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A dynamic mechanical thermal analysis (DMTA) study of polyethylenes [a]

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Abstract

Differences in mechanical α and β relaxations for a family of six polyethylenes (PE) are discussed in terms of structural variations and immobilization of amorphous chains. An amorphous contribution has been identified in the α transition of high density polyethylenes (HDPE). Further, low density polyethylenes (LDPE) with long chain branches are found to sustain more amorphous tension than their linear low density analogs; such tension may be attributed to additional restraints in amorphous regions. Effects of CCl_4 plasticization on the two relaxations are discussed in terms of chain immobilization and free volume. Our data support the assignment of the β transition as the primary glass transition in PE. Relations between relaxation and mechanical toughness of the PE family are also discussed.

INTRODUCTION

Although the relaxation behavior of polyethylenes (PE) has been an extensively studied area, there still exist many unsolved questions, especially regarding the underlying molecular mechanisms for the generally observed relaxation processes. In this study, dynamic mechanical α and β relaxations and the influence of solvent plasticization were investigated for a family of polyethylenes differing in chain architecture and morphology. This study was undertaken in order to provide new information, and it was hoped to clarify some of the controversies in the relaxation literature. This study is also aimed at understanding the influence of amorphous aggregation on physical properties in these polymers. A review of existing relaxation literature will not be made in this manuscript since comprehensive reviews are available elsewhere [1–3].

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EXPERIMENTAL

Materials and sample preparation

Six members of the PE family studied are listed in Table 1. The two linear low density (LD) polymers are random copolymers of ethylene and 1-octene, and are essentially a mixture of a highly branched and a less branched component [13]. Taftmer-P is a random copolymer of ethylene and propylene; the α-olefin comonomer for Taftmer-A is not known with certainty, but is thought to be 4-methyl-1-pentene. Except for LLDPE and ULDPE, all polymers have reasonably homogeneous branching distributions. Films were prepared by compression molding on a Carver 2699 Laboratory Press (1000 psi, 150°C, 10 min) and annealing at 60°C for ten hours before any testing.

Characterization

DMTA measurements were made on a Polymer Lab Mk II DMTA system (tensile mode; frequency 1, 3, 10, 30 Hz; -140–120°C at 2°C min^{-1}; for clarity only the data at 3 Hz are presented). Plasticization was carried out, before the DMTA test, by exposing samples to saturated CCl_4 vapor at room temperature until the sorption of CCl_4 into the polymers reached equilibrium. DMTA of plasticized Taftmer was not carried out as it lost any mechanical strength when swollen. DSC measurements were made on a Perkin–Elmer DSC 7 at a heating rate of 20°C min^{-1}. Sample densities were determined at 23°C using a Tecam density gradient column filled with water and isopropanol. Relevant DSC and density results are summarized in Table 1. When calculating percentage crystallinity from DSC and density data, a two phase model was assumed with $\Delta H_f° = 277.1$ J g^{-1}, $\rho_c = 1.00$ g cm^{-3} and $\rho_a = 0.855$ g cm^{-3} [15].

RESULTS AND DISCUSSION

As generally observed, there are three mechanical relaxations for the PE family (Figs. 1–3), which are identified as α, β and γ in order of decreasing temperature.

α Transition

The α transition temperature (T_α) increases with decreasing branching content (Figs. 1–3). DSC data show that a less branched polymer has higher melting temperature, implying a larger fold length, which supports a crystalline chain mobilization mechanism [1,4] for the α relaxation, i.e., 180° rotation and $C/2$ displacement of chains inside crystals. Polymers with

TABLE 1

Characteristic data for the PE family members

	HDPE	LDPE	LLDPE	ULDPE	Taftmer-A	Taftmer-P
Branch content (*C*/1000)	<1	≈ 25	≈ 11	≈ 16	n/a	≈ 100
MW × 1/1000	115	101	112	110	n/a	20
Density (g cm^{-3})	0.9630	0.9221	0.9214	0.9123	0.880	0.8737
Melt index, ASTM 1238D	0.8	1	1	1	3.6	n/a
X_c (volume) by density	0.745	0.463	0.458	0.395	0.172	0.127
X_c (weight) by DSC	0.788	0.399	0.451	0.358	0.244	0.127
First melting peak (°C)	n/a	79–81	79–81	69–71	50	22
Main melting peak (°C)	137.7	111.3	123.8	123.0	75	41.4

n/a means not applicable.

