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Dynamic mechanical studies on secondary relaxations of ethylene copolymers [☆]

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Abstract

For ethylene copolymers, secondary relaxations control many important functional properties, such as room temperature ductility and subambient impact toughness. The location and intensity of these relaxations could also indicate the local environments of the polymer main chain. For example, the "crankshaft" motions for the methylene sequences give rise to the γ transition and the β relaxation introduced by the side branches. We have undertaken a broad based study of several families of copolymers of widely different chemical compositions including vinyl acetate, methyl acrylate, acrylic acid, and α-olefins. Comparisons have been obtained both from within the family as a function of co-monomer content and between families for the effect of the chemically different side groups. Interesting contrasts have been found. For example, the relative intensity of the β relaxation versus that of the α transition is a function of the crystallinity. Within the family of the ultralow density polyethylenes derived from different polymerization processes, the breadth of the β relaxation is found to be strongly related to the homogeneity of the short chain distribution as independently measured by the temperature rising elution fractionation (TREF) technique.

Keywords: Copolymer; DMA; EAA; EMA; EVA; Relaxation; TREF; ULDPE; VLDPE

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1. Introduction

The polyethylene industry is undergoing a major advancement in technology with the newly introduced metallocene based catalysts [1]. These catalysts copolymerize

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a variety of monomers in a very homogeneous manner. In addition, the traditional high pressure, low density processes have been expanded to produce a greater variety of copolymers. Many of the co-monomers can introduce polar functionalities on the main chain, thus creating the possibility of hydrogen bonding. Because many of the properties, such as low temperature impact toughness, room temperature flexibility, etc., are derived from the subambient relaxation processes, we have undertaken a broad based study on the dynamic mechanical properties of these polymers.

2. Experimental

Several families of copolymers are included in the study; the ethylene acrylic acid (EAA) copolymers of up to 20 wt% acrylic acid produced by Dow Chemical (Midland, MI, USA), ethylene vinyl acetate (EVA) copolymers of up to 70 wt% VA by Quantum Chemical (Cinncinati, OH, USA) and Du Pont (Wilmington, DE, USA), ethylene methyl acrylate (EMA) copolymers by Chevron Chemical (Orange, TX, USA), and several ethylene α-olefin copolymers, the so called very low density and ultralow density polyethylenes (VLDPE, ULDPE) by Dow, Union Carbide (Danbury, CT, USA), Exxon, and Mitsui Petrochemical (New York, NY, USA) up to about 20 wt% in co-monomers. A Seiko (Torrance, CA, USA) dynamic mechanical Analyser DMS-110 was used in the rectangular flexture mode with compression molded samples about 1 mm thick over frequencies of about 0.5 and 100 Hz, and temperatures between −150°C and the melting point at a scanning rate of 3°C min^{-1}. Typically, data at 1 Hz are used for comparisons, while data of all frequencies are used for activation enthalpy calculations. For the activation enthalpy calculation, $\tan\delta$ maximum temperature in units of 1/K (i.e. the reciprocal of the absolute temperature) at a given frequency is plotted against the logarithm of the frequency, and the slope of the resulting plot is used for the calculation. In addition ^{13}C NMR and TREF data for several samples were also incorporated in the study.

3. Results and discussion

3.1. Ethylene acrylic acid (EAA) copolymers

A typical dynamic mechanical spectrum for EAA is shown in Fig. 1. Following the traditional assignment of labeling the transitions α, β, γ from the high temperature side, the prominent transition is the β transition. For the compositions studied the β relaxation was located at about 15°C, with a near constant line width (full width at half maximum height) of about 35°C. The upward shifts of the T_β from slightly below 0°C normally observed for low density polyethylenes [2] are undoubtedly due to the hydrogen bonding of the side groups that hindered the mobility of the main chain. Because the β relaxation is the primary softening mechanism for this material, all samples examined appeared to be quite stiff due to the proximity of the T_g to ambient temperature.

