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Mechanical Relaxation in Polyethylene Crystallized With Various Degrees of Lamellar Orientation

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The mechanical relaxation behavior of a set of well-characterized samples of polyethylene crystallized with different degrees of lamellar orientation is reported. The various samples ranged in morphology from unoriented isotropic samples to ones which showed a high degree of orientation of the *b*-axis along the sample growth direction. The mechanical measurements were made using a torsion pendulum apparatus of standard design, the direction of shear being normal to the *b*-axis for the oriented samples. The temperature range covered was from 100 to 400 °K. No definite effects attributable to orientation were observed for either the γ or β relaxation process, whereas for the α relaxation results for G'' indicate that a slight decrease in peak height resulted from the presence of lamellar orientation, particularly on the high temperature side of this peak. Data for the real and imaginary parts of the complex shear compliance are also discussed.

Key Words: Polyethylene, mechanical relaxation, lamellar orientation, torsion pendulum, shear modulus, shear compliance, orientation effects.

1. Introduction

Density and morphological factors such as lamellar thickness and spherulite size are known to affect the relaxation behavior of crystalline polymers. This dependence on morphology is often very complicated, affecting the loss measures tan δ, G'', and J'' in different ways [1][1] and making it difficult to determine the molecular mechanisms responsible for the various relaxation processes observed.

One of the morphological variables that has been little studied is orientation, despite the fact that in simpler solids, [2, 3, 4] for certain crystal symmetries, and for certain molecular mechanisms, the direction of the applied stress with respect to the crystal axis is known to affect the relaxation behavior. In polyethylene, Takayanagi [5] has reported striking differences between unoriented samples and samples crystallized with preferred orientation of the *b*-axis. The experiments were in tension, the direction of stress being along the *b*-axis. However, the two samples were of somewhat different compositions of polyethylene, and it is not clear to what extent the observed differences were due primarily to orientation.

In addition, Eby and Colson [11] have shown for samples of polyethylene prepared with an oriented surface layer and for the same samples with the oriented layer removed that the mechanical relaxation behavior in shear is measurably different.

It is the purpose of the present paper to report the mechanical relaxation behavior (in shear) of a set of well-characterized samples of polyethylene having different degrees of lamellar orientation, the direction of shear being normal to the *b*-axis for the oriented samples. As will be seen, no definite effects attributable to orientation were found for either the γ or β relaxation process. However, for the α relaxation the experimental results for G'' indicate that a slight decrease in peak height resulted from the presence of lamellar orientation, particularly on the high temperature side of this peak.

2. Experimental Procedure

2.1. Sample Preparation

The samples were prepared from Marlex 6050[2] polyethylene supplied through the courtesy of R. J. Martinovich of the Phillips Petroleum Company. This polymer contains a small amount of thermal stabilizer and has a weight average molecular weight of approximately 90,000.

A quenched sample and two isothermally crystallized samples were obtained using a technique employed by Passaglia and Martin [1] for samples of polypropylene. The polymer was initially prepared as a flat strip by compression molding. The flat strip was subsequently placed between two strips of aluminum cut to the desired dimensions and the sandwich then wrapped tightly in aluminum foil. The wrapped sandwich was mounted between two bronze plates held together by slight spring tension. The entire

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[1] Figures in brackets indicate the literature references at the end of this paper.

[2] Certain commercial materials and equipment are identified in this paper in order to specify the experimental procedure adequately. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards.

assembly was heated in an oven to 165 °C for about 30 min. One sample was quenched in dry-ice and acetone. The two isothermally crystallized samples were prepared in a crystallization bath, one being held at 127.5 °C for three days followed by rapid cooling to room temperature, and the second being held at 129 °C for 12 days, 128 °C for 1 day, 127 °C for 1 day, and then followed by rapid cooling to room temperature.

The oriented samples were prepared according to a method outlined by Seto and Fujiwara [6] and a diagram of the apparatus used is shown in figure 1. The apparatus consisted of a cylindrical copper block separated by a thin layer of transite (~ 1 mm) from a similar copper block which was water cooled. A hole was drilled down the axis of the assembly. The upper block was maintained at approximately 200 °C while the lower block was at room temperature. The polymer sample, contained in an evacuated glass tube of about 2 mm I.D., was lowered slowly through the hole. Crystallization was restricted to a very narrow region in the vicinity of the insulating layer, and by controlling the rate at which the sample was lowered, samples with varying degrees of lamellar orientation were obtained. For this investigation lowering rates were varied from 19.0 mm/hr, at which rate a sample with essentially no orientation was produced, to 0.28 mm/hr for a sample with a relatively high degree of lamellar orientation.