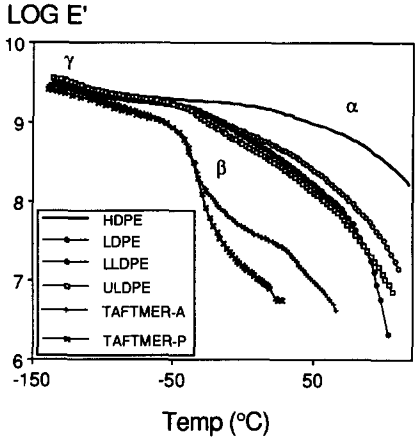

Fig. 1. Storage moduli of the polyethylenes as a function of temperature at 3 Hz.

longer fold lengths should exhibit a higher T_α because chains within thicker lamellar have to overcome higher energy barriers to mobilize [3]. In general, plasticization by CCl_4 does not seem to have much influence on the α relaxation of any of the low density polyethylenes examined (Fig. 4). The α process is controlled by chain mobility in the crystalline phase which is not accessible to solvent.

However, the effect of CCl_4 on the α relaxation of HDPE seems to be significant (Fig. 5). Location of the α peak is shifted from 64°C to 77°C by CCl_4 and an Arrhenius plot yields a much higher activation energy for the plasticized sample. Meanwhile, CCl_4 gives rise to a well defined and prominent β relaxation peak centered at approximately $-60°C$, which for dry HDPE is essentially absent.

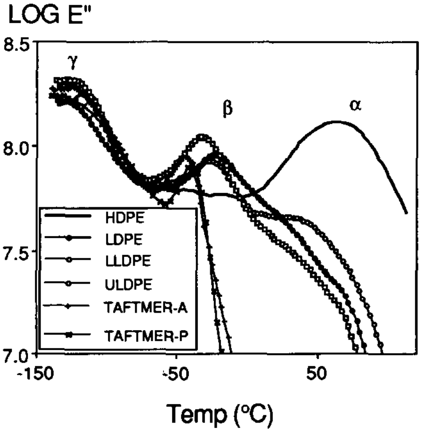

Fig. 2. Loss moduli of the polyethylenes as a function of temperature at 3 Hz.

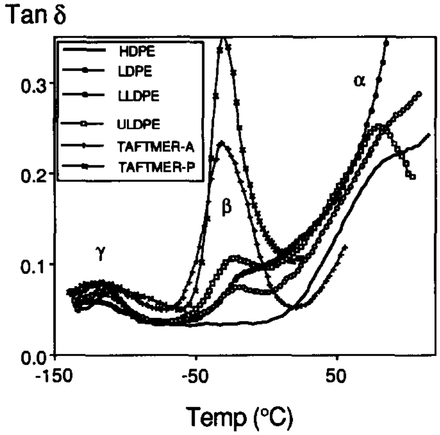

Fig. 3. Loss tangent of the polyethylenes as a function of temperature at 3 Hz.

Previous reports indicate that the mechanical *α* relaxation of melt crystallized HDPE may be resolved into two overlapping components [5,6] arising from the same underlying mechanism, but resolvable because of extremes in lamellar thickness distribution [3]. Our observation suggests that the two components may have different natures: one of them is a crystal controlled process located at higher temperature (insensitive to CCl_4, higher activation energy); the other may be a relaxation originating from the amorphous phase, i.e., the *β* relaxation discussed below.

β Transition

The *β* transition of HDPE is hardly visible in Figs. 2 and 3, although some investigators revealed that HDPE shows a weak, broad *β* relaxation

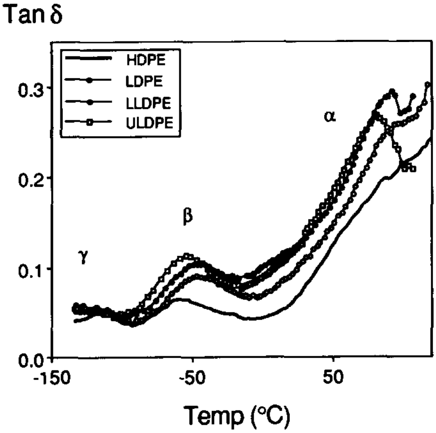

Fig. 4. Loss tangent vs temperature for CCl_4 plasticized polyethylenes at 3 Hz.

