Influence of Thermal and Mechanical Histories on the Viscoelastic Behavior of Drawn Polyethylene

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Synopsis

Storage and loss elasticity complex moduli E' and E'' and temperatures at which the α relaxation takes place are studied with respect to thermal history, deformation speed, and molecular weight distribution of drawn linear polyethylene. Maximum values of E' and E'' increase with draw ratio of the hot-drawn samples, and the α relaxation temperatures increase by around 10°C when the polyethylene filaments are annealed at 110°C. The activation energy of the process, considered as a single one because the symmetrical shape of the maxima, increases with draw ratio, and this increase is less pronounced when the filaments are annealed. Annealing of the filaments produces a decrease in their E' values, but this decrease is almost negligible for filaments obtained from polyethylene with a broad molecular weight distribution. The final crystallinity of the filaments drawn at room temperature and subsequently annealed is higher for the filaments obtained at lower drawing speed.

INTRODUCTION

Dynamic mechanical behavior of crystalline polymers is more complex than that of amorphous ones, and their relaxations depend on molecular weight, molecular weight distribution, and thermal history. When crystalline polymers are oriented by drawing, the variables involved in the process obviously affect the viscoelastic relaxations, but these effects have been rarely reported. The main conclusion reached is that orientation in polyethylene, polypropylene, and poly(oxymethylene) produces a shift in the α relaxation, which is associated to the crystalline part of the polymer, toward higher temperatures when the temperature of the drawing process is increased.[1,2] The values of the storage and loss parts of the elasticity complex modulus, E', and E'', are highest when the drawing is carried out at the temperature of the α relaxation and are higher than those of undrawn samples.

The influence of drawing on the α relaxation of polyethylene is still controversial.[2-4] Thus, it is accepted that undrawn polyethylene samples show α relaxation at higher temperatures than drawn samples. However, the values of E' and E'' for this relaxation of undrawn polyethylene were reported to be either higher[3] or lower[2,4] than those of drawn polyethylene.

The aim of the present work is to study the dependence of the α relaxation on thermal history, drawing speed, and molecular weight distribution of drawn high-density polyethylene.

EXPERIMENTAL

Filaments of two different polyethylene samples were extruded with draw ratios 6, 8, and 10. The extrusion process was carried out at 280°C, cooling at 38°C, and drawing at 95°C. Roll speed controlled the draw ratios.[5] Filaments of draw ratio 6 were subsequently drawn at room temperature by means of an Instron dynamometer, using two different crosshead speeds, 0.1 and 10 cm/min.

The molecular weights of the two commercial polyethylene samples A and B (Marlex 6003 and 6009, respectively) were determined by viscometric measurements in decalin at 135°C. By application of the Mark–Houwink equation[6]

$$[\eta] = 6.77 \times 10^{-4} M_w^{0.67}$$

molecular weights are 1.34×10^5 and 1.27×10^5 for samples A and B, respectively.

Molecular weight distributions of the original samples were obtained by means of a Water Associates 150 C, ALC/GPC apparatus.

Densities of the filaments were measured using a gradient column filled with ethanol–water. Crystallinities were calculated through density results considering 1.000 and 1.172 cm^3/g as the specific volumes of the crystal and wholly amorphous polyethylene, respectively.[7]

Crystallinities were also determined by using a DSC 1B Perkin–Elmer differential scanning calorimeter. Melting enthalpy of wholly crystalline polyethylene was considered to be 70 cal/g.

A Rheovibron dynamic viscoelastometer was used to study the dynamic mechanical behavior of the filaments in the range from room temperature to 110°C, at four fixed frequencies, 3.5, 11, 35, and 110 Hz. The filaments were heated at a rate of 1°C/min while the viscoelastic measurements were performed, and these were subsequently repeated two times. The filaments were loosely heated in a separate device comparing the densities thus obtained with those of the filaments annealed at a fixed position in the Rheovibron chamber.

