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Polyethylene structural heterogeneity by thermal and rheological techniques

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Abstract

Recent advances in metallocene catalysts have created a rich set of structural variations for polyethylenes. Copolymers of unprecedented comonomer content and branching distribution have been commercialized. In this paper, we report progress in our laboratories in characterizing these parameters. For polymers of moderate to high crystallinity, differential scanning calorimetry (DSC) provided very good qualitative data, while temperature rising elution fractionation was more quantitative. However, when the crystallinity is low or near non-existent, a dynamic mechanical technique provided excellent quantitative data. A new method is introduced where the normalized beta relaxation linewidth is used to calculate the branching distribution. Good results for nearly totally amorphous polymers were obtained.

Keywords: Polyethylene; Metallocene catalyst; Structural heterogeneity

1. Introduction

Ever since the Ziegler–Natta synthesis of polyolefins, there has been a desire to create progressively lower density materials by copolymerization. These lower density olefins potentially offer a range of attractive properties such lower moduli (higher flexibility), greater toughness and lower heat seal initiation temperatures. Until recently, the lowest density which was commercially achievable remained near the 0.915 range. However, in the last few years new catalysts, most notably the metallocene compounds based on zir-

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conium, coupled with improvements in process technology, such as series reactor designs, has resulted in a large number of new products of ever-decreasing density.

In the medical industry, these lower density olefins present very interesting possibilities for product designs. For example, the extremely high catalyst activity may lead to materials with very low inorganic contamination, while the high comonomer content and random distribution may provide superior optical clarity for particulate matter (PM) inspection. In addition, some of the softer grades of materials possess good thermoplastic elastomeric properties for innovations in product design. Thus, we have undertaken a systematic study on the relationship between thermal, mechanical properties and the structural, compositional parameters. Previous work has shown that compositional heterogeneity has a great influence on polymer properties [1]. The purpose of this work was to characterize polymer heterogeneity by thermal and rheological techniques. Materials used in this study were ethylene copolymers with butene, hexene, octene and vinyl acetate. Polymer types covered include linear low density polyethylene (LLDPE), very low density polyethylene (VLDPE), ultra low density polyethylene (ULDPE), ethylene vinylacetate (EVA) and ethylene-propylene rubber (EPR). For our purposes, LLDPE covers the density range between 0.91 and 0.925 kg l^{-1}, VLDPE between 0.89 and 0.91 and ULDPE with densities of 0.89 and below.

2. Experimental

Pellets of the materials were first compression molded into ca. 2 mm thick films on a compression molding press at 190°C and the thermal properties measured on a TA Instruments 2910 differential scanning calorimeter (DSC) cell using a 2100 controller. Heating and cooling rates of 10°C and 5°C min^{-1} were used throughout this study. A Seiko dynamic mechanical analyzer (DMA), DMS-110, was used for wide frequency range (0.5–100 Hz) studies over the temperature range of −150 to 150°C. Morphological studies were done using a Reichert FC4E cryo-ultramicrotome to prepare undistorted material blocks for SEM analysis. SEM analysis was done with a JEOL 6300 FESEM after sonic etching in ambient temperature heptane. In addition, other available characterization data were incorporated into this study.

3. Results and discussion

DSC analysis of polyethylenes characterizes the crystalline character of the material. Selected second heat DSC data are shown in Table 1. In a random copolymer the melting point depression is directly related to the amount of comonomer incorporated into the crystallizing segments (Fig. 1). If the comonomer incorporation is not random then the effect of the comonomer is not monotonic on the melting point and a spectrum of melting temperatures is possible. The primary peak melting temperature for the polyethylenes is shown in Table 1.