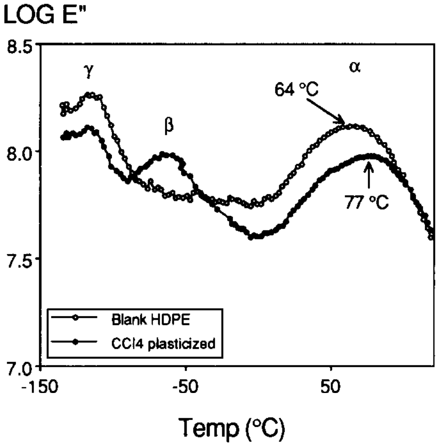

Fig. 5. Comparison between the loss moduli of "dry" and plasticized HDPE.

when quenched from the melt. Unlike HDPE, all low density polyethylenes show well defined *β* relaxations which are more prominent than their γ transitions. Transition intensity seems to be inversely related to polymer crystallinity, with samples of lower crystallinity showing more intense *β* peaks (Fig. 3). Plasticization of HDPE by CCl_4 gives rise to a prominent *β* peak centered at about −60°C (Figs. 4 and 5), which reproduces the observation by Paauwe and Knox [7]. For low density polyethylenes, CCl_4 increases the intensity of their *β* transitions and shifts them to lower temperatures, but not as low as the new HDPE *β* peak.

Although the amorphous origin of the *β* relaxation is generally recognized, its molecular mechanism is still a controversial issue. There have been three main hypotheses: (1) diffusional motion of branch points, (2) relaxation of crystalline–amorphous interfacial components, (3) glass–rubber transition of constrained amorphous components [1]. The branch point motion hypothesis was invoked since the intensity of the *β* relaxation in PE was found to be related to branch content [8,9]. The interfacial relaxation mechanism was proposed to explain Raman spectroscopy data [3] which revealed three components in solid HDPE: crystalline, liquid-like amorphous, and an interfacial component. The *β* relaxation intensity was proportional to the interfacial component content, and it was concluded that the *β* transition was due to relaxation of chain units located in the interfacial region; consequently, its existence requires the presence of a crystalline phase [3].

Our results do not seem to favor either the branch point or the interfacial mechanism. The branch point hypothesis cannot explain the solvent-induced *β* peak in HDPE, which is essentially free of branching. The interfacial relaxation mechanism is not supported by the intense sharp *β* relaxation of Taftmer-P, which is almost completely amorphous and should contain a

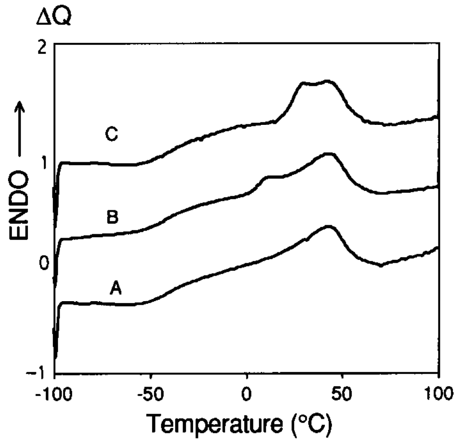

Fig. 6. DSC thermograms of Taftmer-P samples with different thermal histories: A, sample quenched from 100 to −100°C; B, quenched from 100 to 0°C, annealed at 0°C for 15 min and then quenched to −100°C; C, quenched from 100 to 15°C, annealed at 15°C for 15 min and then quenched to −100°C. Rate of quenching for all samples is 500°C min^{-1}.

much smaller amount of interfacial component compared with other low density polyethylenes. This assumes that interfacial material exists in a region of approximately the same thickness surrounding "crystallites" of comparable size. On the other hand, the features of the β relaxation of Taftmers, i.e., the sharp drop in modulus, the rubbery plateau above T_g (Taftmer-A, Fig. 1), and the dependence of transition intensity on percentage crystallinity (Figs. 1 and 3), are all characteristics of a primary glass relaxation in a low crystallinity polymer. DSC thermograms of the Taftmers also revealed a T_g-like transition around −35°C (Fig. 6). Due to the rapidity of crystallization, Taftmer cannot be supercooled into a completely amorphous state, even when quenched at 500°C min^{-1}. Differences in thermal history lead to significant changes in Taftmer's melting behavior but seem to have little effect on the T_g-like transition. This implies that the transition is not closely related to the crystalline phase. On the other hand, the intensity of this transition also shows a dependence on fractional amorphous content, as shown in Fig. 7. All of these results support the glass transition mechanism. The glass transition mechanism can also readily explain the β relaxations of other family members, as well as the majority of the literature data.