However, inasmuch as the drop rate also influenced the crystallization temperature—a rapid drop rate corresponding to a low crystallization temperature—a variation in the crystalline lamellar thickness also resulted. That is, the lamellar thickness, or correspondingly the density [7], increased with an increase in the degree of orientation.

Samples grown in this manner show orientation of the *b*-crystallographic axis along the sample growth direction as indicated by the wide angle x-ray photographs presented in figure 2 for four of the samples studied. For samples 3 and **6**, orientation is indicated by arcs representing the (110), and (200) reflections for sample 3, and (110), (200), and (020) reflections for sample 6, whereas for the unoriented quenched or fast cooled samples (1 and 2) (the fast cooled sample was produced in the apparatus just described) uniformly continuous rings are observed corresponding to these reflections.

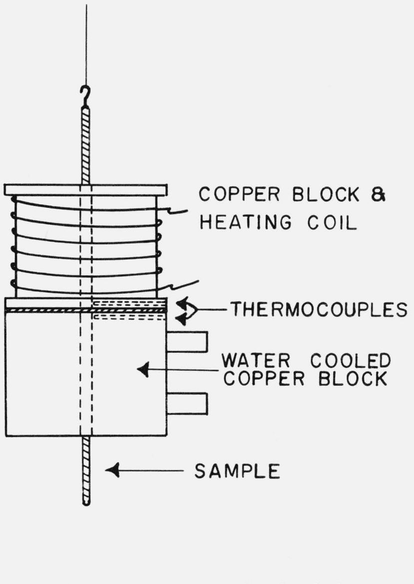

FIGURE 1. *Apparatus for growing oriented polyethylene samples.*

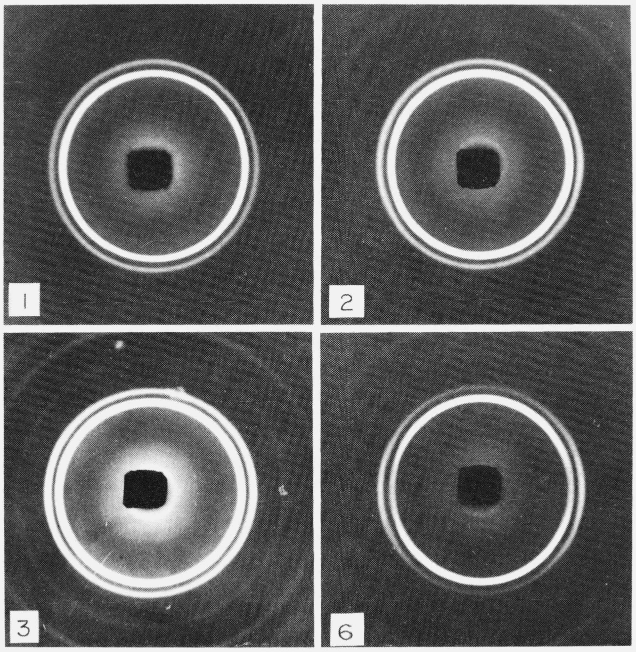

FIGURE 2. *Wide angle x-ray photographs of polyethylene samples: Sample 1, unoriented quenched; Sample 2, unoriented, grown in apparatus described in figure 1; Sample 3, slightly oriented; Sample 6, highly oriented.*

A further indication of the orientation obtained is provided by figure 3 which shows photomicrographs of sections cut longitudinally from the same four samples referred to in figure 2. Here ringed spherulites typical of polyethylene are observed for the unoriented samples. However, for the highly oriented sample 6, the dark bands caused by the twisting of the crystalline lamellae no longer form rings but are now nearly straight lines indicating that a large fraction of the lamellae run parallel to the sample growth direction.