RESULTS AND DISCUSSION

The α Relaxation in Oriented Filaments

Without Thermal Treatment

In Table I, we have listed the results referred to the α relaxation for oriented samples at different draw ratios without any further thermal treatment. The α relaxation is the temperature at which the dynamic loss modulus (E'') maxima take place, together with the numerical values of the moduli at the maxima. The correlation between the E'' values and the draw ratio shows that E'' increases with orientation and crystallinity, and the peak temperature is about 10°C lower than the temperature for annealed filaments, as was previously reported.[4]

Moreover, the activation energy has been calculated assuming a single process for the α relaxation, according to the symmetrical shape of the α maxima (Fig. 1). The values of the activation energy are about 20 kcal/mol, values which can

TABLE I
Alpha Relaxation Data for Original Filaments

Sample	Draw ratio λ	$E''_{max} \times 10^{-8}$, N/m^2		T_α, °C		ΔH, kcal/mol
		110 Hz	3.5 Hz	110 Hz	3.5 Hz	
	6	7.64	4.44	67	29	19 ± 2
A	8	8.00	6.32	59	30	24 ± 3
	10	10.80	6.44	65	41	29 ± 3
	6	4.84	4.52	64.5	33.5	23 ± 2
B	8	7.52	6.56	62	33	25 ± 3
	10	8.56	7.60	59	33	26 ± 3

be predicted by the relation $\Delta H = 0.060 T_{(1\ Hz)}$ established by Heijboer.[8] The dispersion of the activation energy values is higher for unannealed samples than for thermally treated samples, although there is an increase of this energy with the draw ratio. This effect is more pronounced with samples of higher molecular weight.

The increasing values of E'' with draw ratio and crystallinity show that the orientation process increases the crystalline orientation with a corresponding increase in the activation energy. These results are comparable to those found for different polyolefins.

The temperatures for the α relaxation correspond to the values found for polyethylene and chlorinated and oxidized polyethylene.[4,9-13]

Thermally Treated Filaments

The thermal history of the filaments has an important influence on the values of E' and E''. When the filaments are used for the first time in the dynamic experiments, the annealing treatment imposed on the samples in order to perform
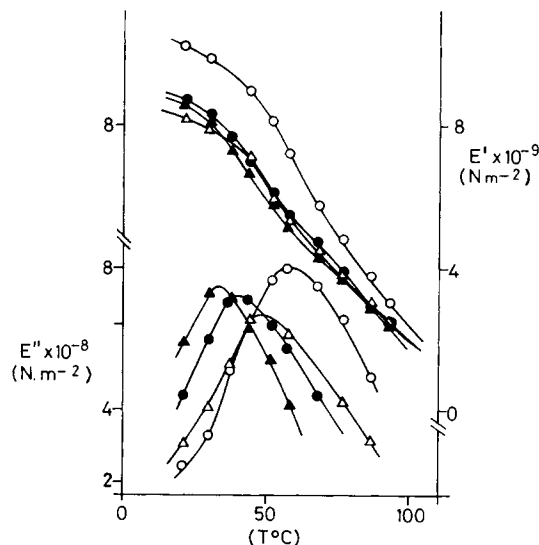

Fig. 1. Temperature dependence of storage (E') and loss (E'') parts of the complex modulus for original filament of polyethylene B having draw ratio 10. Measurement frequencies are: 110 (O), 35 (△), 11 (●), and 3.5 Hz (▲).

the measurements modifies the values of the moduli and the temperature for the α relaxation. The loss moduli, at a given draw ratio, decrease when the samples are annealed, and the α relaxation temperature is about 10–15°C higher than in the unannealed samples, although there is practically no variation with the draw ratio. It must be noted that these values are not reversible, and they remain unchanged after consecutive heating runs, as shown in Figure 2.