Among the samples examined, there is a wide range of melting temperatures and crystallinities. These values only reflect part of the material response. The melting curve

Table 1

Thermal analysis of polyethylenes

Sample	T_m (in °C)	Hf/(J g^{-1})	% Crystallinity[a]
ULDPE#1	69.5	59.8	20.4
ULDPE#2	71.8	62.0	21.2
ULDPE#3	118.4	74.8	25.6
ULDPE#4	55.3	38.0	13.0
VLDPE	123.8	125.6	42.9
EVA#1	84.1	74.8	25.6
EVA#2	69.9	60.3	20.6
EPR #1	47.9	35.9	12.3
EPR #2	(20)	–	ca. 0.0

[a] Hf = 292 J g^{-1} is taken to be 100% crystalline polyethylene.

is a reflection of the lamellar thickness distribution which is in turn a function of the sample history and composition. In several of these materials the melting curve exhibits multiple endothermic peaks even though the material is a single grade of polyethylene. Multiple melting peaks indicate several distinct lamellar thickness populations. This indicates that the comonomer distribution is heterogeneous. This type of melting response occurs with most LLDPE type resins due to the multiple catalytic active sites with different reactivities towards comonomers. Much narrower melting curves are seen in conventional linear HDPE homopolymers, high pressure LDPE or EVA copolymers. This is illustrated in Fig. 2.

Even though we can detect heterogeneity among crystallizible components with DSC it is difficult to quantify because of the difference in specific heat which accompanies increased comonomer incorporation. Another area of difficulty occurs when one or more

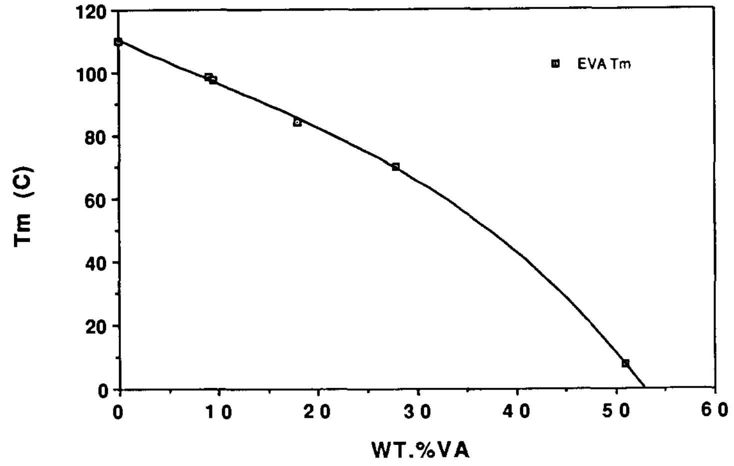

Fig. 1. DSC analysis of EVA copolymers: melting temperature versus percent vinyl acetate.