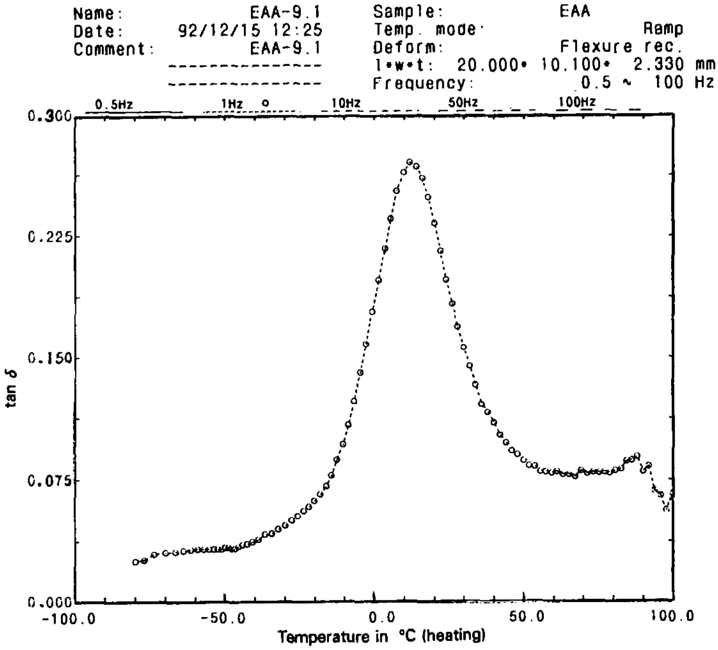

Fig. 1. 1 Hz tan δ spectrum of ethylene acrylic acid (EAA) with 9% AA.

3.2. Ethylene vinyl acetate (EVA) copolymers

Some of the representative spectra of the EVA system are presented in Fig. 2. It can be seen that as the VA content increases, the β relaxation first decreases in temperature and then starts to increase toward higher temperatures at a relatively high VA content. Nielson [3] reported some early dynamical results on EVA of different compositions where he observed a near constant β peak for lower VA

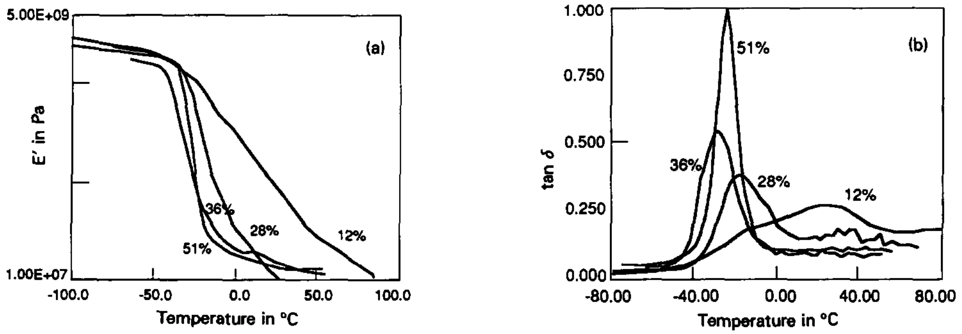

Fig. 2. Ethylene vinyl acetate (EVA) spectra with VA contents of 12, 28, 36 and 51 wt%: (a) modulus; (b) tan δ.

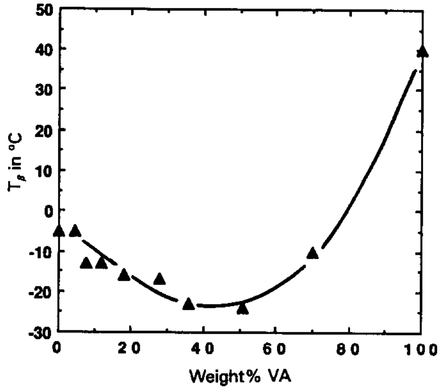

Fig. 3. Locus of EVA tan δ (1 Hz) maxima vs. VA content.

content samples at a constant −25°C, and extrapolated the upturn in the β transition in higher VA compositions to about −120°C, coinciding with the γ transition of polyethylenes. However, in contrast to Nielson's constant transition temperature at about −25°C to up to 40% VA content, we observed a steady decrease of the β transition temperature from that of the LDPE with increasing VA content (Fig. 3). Simultaneously with the relaxation maxima movements, the observed line width steadily narrowed with VA content to about 10°C (full width half height) for the 70 wt% copolymer (Fig. 4). In agreement with Nielson, the β relaxation after the last traces of ethylene crystallinity had disappeared, started to turn upward, ending at about 40°C for the 100% polyvinyl acetate.

The steady narrowing of the line width indicated a monotonic increase in cooperativity of the relaxation process, and indirectly the homogeneity of the local environment of the side branches. Of course, the ultimate uniformity is achieved by the 100% vinyl acetate sample where the VA side group becomes perfectly alternating with a methylene unit on the main chain.

