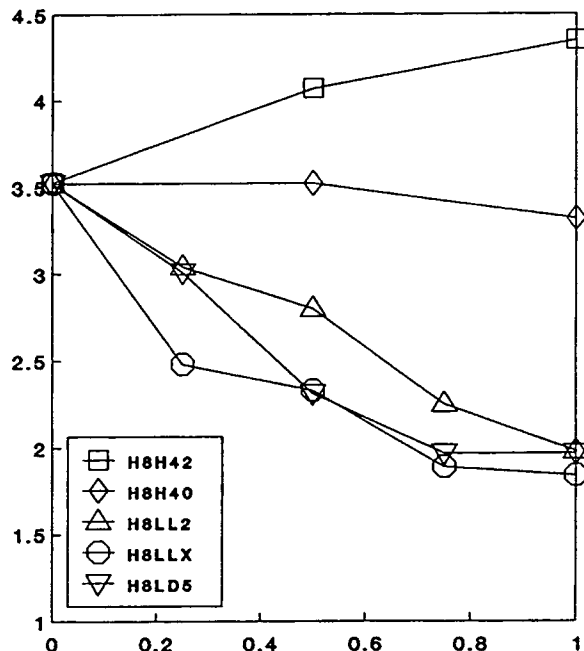


Figure 6 Change of $\langle \sin \delta \rangle_\alpha / \langle \sin \delta \rangle_\beta$ with weight fraction of branched component.

from this figure that the α relaxation decreases with increasing weight fraction of branched component for the blends H8LL2, H8LLX, and H8LD5 while it is fairly constant or even higher than the linear component for the HDPE-HDPE blends. This decrease is related to the decrease in crystallinity with increasing composition of the branched component as the intensity of the relaxation depends on the degree of crystallinity within the samples.

β Relaxation

The β process is still a source of discussion. Nowadays, agreement has been reached about the existence of this relaxation in linear polyethylene (LPE), about the nature of its broadness (the presence of the crystalline phase, which exerts a certain stress on the amorphous phase immobilizing segmental reorientations), and about the region where this process takes place^{3,4} (in the amorphous region and not only in the interfacial zone as some authors have proposed.²³ This relaxation, moreover, is usually presumed to be of the same nature in LPE and branched polyethylene (BPE). The molecular interpretation for this process considers it as the consequence of the relaxation of different entities within the amorphous region, i.e., folds of various lengths, cilia, floating chains, and tie chains,⁴ each of them requiring a different energy and all of them contrib-

uting to the final spectrum. It is reasonable to consider that the shortest relaxation times are associated with motions of very loose folds and relatively nonextended tie chains; longer times with tighter or more extended tie chains and not so loose folds and tight folds must be unable to relax.

Figure 7 shows the change of the β relaxation temperature (T_β) as a function of the weight fraction of branched molecules. The values for the single components were already reported in a parallel paper,⁹ paying special attention to the low T_β values found for materials H8065 and LLXZ07. The low value found for this last material can be explained by its low crystallinity, resulting in the existence of a greater number of conformations available to reorientation. The addition of the branched materials gives rise to an increase of T_β with regard to the one corresponding to the linear component in all cases, even when, as in the blend H8LLX, the T_β values of the single components are of the same order of magnitude. The intermediate T_β values, between the two corresponding to the single components, found for the blends H8H42, H8H40, H8LL2, and H8LD5 as well as the maximum found for the blend H8LLX represent a noticeable behavior. In order to discuss these results, it is interesting to express this relaxation, according to the aforementioned molecular interpretation, as the result of two competing effects, the first effect accounting for the stress exerted on the amorphous phase by the lamellae and the second

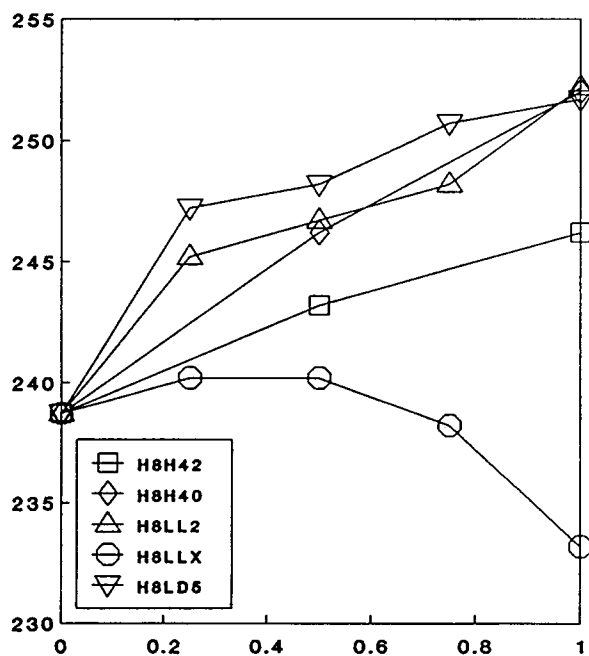


Figure 7 Variation of T_β (β relaxation temperature) as a function of weight fraction of branched component.