The effect of the heat treatment on the α relaxation has been analyzed in polyethylene single crystals[13,14] and in low-molecular-weight polyethylene.[15,16] The α mechanism has been associated with the crystalline phase, and different approaches concerning the details of this molecular motion have been taken.[17-21] Thus, the α relaxation is considered to be a complex process associated with chain rotation–translation, twisting in the lamellae, reorientation of the chain folds, tightening of interlamellar links, and removal of cilia by lamellae thickening.[17] Other different sources of molecular motions have also been considered.[22-27]

Many studies have been carried out on the mechanical and dielectric relaxation behavior of n-paraffins to explain the mechanical properties of polyethylene, but different studies indicate that n-paraffins may not represent good model compounds for polyethylene.[16]

The α relaxation, thus, seems to be a very complex process associated not only
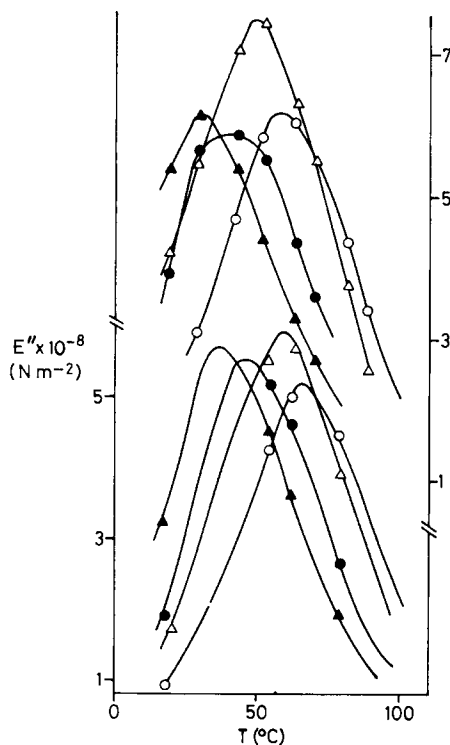
Fig. 2. Temperature dependence of loss part (E'') of the complex modulus for a filament of polyethylene A drawn by Instron to draw ratio 8, at crosshead speed 1 mm/min. Upper curves correspond to the first run of measurements. Solid lines of lower curves correspond to the same filament, after annealing at 110°C, during the second run of measurements (points omitted). Singular points superimposed on these curves correspond to further annealing during the third run. Measurement frequencies are: 110 (O), 35 (△), 11 (●) and 3.5 Hz (▲).

with the crystalline phase but also with the amorphous phase. Takayanagi et al.,[23,24] following previous suggestion of Markovitz et al.,[25] have considered the α relaxation as two overlapping processes which allow to resolve the experimental results in two different peaks with different activation energies.

As was commented above, we have not attempted to resolve the α relaxation because the relaxation was very symmetrical and appeared at higher temperatures when the samples are annealed, as is the behavior of polyethylene single crystals. It is clear that this process envisages a contribution to the α relaxation from both parts, crystalline and amorphous, and the orientation and the thermal treatment modify the size of the amorphous layer and the size of the crystallities. These modifications lead to slight differences of crystallinities in the samples, as has been shown. Conformational or localized defects may be excluded because, in any case, they are only a very weak contribution to the total process.

Influence of Deformation Rate on α Relaxation

The orientation at room temperature of filaments with $\lambda = 6$ to draw ratios 8 and 10 produces samples with different characteristics depending on the deformation rate. Thus, when the rate is 100 mm/min, the maximum stress resistance is 21 N, and it is only 12 N when the rate is 1 mm/min.

The total crystallinity practically does not change with the deformation rate. However, annealing increases the crystallinity, and this increase is higher when the samples have been slowly deformed and the possibilities for orientation and reorganization are more favored.