A summary of the characteristics for each sample studied is given in table 1. The densities were measured by the displacement technique using distilled water. The low angle x-ray spacings were determined photographically using a Rigaku-Denki low angle x-ray camera. The column at the far right indicates a rough qualitative estimate of the degree of lamellar orientation for each sample.

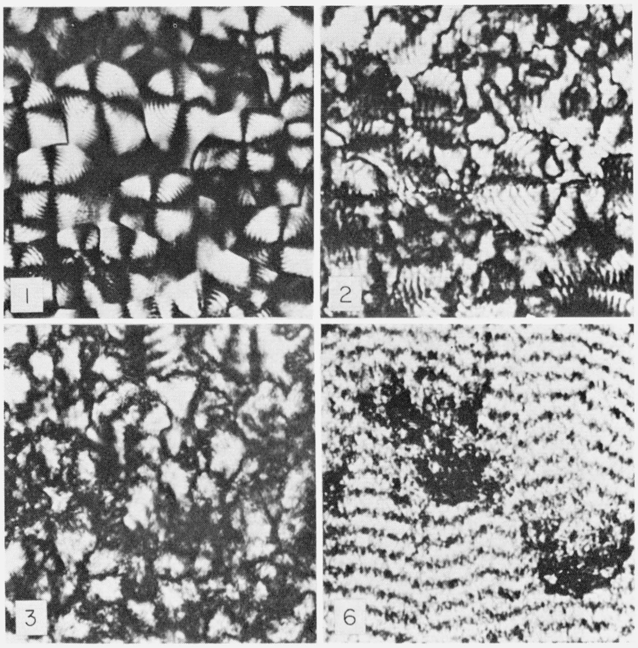

Figure 3. *Photomicrographs of polyethylene samples: Sample 1, unoriented quenched; Sample 2, unoriented, grown in the apparatus described in figure 1; Sample 3, slightly oriented; Sample 6, highly oriented.*

Table 1. *Summary of sample characteristics*

Sample	Density	Approximate Low angle spacings		Degree of orientation
	g/cm³	l_1(A)	l_2 (A)	
1 (Quenched)	0.9516 (24.0 °C)	232	Not measurable	None.
2	.9623 (26.6 °C)	256	119	None.
3	.9704 (26.0 °C)	316	156	Poor.
4	.9710 (25.8 °C)	322	156	Medium.
5	.9730 (24.8 °C)	377	183	Good.
6	.9714 (26.6 °C)	385	164	Good.
7 (Isothermally crystallized)	.9664 (26.5 °C)	275	135	None.
8 (Isothermally crystallized)	.9836 (25.5 °C)	Not measurable	204	None.

It will be noticed, as previously mentioned, that orientation, lamellar thickness, and density all vary in the same direction from sample to sample. That is, due to the manner of sample preparation, an increase in orientation is accompanied by an increase in lamellar thickness and density. This has the unfortunate consequence of making it difficult to correlate an observed change in mechanical properties with a morphological change.

2.2. Apparatus

The mechanical measurements were obtained using a torsion pendulum apparatus which has been described in some detail previously [8].

The samples were made to the proper dimensions so as to provide an operating frequency of about 1 Hz. In the case of the quenched and isothermally crystallized samples, which were flat strips, the thickness dimension varied from position to position on each sample by up to 5 percent, while variations in the other dimensions were small enough to be considered negligible. Therefore, an average sample thickness determined from measurements taken at 10 different positions on each sample was used in calculating the real part of the shear modulus, G'. For each cylindrical rod sample, the diameter of which varied over its length by up to 3 percent, six measurements were made. From these an average diameter was determined for computation purposes.

2.3. Effects of Thermal Expansion

As is customary in studies of mechanical relaxation in polymers, we have neglected dimensional changes with temperature in calculating the moduli, using the dimensions measured at room temperature for this purpose. Generally this is justifiable inasmuch as changes in modulus resulting from thermal expansion are small compared with observed changes in the modulus. It is also justified when relative difference among samples is of interest and the samples are all isotropic. When samples of different orientations are compared, however, the known anisotropy [9] of the thermal expansion of polyethylene must be considered.