In semi-crystalline polymers, it is universally observed and well rationalized [10] that glass–rubber relaxation strength will be depressed by crystallinity. In addition, the transition is usually broadened and shifted to higher temperatures because of the constraint on amorphous chains by the crystalline component. A general picture might be that there is competition between the thermodynamic driving force for crystallization, which tends to draw chains from the amorphous phase and reels them into a crystal lattice,

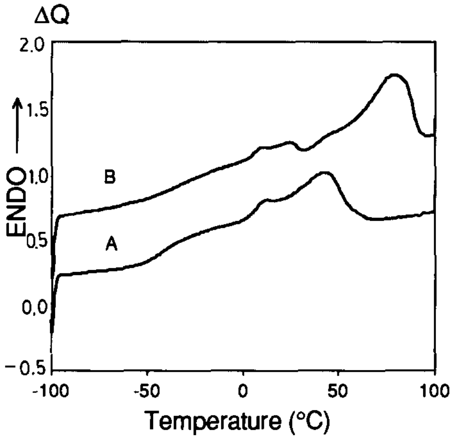

Fig. 7 DSC thermograms of A, Taftmer-P; and B, Taftmer-A. Both samples were quenched from 100 to 0°C, annealed at 0°C for 15 min and then quenched to −100°C.

and the rubber elasticity of amorphous chains, arising from their reduced conformational entropy, which resists the "reeling in" process. A balance between the two forces leaves amorphous chains under tension, which may significantly reduce their mobility, making them more "rigid" compared with chains in a completely amorphous and unrestricted state. This implies that either a higher temperature or a plasticizer is needed for relaxation to occur.

Based on this concept, the effect of chain branching on T_g should be two edged. First, any side chains attached to the $-(CH_2)_n-$ backbone tend to reduce its inherent flexibility and raise its T_g, an effect that can generally be described by Wood's equation [11]. On the other hand, randomly distributed side chains destroy main chain regularity and reduce inherent crystallizability. This latter effect will increase fractional amorphous content, weaken the restraint on amorphous chains, and subsequently enhance relaxation strength and lower the relaxation temperature. The dependence of the β relaxation on branch content, shown in Fig. 3 and observed by many others, can be satisfactorily explained by this mechanism.

HDPE cannot display an apparent glass transition because its high crystallinity severely diminishes the relaxation intensity and exerts high tension on its amorphous chains. This effect broadens the relaxation process and shifts it to higher temperatures, causing the β peak to merge with the α. On the other hand, low density polyethylenes, due to their lower crystallinity and reduced amorphous tension, can display an obvious glass transition, as do other moderately crystalline polymers. An increase in amorphous fractional free volume by CCl_4 plasticization shifts the β peaks to lower temperatures and moderately increases their height. This latter effect may be attributed to the mobilization of chain segments normally constrained by crystals. The solvent induced β peak of HDPE presumedly results from the creation of more "mobile" amorphous chains (increasing intensity) and/or increases in their mobility (lowering T_g). The T_β of CCl_4 plasticized HDPE is the lowest among the family, indicating that the side chain free backbone of HDPE is inherently the most flexible.

It can be seen from Fig. 2 that LDPE exhibits a somewhat higher T_g than LLDPE and ULDPE. Khanna et al. also observed this phenomenon and attributed the higher T_g of LDPE to its bulkier long chain branching [12]. This interpretation is questionable since, from the side chain argument, LDPE should have a lower T_g because of its longer and hence more flexible side chains. Our explanations are as follows. Based on Woods' equation, LDPE would be expected to have a higher inherent T_g since LDPE has more short chain branching than the linear low density PEs. In addition, there may be more crystalline–amorphous connections in LDPE than in LLDPE or ULDPE because LDPE has a narrower side chain distribution. Finally, LDPE contains flexible long chain branches which are themselves capable of crystallization. During the crystallization process, these long chain branches may be drawn into a crystal lattice excluding, however, long chain branch points. The rejected branch points, with arms held in crystals, act as additional crosslinking points that lead to further restraint on the amorphous phase. Our recent gas permeability measurements on these polymers also give supportive evidence for this hypothesis [13].

Relaxation behavior and physical properties

Comparing the uniaxial tensile toughness of these polymers, it was found that HDPE is "thermodynamically" the toughest material in the family; the energy required to deform unit volume of material is highest for HDPE [13]. In practice HDPE only showed superior toughness at relatively low draw rates, i.e. < 10 cm min^{-1}. When this rate is exceeded its toughness drops abruptly and it becomes more "brittle" than its low density cousins, simply because the sample would rupture before large scale plastic deformation could take place. However, when plasticized by CCl_4, HDPE could be readily drawn, and indeed showed the highest toughness at all draw rates investigated [14]. Together with relaxation data, these observations suggest that the poor high rate drawability of dry HOPE may have its origin in its highly constrained amorphous phase. At higher draw rates, less mobile amorphous chains are unable to move fast enough to orient themselves with the drawing stress, dissipate energy and diminish local stress concentrations. However, they can do so when the strain rate is low or when chain mobility is enhanced by extra free volume.

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