Effect on the Elastic Modulus of High-Density Polyethylene of Differing Thermal Treatments

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SYNOPSIS

The effect of different thermal treatments on the elastic modulus of high-density polyethylene has been studied in order to determine which of the parameters defining the polymer morphology has the major effect on the modulus. After examination of the effects of crystallinity, spherulite size, and lamellar thickness, it is concluded that it is the spherulite size which plays the dominant role in controlling the magnitude of the modulus. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The heat treatment which is applied during processing is one of the main factors which affects the mechanical properties of polymer end products. Since polymers differ from metals or ceramics in that the elastic modulus may vary with its morphology, this article is primarily concerned with the dependence of the modulus on the heat treatment. The physical significance of the modulus in terms of molecular movements is still unresolved, and, in any case, it is strongly dependent upon the time scale of the experiment. In this article, the modulus will be taken as the ratio of applied stress to measured strain at a time scale of approximately 0.1 s. The physical significance of the quantity will be discussed in a later article.[1]

Experiments have been carried out to develop an understanding of the relationship between the microstructures of high-density polyethylene developed by different thermal treatments and the mechanical properties of the polymers which result from these microstructures. The ultimate aim is to develop an understanding which will enable polymer engineers to control the mechanical properties of the end products, by changing the microstructure through thermal or other treatment.

Effect of Thermal Treatment on Polyethylene Morphology

The crystallinity, spherulite size, and lamella thickness are all significantly dependent upon the applied thermal treatment. Experiments have therefore been carried out to determine the extent to which crystallization temperature, crystallization time, and cooling rates affect these aspects of the morphology and, hence, the elastic modulus of high-density polyethylene.

A change in the crystallization temperature affects not only the rate of crystallization but also the size of spherulites which are formed. The critical nucleus dimensions for growth decrease with increasing undercooling for a given surface free energy. At small undercooling, the critical size required for the formation of the equilibrium nucleus is relatively large and few spherulites develop. At large undercooling, the critical size required for the equilibrium nucleus is much smaller, and many spherulites develop.[2,3]

The crystallization time will affect the overall crystallinity. The subsequent or secondary crystallization is normally accompanied by an increase in the density of spherulites with time. Since the secondary crystallization takes place at temperatures higher than the initial crystallization temperature, this is also responsible for increased lamellae thickness.[4,5] Similarly, increasing the holding time at the crystallization temperature increases the lamella thickness.[6,7]

Introducing different cooling rates to the polymer is equivalent to introducing different undercooling and, hence, different crystallization temperatures.[8] In industrial practice, the effect is to introduce different spherulite dimensions.

EXPERIMENTAL

The polymer used was high-density polyethylene supplied in powder form without additives by Hoechst and designated GA7260 (M_w = 97,900 and M_n = 10,000). Samples were compression-molded at 180°C in an induction-heated platen press and, subsequently, a number of different treatments were applied to these samples.

In the first group of samples, different cooling rates were applied to the molten polymer in order to induce different morphologies. Slow cooling was achieved by leaving the polymer melt in the platen press at the maximum pressure to air cool it to room temperature. Samples made from this type of plaque were termed "air-cooled (AC)" samples. Fast cooling was achieved by plunging the complete mold assembly containing the molten polymer into the ice-water mixture. Samples made from this type of plaque were termed "water-quenched (WQ)" samples.

In a second series of experiments, instead of slow or fast cooling, the polymer was crystallized in a second platen press which had been preset to the desired temperature. After holding the polymer at different crystallization temperatures for 150 min at atmospheric pressure, it was plunged into the ice-water mixture. The crystallization temperature was varied between 100 and 129°C with the idea of controlling the lamellar thickness. After the initial heat treatment at 180°C, the polymer was held in a platen press at specified crystallization temperatures for 150 min. As the crystallization temperature approached 100°C, the change in lamellar thickness due to variation in the crystallization temperature levels off, and for a crystallization temperature higher than 125°C, the time required for complete crystallization increases drastically.[9] Therefore, crystallization temperatures lower than 100°C and higher than 129°C were not applied.

In the last group of samples, for a given crystallization temperature, different crystallization times were applied. After the initial treatment at 180°C, the plaques were held at T_c = 125 or 120°C in a platen press under atmospheric pressure for 150, 240, 600, 1500, 2400, and 6000 min and then plunged into the ice-water mixture. Samples are designated so that following the group number the first four digits refer to the crystallization time and the last three digits refer to the crystallization temperature.

Crystallinity and Morphology Determination

Crystallinity of the samples was determined by density and by DSC. The densities were determined by using a density gradient column. The enthalpies of fusion were determined from the melting endotherms obtained with a Perkin-Elmer DSC2B at a heating rate of 10 K/min. The enthalpies of fusion were converted to degrees of crystallinity by taking 69 cal/g as the enthalpy of fusion of the perfect polyethylene crystal.[10,11]

A small-angle light-scattering method was used to measure the spherulitic dimension of the polymer samples. The sample which had been cut into a 10 μm section using a sledge microtome was placed between a microscope slide and a coverslip. When a monochromatic laser beam wavelength of 632.8 nm was passed through the system, a four-leaf H_v SALS pattern was obtained for samples which had a well-defined spherulitic structure.[12] A photoelectric cell was used to scan the H_v SALS pattern in order to locate the maximum intensity. The scattering angle θ, the angle between the main beam and the scattered light at maximum intensity, and the wavelength of the laser beam were used to calculate the average spherulite radius R.