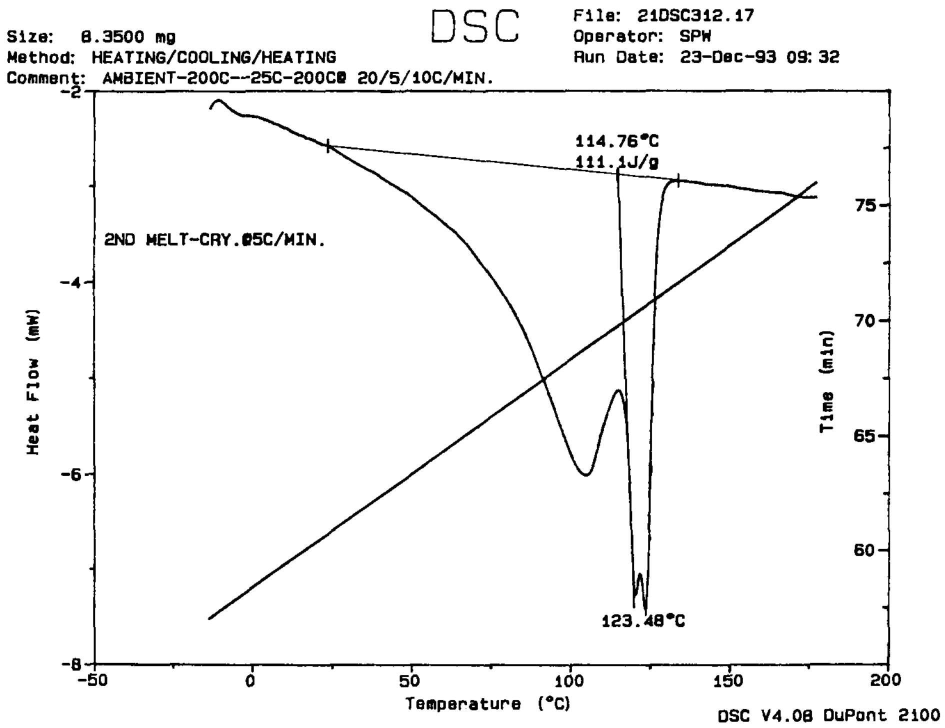

Fig. 2. DSC analysis of a VLDPE.

of the components is amorphous. The observed effect of this will be to reduce crystallinity at the same melting temperature. This is illustrated in Table 1. Two samples, ULDPE#3 and the VLDPE, exhibit a similar melting temperature but very different crystallinities.

Another way to characterize polyethylene heterogeneity is through temperature rising elution fractionation (TREF), [2]. This technique fractionates material based on differences in crystallizibility during very slow crystallization from dilute solutions. Application of this technique to various polyethylenes is illustrated in Fig. 3. It is very obvious that the short chain branching distribution is very different for the three samples. This short chain branching distribution can be readily quantified in a manner analogous to gel permeation chromatography (GPC). This is illustrated below:

$$\mathrm{SCBD} = \frac{(\sum N_{i\mathrm{SB}}\mathrm{SB}_i^{\,2})/(\sum N_i\mathrm{SB}_i)}{(\sum N_i\mathrm{SB}_i)/(\sum N_i)} \qquad (1)$$

where N_i is the concentration (detector response) of a given fraction and SB_i is the degree of short chain branching (CH3/1000 carbons).

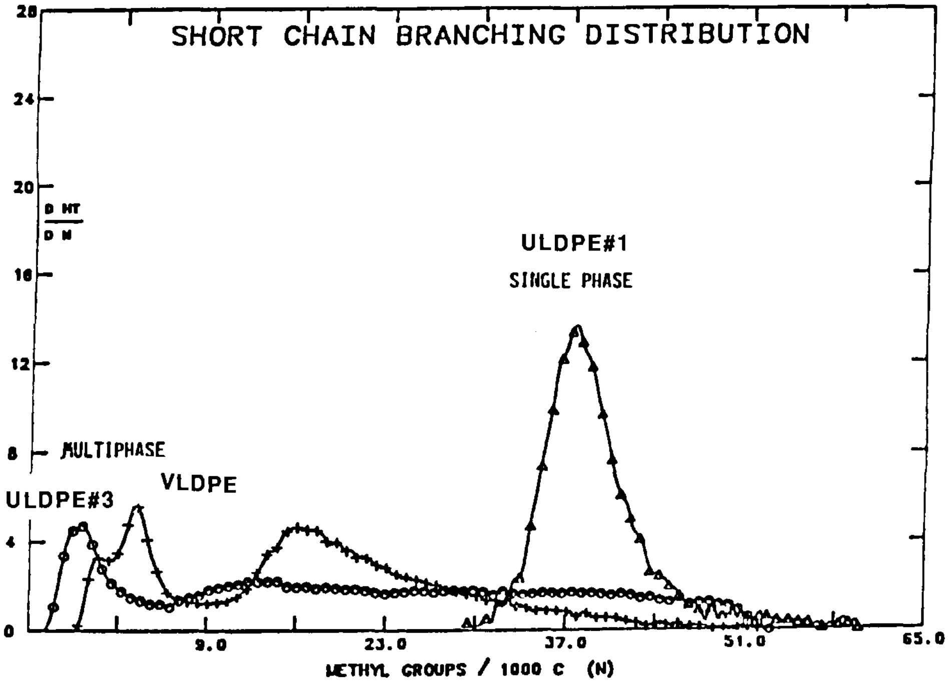

Fig. 3. Short chain branching distribution.