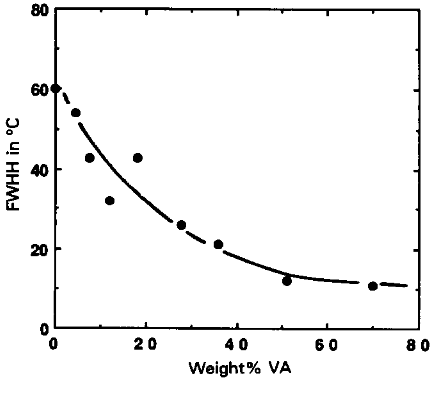

Fig. 4. Relaxation line width of tan δ (1 Hz) full width half height for EVAs.

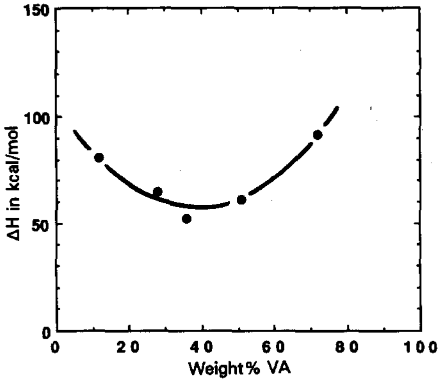

Fig. 5. EVA β relaxation activation enthalpy vs. VA content.

The activation enthalpy calculated from the multi-frequency data (Fig. 5) also exhibited a parabolic functional dependence. This could be rationalized by the observation that at low VA contents, the added side branches are "dilute" and do not interact with each other. The lowering of the activation energy comes from the perturbation of the linear polyethylene main chain. However, as the branches become significant through hydrogen bonding between the acetate groups (both the intra- and intermolecular manner), thus hindering the rotational movement and relaxation of the main chain. This added hindrance could account for the increases in both the location (temperature) and the activation enthalpy.

3.3. Ethylene methyl acrylate copolymers

Methyl acrylate is an isomer of vinyl acetate. The structural comparison between the two is given in Fig. 6. In vinyl acetate, the linkage between the side group and the main chain is via an ether oxygen, while in the case of methyl acrylate it is through a carbon–carbon bond. Similar to dielectric data reported by Buerger and Boyd [4], we observed a decrease in the β relaxation temperature with MA content, and the accompanying narrowing of the line width. However, when compared with the EVA series on an equal melting point or equal crystallinity basis, a much steeper function is very apparent (Fig. 7). This could be due to the packing and bond rigidity differences between the ether linkage and the carbon–carbon bond linkages to the main chain. Our data indicate that the carbon–carbon bond provided much

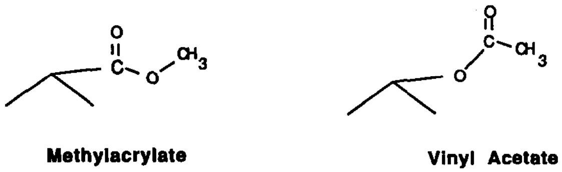

Fig. 6. Structural comparison of ethylene vinyl acetate and ethylene methyl acrylate.

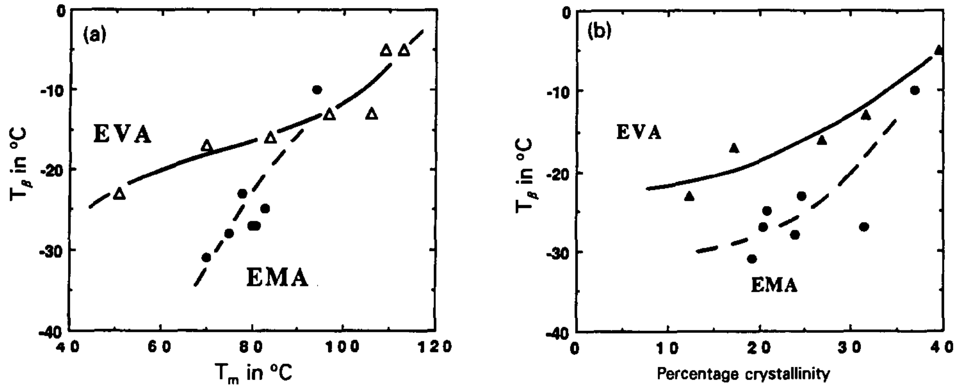

Fig. 7. β Relaxation maxima for EVA and EMA as functions of, (a) melting point, and (b) crystallinity.

more effective coupling (most probably via the barrier to free rotation) to the main chain which resulted in a greater depression of the relaxation temperatures.