The lamella thickness was measured by DSC. These measurements were based on the fact that lamellae with small dimensions melt at lower temperatures and the melting temperature increases with increasing lamellar thickness. If it is assumed that at a given temperature for a melting sample of polymer the rate of heat input is proportional to the fraction of lamellae whose thickness is given by the Thomson formula, then the distribution of lamellae thickness can be obtained directly from the DSC melting curve.[13] A heating rate of 10–20 K/min was suggested to be the most appropriate heating rate for semicrystalline polymers on the basis of optimizing the relation of the recrystallization and reorganization rate of the polymer to the DSC scanning rate.[14]

The elastic moduli of samples cut into a 6.4 × 45.7 mm dimension from 0.5 mm-thick molded plaques were measured on a Rheometrics solids analyser (RSAII) at two different temperatures of T = 28 and 48°C. All tests were done using a dual cantilever bending fixture. The sample extension at elevated temperatures was compensated by the spring-loaded clamps in the fixture. The elastic modulus was re-

Table I   Effect of Morphology–Crystallinity on Elastic Modulus for AC and WQ Samples

Group I	Spherulite Size (μm)	Lamellar Thickness (Å)	Crystallinity by DSC (%)	Elastic Modulus (GPa)
AC	19.0	155.4	74.9	4.1
WQ	10.5	128.1	66.7	3.1

corded at a static strain sweep mode at a strain of 0.1%.

RESULTS AND DISCUSSION

To examine the dependence of elastic modulus on morphology–crystallinity, the different microstructures produced by various heat treatment have to be analyzed. A difference in crystallinity values was found between the density and the enthalpy of fusion (DSC) methods. The authors claim that as the crystallinity of the polymer increases amorphous chains—between the crystallites, particularly in the interfacial region—become more and more oriented and go into an ordered state, increasing the overall density of the polymer. Crystallinity calculations based on density ignore the increase in the amorphous density and refer to a constant amorphous density, consequently resulting in a discrepancy between the crystallinity values measured by a density method and by a DSC method. These differences can also be explained by a comparative analysis of the Raman spectrum together with the degree of crystallinity results obtained by the two methods. Strobl and Hagedorn described a way of obtaining the level of crystallinity in semicrystalline polyethylene from an analysis of the Raman spectrum. Their analysis of the Raman spectrum not only provides a means of determining the fraction of crys-

talline and amorphous phases but also the fraction of interfacial material between crystalline and amorphous phases.[15]

This analysis of Raman spectrum was used by Glotin and Mandelkern in a study of the morphological structure of the polyethylene and the difference between crystallinity determination by density and DSC methods.[16] They concluded that the degree of crystallinity determined from density measurements is equal to the sum of the crystalline and interfacial contents obtained from the Raman analysis, while enthalpy of fusion measurements yields values equal to the crystalline content. Therefore, the difference between crystallinities measured by density and enthalpy of fusion is actually equal to an interfacial contribution. The difference in crystallinities measured in this investigation also supports the proposition of an interfacial contribution. It is found that, as the crystallinity increases, the difference between crystallinity values obtained by density and crystallinity methods decreases. Decreasing divergence between the two methods of crystallinity determinations with increasing crystallinity is consistent with the fact that the difference between the two methods of crystallinity determination is due to the effect of a noncrystalline-interfacial region.

Table I shows the measured elastic modulus and morphology–crystallinity results for the samples subjected to markedly different cooling rates. The

Table II   Effect of Morphology–Crystallinity on Elastic Modulus at Constant Time Duration but at Different Crystallization Temperatures

Group II	Spherulite Size (μm)	Lamellar Thickness (Å)	Crystallinity by DSC (%)	Elastic Modulus (GPa)
0.150.100	11.3	132.0	65.0	3.207
0.150.105	11.9	129.0	68.6	3.417
0.150.110	13.3	136.6	68.9	3.438
0.150.115	16.6	145.0	70.9	3.482
0.150.120	20.4	162.7	72.1	3.541
0.150.125	—	185.7	72.3	3.655
0.150.127	—	189.8	73.4	4.358
0.150.129	—	200.6	69.6	3.911

Table III **Effect of Morphology–Crystallinity on Elastic Modulus of Various Crystallization Time at a Constant Crystallization Temperature of 120°C**

Group III	Spherulite Size (μm)	Lamellar Thickness (Å)	Crystallinity by DSC (%)	Elastic Modulus (GPa)
0150.120	20.4	162.7	72.1	3.54
0240.120	19.9	163.7	72.9	3.55
0600.120	19.8	169.8	74.2	3.63
1500.120	20.4	178.7	75.1	3.57
2400.120	19.9	174.2	76.0	3.68
6000.120	20.2	180.1	75.8	3.59

results suggest that the AC samples do have a higher elastic modulus than that of the WQ samples; however, since the spherulite size, lamellar thickness, and crystallinity are all larger for the AC samples, it is not possible to associate the higher modulus with any of the specific morphological features.

Table II shows the elastic moduli and morphological parameters for samples crystallized for a constant time duration of 150 min at different crystallization temperatures of 100–129°C. Increasing crystallization temperature seems to increase not only the spherulite size and lamellar thickness but also the crystallinity of the samples. Therefore, the observed elastic moduli cannot be attributed to a specific parameter.

Table III shows the elastic moduli and morphological parameters for samples crystallized for different times at a constant crystallization temperature of 120°C. While crystallinity and lamellar thickness both increase with holding time at a crystallization temperature of 120°C, spherulite size and elastic modulus change little with holding time. It can be concluded that in spite of an increase in lamellar thickness (~ 20 Å) and an increase in crystallinity (~ 4%), the elastic modulus does not seem to change significantly and it can be related to a constant spherulite size. There appears to be little relationship of elastic modulus to morphological parameters other than to spherulite size and so further analysis will be concerned with the role of these morphological units in determining the measured elastic modulus.

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