TREF is the best technique for quantitative characterization of polymer heterogeneity provided that the materials are mostly crystallizible. However, it suffers from the same difficulty as DSC analysis; amorphous components cannot be fractionated by this technique. Typically, as the comonomer content approaches about 20 mol%, the residual crystallinity becomes negligible. Thus the distribution of branches in the amorphous phase cannot be fractionated based on crystallizability. In addition, the technique is also very time consuming and labor intensive without automation. Also, without solvent recycling, a large amount of waste solvent is generated in the experiment. However, if one is interested in physically isolating the fractions, TREF is the only method available.

DMA is another technique which is sensitive to the structural heterogeneity of polyethylene. The tensile (Young's) modulus and 1 Hz dynamic elastic modulus at ambient temperature were found to be linear functions of the crystallinity. By scanning the material response over a range of temperatures and frequencies it has been found that the material exhibits relaxations which are characteristic of different structural units of the material [3].

The beta relaxation has been shown originate from the amorphous phase near the branching points [4]. The sensitivity of the beta relaxation to structure and branching is illustrated in Fig. 4. These data shows how the beta transition temperature changes with increasing vinyl acetate content among EVA copolymers. Since the melting temperature is a function of VA content, the melting temperature also correlates with the beta relaxa-

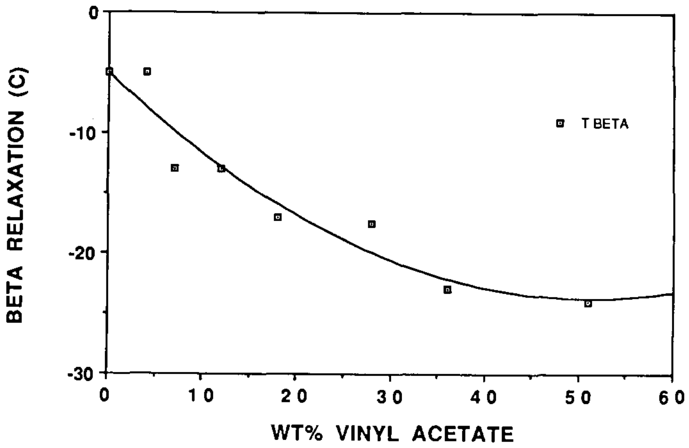

Fig. 4. DMA of EVA: beta relaxation temperature versus percent vinyl acetate.

tion temperature. The beta relaxation temperature also correlates with the melting temperature among the polyethylenes (Fig. 5).

It was noted previously that the width of the beta relaxation correlated with the short chain branching distribution (SCBD) defined from the TREF analysis [5]. Further, the relaxation linewidth is also influenced by the comonomer content. EVA copolymers polymerized at high pressure by a free radical process are known to exhibit a rather narrow comonomer distribution [2]. The full width at half height (FWHH) for the beta relaxation of EVA copolymers as a function of the comonomer VA content is shown in Fig. 6. Data by Schmieder and Wolf [6] on chlorinated polyethylenes, which is also known to be a random process, fit nearly identically to EVA on a molar basis. This identical depend-