being related to the morphology of the intercrystalline zone.²³ On passing from the highly linear polyethylene (H8065) to the highly branched one (LLXZ-07), there are two main structural changes taking place: (i) the lamellar thickness decreases while the amorphous layer thickness increases and (ii) the intercrystalline region becomes more concentrated in nonadjacent reentries, loose loops, and reentries in other lamellae. On blending, the same structural changes take place but in a more controlled way. The increase of the amorphous layer thickness with increasing content of branched material implies a certain release of the stress exerted on the intercrystalline region by the lamellae as well as an increase of the free volume in the intercrystalline phase due to the increase in concentration of loose loops, nonadjacent reentries, and cilia. According to this model, an increase in branch content should be associated with a decrease in the relaxation temperature. This is precisely the origin of the contradiction. It is reasonable to think that due to the broadness and poor resolution of this process in the HDPE samples the calculated T_β values could be underestimated, at least for materials H8065 and H4255, but the intermediate T_β values for the blends compared to those of the single components again evidence the contradiction.

With the existing theories of the β relaxation, therefore, serious contradictions appear when intending to explain the experimental behavior. It might be possible, for this reason, to reopen the polemic whether the nature of this relaxation for fairly linear polyethylene (in this case H8065 and H4255) and for BPE is the same or not and whether there are other factors to consider (morphological, kinetic, etc.).

γ Relaxation

Contrary to what happens in the case of the β relaxation, in this case the molecular interpretation given elsewhere^{3,4} appears to be correct: an increase in branch content implies the increasing release of the stress exerted on the amorphous phase by the crystals, the conformational reorientations responsible for this process becoming easier.^{7,8}

On blending, the same results are found (Fig. 8). As far as the weight fraction of branched component increases, the γ relaxation temperature (T_γ) decreases. The type of crystallization (colamellar formation in the case of the blends H8H42, H8H40, H8LL2, and H8LLX and segregation for the blend H8LD5) brings about some differences in the behavior of the different blends. If we account for the

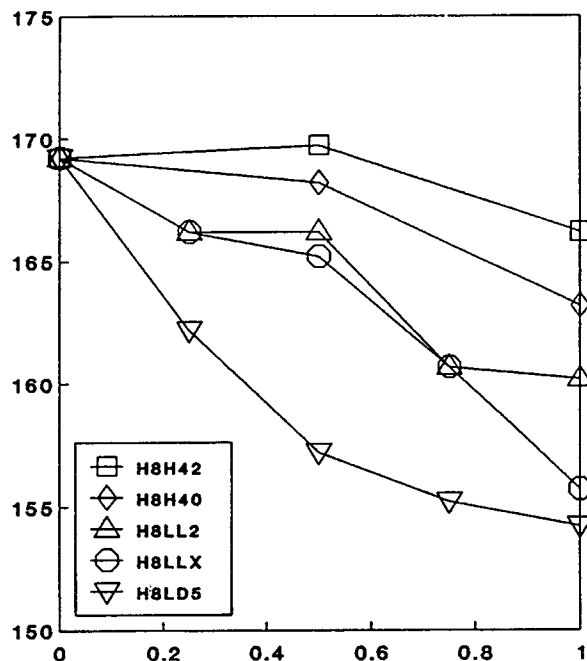


Figure 8 Change of T_γ (γ relaxation temperature) with weight fraction of branched component.

two HDPE-LLDPE blends, it is apparent that, regardless that they have different branch content and different crystallinity for the same weight fraction of the branched component, both show the same T_γ though the T_γ values for the LLDPE samples are different. On the other hand, if we compare the blends H8LLX and H8LD5, which show similar branch content and similar crystallinity over the entire composition range, they present very different T_γ values, the latter displaying always lower values than the former. Thus, the type of crystallization occurring in each system (colamellar formation or segregation) appears to influence the position of the γ relaxation more than crystallinity.

Finally, no significant changes have been detected on the strength of this relaxation on varying the fraction and the type of branched component. Similar results have been reported elsewhere.³

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