The moduli are sensitive to the transverse dimensions of the specimen, being inversely proportional to the cube of the thickness for a flat specimen, and to the fourth power of the radius for a cylindrical one. Now, it is known [9] that the *a*-axis of polyethylene has by far the largest expansivity, and our oriented samples are such that this dimension is preferentially normal to the growth direction, whereas in the unoriented sample it has, of course, no preferred direction. This will cause differences in the thermal expansion of the dimension normal to the growth direction, which in turn will cause relative differences in the moduli for the two types of samples at any temperature but room temperature. Without actual measurements on our samples it is impossible to make a quantitative correction for this, but using the data of Swan [9] it can be estimated that the isotropic sample moduli should be lowered by several percent relative to the oriented sample moduli at liquid air temperature, and raised by somewhat less at the highest temperatures achieved. The effect of this difference on the observed differences in the curves will be commented on below.

3. Results

The experimental data for the imaginary and real parts of the complex shear modulus as functions of temperature are presented in figures 4 and 5 respectively. For clarity the data for samples 4 and 5 have not been included, but the results for them will be commented on when necessary.

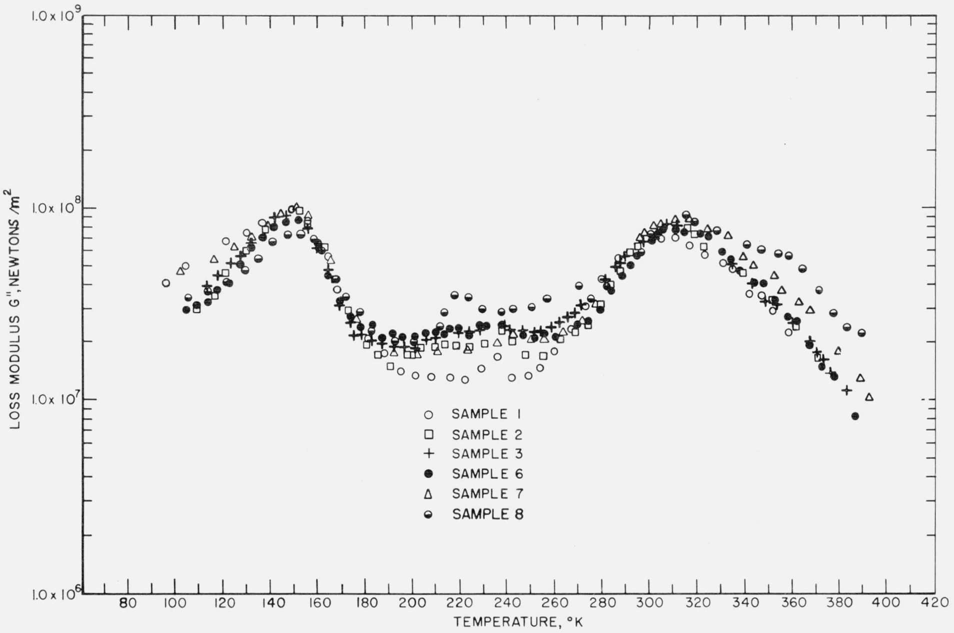

FIGURE 4. *Loss modulus,* G″, *versus temperature for unoriented and* b-*axis oriented polyethylene samples.*