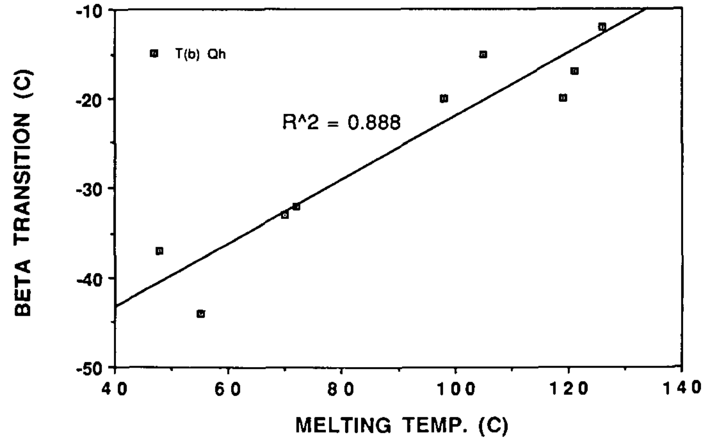

Fig. 5. DMA of polyethylenes: beta relaxation temperature versus melting temperature.

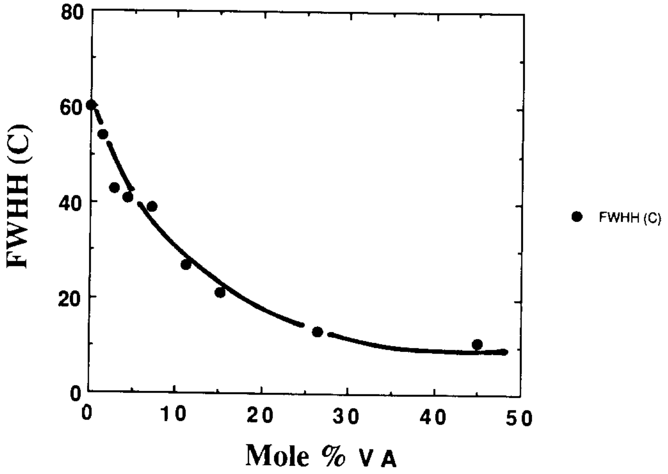

Fig. 6. Beta relaxation linewidth versus vinyl acetate content.

ence on very different branch units indicates that at least for ethylene copolymers, this phenomenon is quite universal. Hence the linewidth dependence of EVA and chlorinated PEon comonomer content can be used as a reference point representing a narrow SCBD case. For the time being, the slight complications of long branches in these reference cases will be ignored, leaving open the possibility that some narrowly distributed linear copolymers could exceed these reference cases in narrowness in SCBD. After normalizing the beta relaxation FWHH to that of the EVA or chlorinated polyethylene at equal molar comonomer contents, we find an excellent dependence with the SCBD determined by TREF (Fig .7). This normalized linewidth SCBD plot can then be used to determine

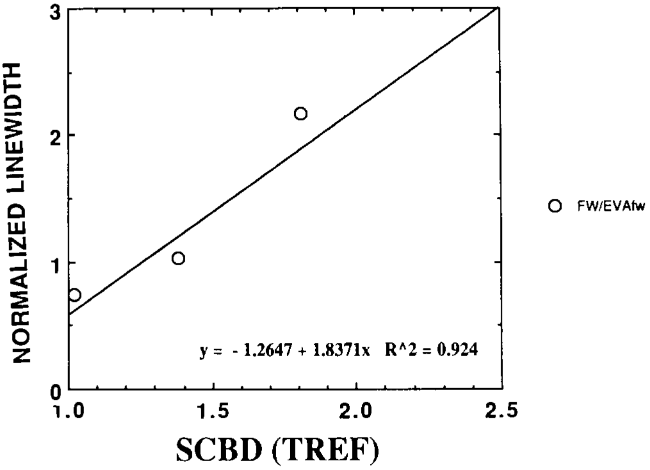

Fig. 7. Normalized beta linewidth versus short chain branching distribution.