Table II shows the results for E'', T_α, and ΔH for samples deformed at two different rates and two different draw ratios, without and with thermal treatment. The variation of the loss moduli shows a decrease with the rate of deformation. The E'' maxima show smaller variations than in the untreated filaments; this fact is due to the invariance of E' in the deformed samples. The different behavior of the annealed samples is due, firstly, to the invariance of E' and damping in the deformed samples and, secondly, to the temperature of deformation. As the deformation and the original drawing processes were performed at room temperature and 95°C, respectively, this difference in temperature affects the shrinkage phenomenon.[28]

TABLE II
Alpha Relaxation Data for Filaments Drawn by Instron Machine

Sample	Final λ	Drawing sped mm/min	$E''_{max} \times 10^{-8}$, N/m^2)		T_α, °C		ΔH kcal/mol
			110 Hz	3.5 Hz	110 Hz	3.5 Hz	
A	8	1	6.24	6.20	58	31	28 ± 3
	10		9.2	8.40	60	30	25 ± 3
A (annealed)	8	1	5.2	5.72	65	36	24 ± 3
	10		8.72	8.80	70	38.5	26 ± 3
A	8	100	4.88	5.00	61	30	22 ± 2
A (annealed)	8	100	4.88	5.36	71	48	22 ± 2
B	8	1	5.84	5.60	61	30.5	23 ± 2
	10		8.08	6.96	61.5	30.5	23 ± 2
B (annealed)	8		5.68	5.68	63	33	21 ± 2
	10	1	8.76	7.36	64.5	33	22 ± 2
B	8	100	6.36	4.76	62.5	32.5	23 ± 2
B (annealed)	8	100	5.96	5.84	61	31	22 ± 2

Here, again, the symmetry of the E'' vs. T curves (Fig. 3) is quite unquestionable, and there is no possibility of assuming two diferent peaks. In this situation, the activation energy is determined and the values are of the same order as in undeformed samples (Table II).

Influence of Molecular Weight Distribution on α Relaxation

All mechanical properties of linear polyethylene are dependent on molecular weight and on the crystallization and orientation conditions.[29-31] Molecular weight distribution plays a fundamental part on behavior, because thermal and mechanical histories are influenced by the contribution of the molecular species in the system.

In our case, samples A and B differ very little in viscosity-molecular weight average, although the melt indexes are quite different (0.3 and 0.9 g/10 min, respectively). An analysis of GPC of the two samples shows that the molecular averages and the dispersities are very different (Table III). These values indicate that the polydispersity is lower for sample A. However, the melting temperatures and the crystallinities are very similar, and there are no significant differences, as must be expected for these unfractionated systems. With annealing, the crystallinity increases slightly more in sample A than in sample B, and the differences between the calorimetric and the density cristallinities agree with previous reports.[13,30]
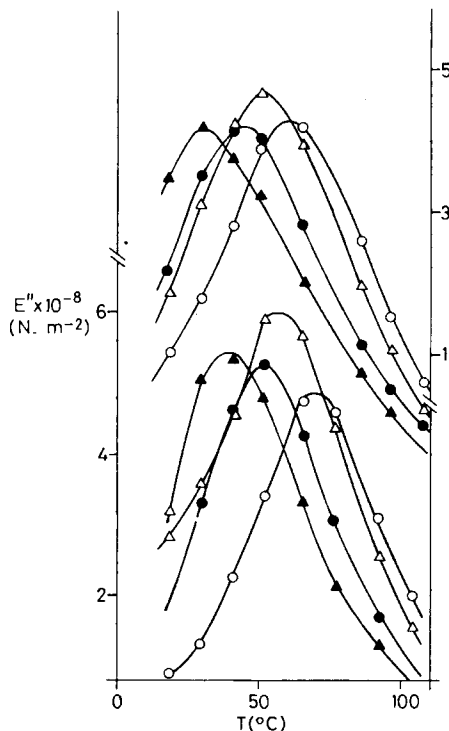

Fig. 3. Temperature dependence of loss part (E'') of the complex modulus for a filament of polyethylene A drawn by Instron to draw ratio 8, at crosshead speed 100 mm/min (upper curves). Lower curves correspond to the annealed filament.