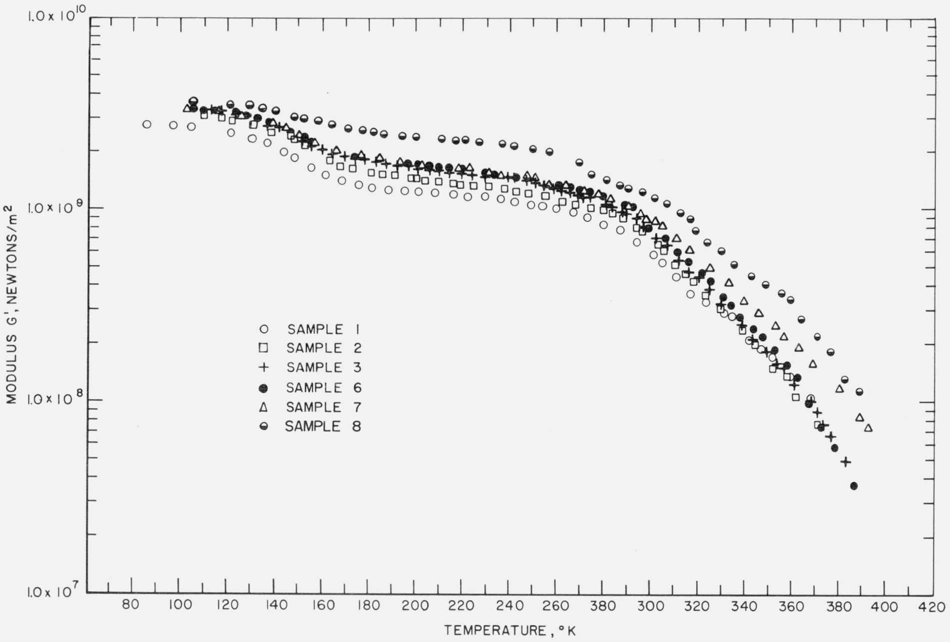

FIGURE 5. *Storage modulus,* G′, *versus temperature for unoriented and* b-*axis oriented polyethylene samples.*

In order to facilitate a more direct comparison of our results with other data reported in the literature the loss modulus G'' will be used for discussion purposes rather than the logarithmic decrement which is customarily reported. From figure 4, which gives the results for G'', the three regions of mechanical relaxation characteristic of polyethylene are observed. We shall here follow the notation generally used and refer to the high temperature relaxation (~ 313 °K) as the α process, the low temperature

TABLE 2. *Experimental results for the observed α- and γ-relaxations*

	γ Relaxation peak				α Relaxation peak			
Sample	T_{max}	ν_0	$G'(T_{max})$	$G''(T_{max})$	T_{max}	ν_0	$G'(T_{max})$	$G''(T_{max})$
	°*K*	*Hz*	*Newtons/m²*	*Newtons/m²*	°*K*	*Hz*	*Newtons/m²*	*Newtons/m²*
1	152	0.840	1.75×10^9	1.0×10^8	303	0.476	5.60×10^8	7.5×10^7
2	152	1.29	2.17×10^9	9.8×10^7	310	.704	5.50×10^8	7.8×10^7
3	146	1.26	2.44×10^9	9.1×10^7	311	.597	5.60×10^8	8.1×10^7
4	146	1.26	2.40×10^9	9.1×10^7	311	.599	5.40×10^8	8.0×10^7
5	146	1.40	2.25×10^9	8.0×10^7	311	.735	6.1×10^8	7.9×10^7
6	151	1.37	2.40×10^9	8.8×10^7	313	.685	5.80×10^8	7.9×10^7
7	151	1.46	2.47×10^9	1.0×10^8	316.5	.727	6.16×10^8	8.9×10^7
8	152	2.53	3.04×10^9	7.4×10^7	315	1.34	8.87×10^8	9.29×10^7

relaxation (~150 °K) as the γ process, and the less well defined relaxation in the region from 200 to 250 °K as the β process.

For convenience a resumé of the experimentally determined parameters for the α and γ relaxation peaks is given in table 2 for the samples investigated. Included in the table are the temperature of the peak maximum, the experimental frequency at that temperature, and the values of G' and G'' at the peak maximum. Because of the rather poor resolution of the β relaxation process and also as a result of some overlap of both the α and γ relaxations in this temperature region, the determination of a peak maximum is too uncertain in most cases and thus no values have been included for this relaxation process.

It is apparent from figure 4 that the behavior in all three regions is dependent upon the morphological characteristics of the specimens. These differences are particularly evident in the α and β relaxations, and less so in the γ. Indeed, when account is taken of the differences in thermal expansion as mentioned above, only slight differences remain at the γ peak, and these are such that the higher density samples have lower relaxations. For the quenched and isothermally crystallized specimens a tail appears on the low temperature side of the γ loss peak suggesting that for these samples relaxation mechanisms exist which are not observed in the others.

In the β region, results for the quenched and isothermally crystallized samples (1, 7, and 8) indicate that the magnitude of G'' increases as the density, and correspondingly the lamellar thickness, increases. For the two oriented samples (3 and 6), the densities of which are intermediate to those for samples 7 and 8, the magnitude of G'' falls within the values found for samples 7 and 8. Therefore, it is concluded that the observed differences in these samples are not due to orientation, but to density and/or lamellar thickness differences.