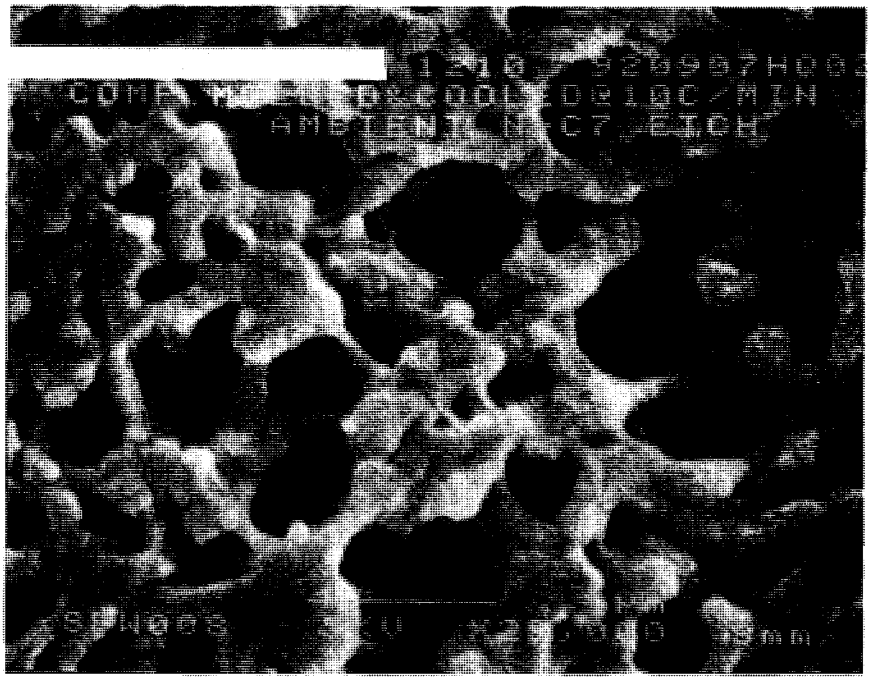

Fig. 8.

distributions of unknown copolymers. Furthermore, the same "calibration" plot can be extended for non-crystalline samples beyond the fractionation capabilities of TREF.

To test the validity of this proposed hypothesis, we used two ethylene-propylene rubbers containing 45 wt% ethylene and 75 wt% ethylene which exhibited 0% and 12% crystallinity, respectively. The normalized beta linewidth of the amorphous EP rubber yielded a SCBD <1.01, a very narrow branching distribution. The normalized beta linewidth of the second product yielded a SCBD of 2.40, a much broader distribution. These two materials were both made by the same supplier. We suspect that the two materials were made with different catalyst systems and process conditions for the very different SCBD. Reportedly, for the ethylene propylene system, vanadium based catalysts produce very narrow distributions while titanium catalyzed products very broad.

The DMA technique works very well with amorphous to low crystallinity materials such as VLDPE. For higher crystallinity materials of 0.92 or greater density the beta relaxation became indistinct and merged into part of the alpha relaxation. This overlapping relaxation and the accompanying reduction in beta intensity makes the technique less sensitive above these densities. Another technique to characterize the material heterogeneity is electron microscopy. This technique works on any material regardless of crystallinity. The primary task is to create image contrast which can be associated with heterogeneous material fractions in the dimension scale of analysis. For crystalline materials this contrast can be created with selective solvent extraction of a particular soluble amorphous component or selective oxidation of a particular component. For amorphous materials the primary technique of contrast generation will be through selective oxidation. This is illustrated in Fig. 8 The size and concentration of any particular component can then be quantified through image analysis techniques.

4. Summary

Material heterogeneity is an important factor which has a major influence on product performance. Polymer heterogeneity can be quantitatively characterized with thermal analytical techniques. Among fairly crystalline polymers, material heterogeneity can be qualitatively assessed by a single DSC run to investigate the melting temperature and crystallinity. To quantify the heterogeneity, it will be necessary to characterize the material with TREF and electron microscopy. Among the lower crystallinity polymers DSC also provides a qualitative assessment of heterogeneity. For these materials quantitative characterization can be equally achieved with TREF, DMA or electron microscopy. For very low crystallinity or amorphous materials only DMA or electron microscopy can be effective in the characterization of material heterogeneity. No one technique can be used to realistically characterize materials over the complete range of composition .

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