TABLE III
Average Molecular Weights for Polyethylene Samples

	Sample A	Sample B
$\overline{M}_n$	15,300	11,700
$\overline{M}_w$	130,600	146,600
$\overline{M}_z$	785,300	994,500
$\overline{M}_w/\overline{M}_n$	8.5	12.5

For sample A, the decrease in E' when the sample is annealed is more pronounced than in sample B. Figures 4 and 5 show these values, referred to the temperature at which the maximum in the α relaxation appears, although the conclusion is the same when moduli E' are taken at other temperatures.
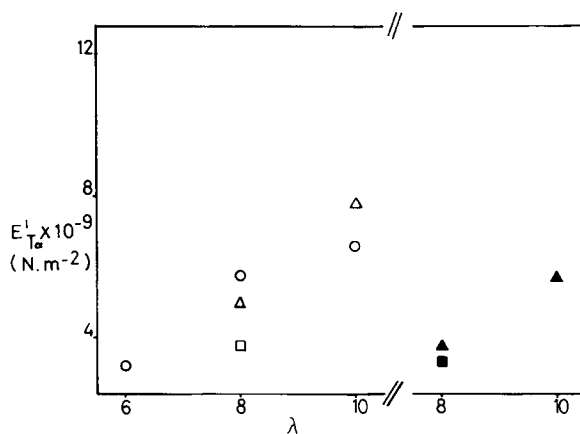

Fig. 4. Dependence of storage part (E') of the complex modulus on draw ratio for filaments of polyethylene A drawn by Instron at two crosshead speeds: 1 mm/min ($\triangle$) and 100 mm/min ($\square$). Filled symbols correspond to the annealed filaments.
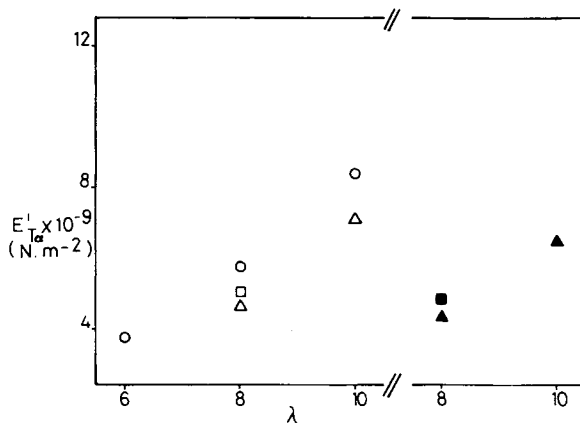

Fig. 5. Dependence of storage part (E') of the complex modulus on draw ratio for filaments of polyethylene B drawn by Instron, at two crosshead speeds: 1 mm/min ($\triangle$) and 100 mm/min ($\square$). Filled points correspond to the annealed filaments.

Another difference is that, when the samples are deformed at room temperature from $\lambda = 6$ to $\lambda = 8$, the values of E' are lower than those of the original oriented filaments, although this decrease in E' is independent of the deformation rate for sample A but not for sample B.

The main conclusion from these experimental results is that the molecular weight distributions influence the distribution of the crystallite sizes and the amorphous layers for the same thermal or mechanical history. For a narrower molecular weight distribution, more homogeneity in sizes must be expected from general conclusions on the influence of molecular weight on the crystallization conditions, and variations in mechanical parameters are related with more homogeneous microstructures which can be obtained by orientation and annealing. When the molecular weight distribution broadens, the distribution of sizes is also wider and the final result is, again, a less significant variation. Moreover, the annealing temperature is high enough to completely melt the very low-molecular-weight species which are present in sample B. Therefore, there is no contribution of these species to the total increase in crystallinity.

Complete analysis of the influence of molecular weight requires fractionated material, and further analysis of this problem is in preparation.

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