The results for G'' above room temperature reveal that the α relaxation is comprised of at least two peaks, one peak (α) having a maximum centered near 315 °K, and a second weaker peak, appearing as a shoulder, at higher temperatures in the vicinity of 360 °K. This secondary loss peak will be denoted by α′. For the unoriented samples both the α and α′ relaxations increase with increasing density, but the α′ process is not observed in the quenched sample. The behavior of the oriented samples, however, deviates to a small extent from this trend since in the region of maximum loss, for both the α and α′ peaks, values for G'' are somewhat smaller than would be expected from density considerations alone, based on the results for the unoriented specimens. This will be demonstrated more explicitly later for the main α peak.

The data indicate no significant dependence of the temperature of the maximum on morphology in the γ region, whereas the α peak is shifted slightly to higher temperatures as the density increases (see table 2). This may be due to the dependence of the temperature of the α maximum on lamellar thickness [10].

In figure 5 the data representing the real part, G', of the modulus are given. These data require little comment except that over the entire temperature range covered, G' for the unoriented samples increases with increasing density; and, within the experimental accuracy, the data below room temperature for the oriented samples show no significant deviations from this behavior. However, above room temperature through the region of the α relaxation G' appears to drop off more steeply for the oriented samples than for the unoriented ones.

4. Discussion

It is impossible from the data in figures 4 and 5 to ascribe unambiguously the observed differences in the behavior of the samples to any single morphological parameter. However, the consideration of other published work does permit a fairly definite statement about the effect of orientation.

Illers [10] has carried out experiments employing torsional shear stresses (~ 1 Hz) on samples of unoriented polyethylene crystallized isothermally from the melt. His results showed that both the α and γ relaxations involve at least two processes. That is, weaker secondary loss peaks were observed as shoulders, one being on the low temperature side of the γ peak, and a second on the high temperature side of the α peak. It was found that as the sample density, or lamellar thickness, increases, the magnitude of both components of the γ peak decreases, whereas the β peak as well as both the α and α′ relaxations show increases. At the same time values for the modulus, G', were found to increase as the density increased.

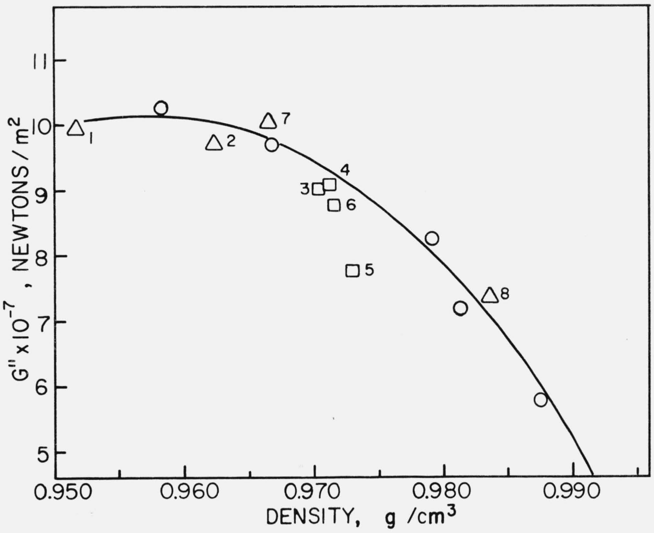

FIGURE 6. *Loss modulus,* G″, *at the peak maximum versus density for the γ relaxation in polyethylene: Δ-unoriented samples, □-oriented samples, ○-data of Illers.*
The solid line represents a least squares fit to all the data points for unoriented samples.

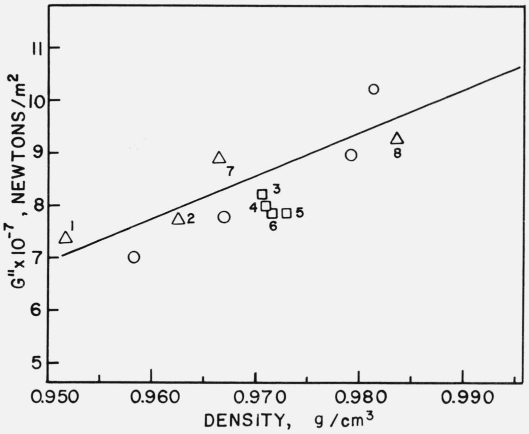

FIGURE 7. *Loss modulus,* G″, *at the peak maximum versus density for the α relaxation in polyethylene: Δ-unoriented samples, □-oriented samples, ○-data of Illers.*
The solid line represents a least squares fit to all the data points for unoriented samples.