Ethylene α-olefin copolymers: very low density PE (VLDPE) and ultra low density PE (ULDPE)

For linear polyethylenes produced by copolymerization of ethylene and α-olefin co-monomers, there is a steady decrease of the β relaxation temperature (Fig. 8) from slightly above 0°C to about −40°C corresponding to density or amount of co-monomer incorporation. Simultaneously, the relaxation intensity, as measured by tan δ peak height, steadily increases with the amorphous content (Fig. 9). These observations indicated that the β relaxation may contain important structural information. Over the entire composition range studied and samples from different polymerization processes, a variety of line widths was observed. In general, samples produced with known "homogeneous" co-monomer placements exhibited a steady

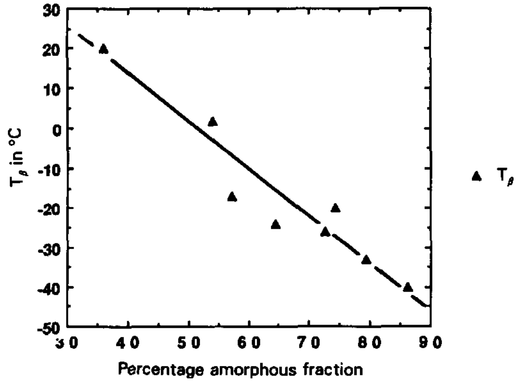

Fig. 8. Linear VLDPE and ULDPE β relaxation vs. amorphous content.

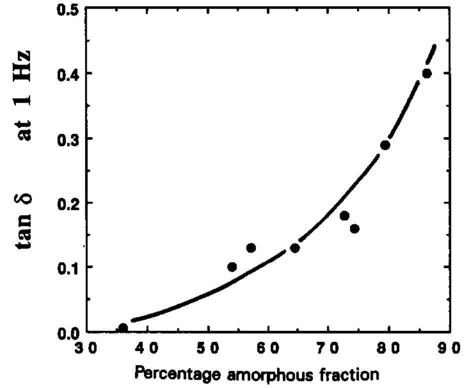

Fig. 9. Linear ULDPE β relaxation strength (tan δ magnitude) vs. amorphous content.

narrowing of line width as with EVA and EMA copolymers. Samples from multiple active site catalysts typically showed a much broader line width compared with homogeneous samples of a similar co-monomer content.

Since the β relaxation is believed to originate from near the branch points, we speculated that the line width may be related to the short chain branching (SCB) distribution. For the three samples for which independent short chain branching data were available by the temperature rising elution fractionation (TREF) technique [5], the line widths measured as full width at half height (FWHH) were correlated with the SCB distribution. The SCB distribution was calculated in a similar fashion to molecular weight distribution (MWD) as the ratio of the second and first moments from the normalized detector intensity SCB plot. Fig. 10 indicated an excellent correspondence of the two functions. This relationship clearly indicates that the location (in temperature) and the intensity (peak height) for the β relaxation are closely related to the branch density and branch distribution. If this relationship can be confirmed by further experiments, the dynamic mechanical method could offer powerful structural insights into these complex copolymers.

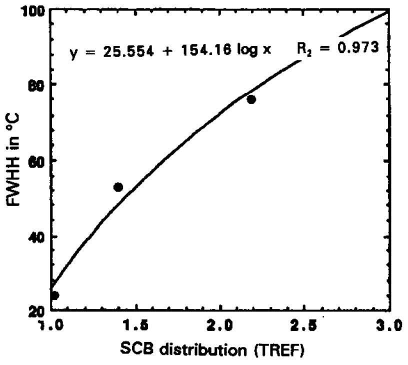

Fig. 10. Linear VLDPE β relaxation line width (FWHH) vs. short chain branching distribution by TREF.

4. Summary

Several ethylene copolymer families were studied by dynamic mechanical analysis (DMA). The β relaxation for EAA was significantly elevated, most probably due to the restricted motions from hydrogen bonding of the side chains. The EVA and EMA series showed significant depression of the β peak, with EMA showing a stronger dependence. The ethylene α-olefin copolymers' β relaxation was found to monotonically decrease with co-monomer content, while the relaxation intensity increased. For the VLDPE and ULDPE samples examined, it was found that the location and line width could be related to co-monomer content and distribution. Preliminary confirmations of this relationship with short chain branching were also obtained by TREF.

Acknowledgment

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