In addition, investigations by Eby and Colson [11] and by Flocke [12], using similar techniques, indicate analogous results for samples of polyethylene quenched from the melt and slowly cooled from the melt. However, in the latter two investigations no distinct secondary maxima, or shoulders, associated with the γ process were observed, although the data of Eby and Colson indicate a definite tail on the low temperature side of this peak, the tail being slightly higher for the quenched sample.

Although quantitative correlation is difficult, our own results show the same trends as observed by these workers. With regard to the γ and α relaxations, it is instructive to plot the values of the loss modulus, *G″*, at the peak maximum as a function of sample density, and these plots are given in figures 6 and 7 respectively. Included in the figures are the data of Illers [10], as well as our own.

The solid lines represent a least squares fit to the data points for the unoriented samples including the data points of Illers.

For the γ relaxation it is seen from figure 6 that our own results for the unoriented samples are in good agreement with the data of Illers. Moreover, except for sample 5, the data points for the oriented samples show no significant deviations from this trend. The point for sample 5, however, does depart somewhat from the trend observed for the others. Examination of photomicrographs along with low angle x-ray photographs indicate that sample 6 has a higher degree of lamellar orientation than does sample 5, although 5 has the greater density. Consequently, it is not certain that the lower peak height observed for this sample is a result of orientation or represents an inconsistency in the data. We would conclude from these data that the magnitude of the γ relaxation is not dependent upon orientation, but obviously depends upon density and/or lamella thickness.

These conclusions may be contrasted with the measurements of Takayanagi [5] who, as mentioned in the introduction, found distinct differences in the region of the γ relaxation, between oriented and isotropic samples in tension. However, the oriented specimen was of a different type of polyethylene from the isotropic specimen, and it is not clear that the observed differences were not due to polymer type.

A similar plot is shown in figure 7 for the α relaxation. Again, our own results for the unoriented specimens, 1, 2, 7, and 8 show the same trend as do those of Illers, although here the agreement is not quite as good as in the case of the γ process. However, the data points for the oriented samples 4, 5, and 6, which are all well oriented, fall consistently below the line fitted to the points for the unoriented specimens.

It might be mentioned that if our own data alone are considered an alternative interpretation is possible. That is, a line fitted to the points for samples 1 through 6 will fall well below the points for the isothermally crystallized samples 7 and 8. Since these two samples were prepared somewhat differently one might conclude that the observed effect was a result of the method of crystallization rather than orientation. However we see no reason to exclude Illers' data from consideration, especially in view of the fact that our own results for unoriented samples show the same trends as do his. Therefore, it is concluded that for this process, in addition to density and/or lamellar thickness effects, orientation does have a small effect, and in such a manner that the loss modulus, *G″*, decreases as the degree of lamellar orientation increases, for the type of orientation our samples have.

Concerning the two weaker secondary relaxations also observed, it can be further stated that it appears reasonable to associate the tail, observed both from the present work and from that of Eby and Colson [11], with the loss mechanism found by Illers on the low temperature side of the γ relaxation peak. However, due to the as yet obscure nature of this process, no statement can be made with respect to possible orientational effects. On the other hand, the α' shoulder does appear to be influenced by orientation since, as mentioned earlier, the loss modulus data for the oriented samples 3 and 6 in the region of this shoulder fall below that for sample 7, a sample of lower density than either 3 or 6 (see fig. 4).

The orientation in these samples is such that the *b*-axis of the unit cell is preferentially along the rod axis, the *a*- and *c*-axes being randomly oriented normal to this direction. Since the deformation is torsional and the oriented samples are cylindrical, the strain is such that the *a*-*b* and *b*-*c* faces of the crystal are preferentially sheared in these samples. Inasmuch as the oriented specimens show a lower G'' than the unoriented specimens in both the α and α' regions, it may be tentatively concluded that the relaxation is preferentially activated by shearing the (010), (010), and (100), or (010) and (001) faces of the crystal. When our results are compared with those of Eby and Colson [11], it appears most likely that the relaxation is preferentially activated by shearing of the (010) and (100), or (010) and (001) faces of the crystal, but the tenuous nature of the conclusion is apparent.

Moreover, it may very well be that the relaxation is associated with some aspect of the lamellar "superstructure" rather than processes within the primary crystals. In this regard, the results could just as well be rationalized by saying that the α and α' relaxations are preferentially activated by shear such that fold planes try to move past one another. This would imply that the process is associated with the fold planes themselves or perhaps associated with movement of the chains because of their coupling to the fold planes. Beyond this one cannot say on the basis of these results.

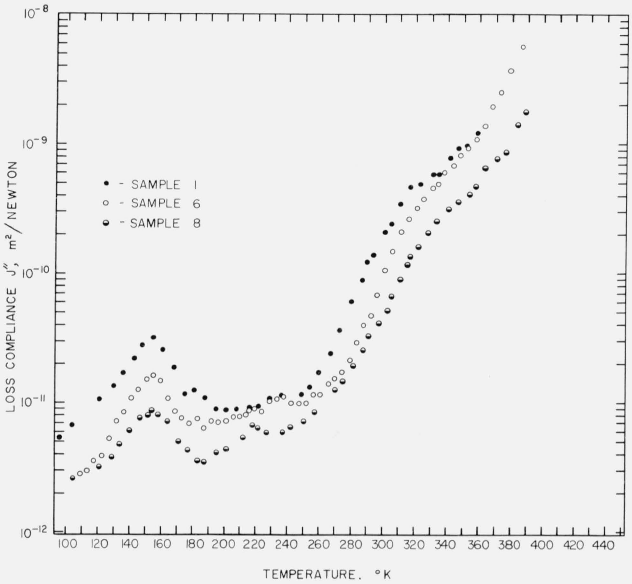

FIGURE 8. *Loss compliance, J″, versus temperature for polyethylene: Sample 1, quenched, unoriented; Sample 6, highly oriented; Sample 8, isothermally crystallized, unoriented.*

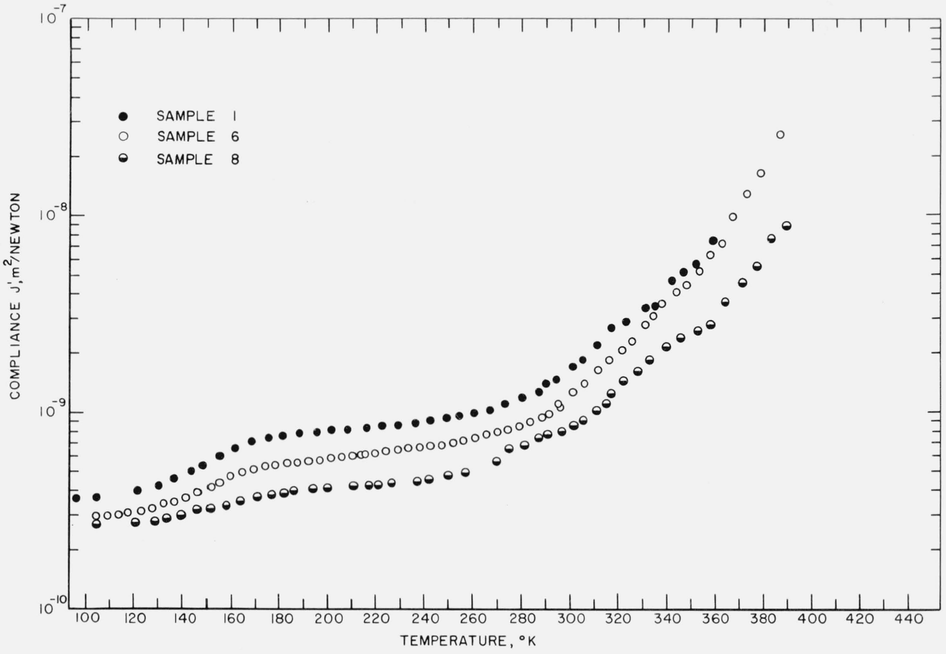

FIGURE 9. *Storage compliance, J′, versus temperature for polyethylene: Sample 1, quenched, unoriented; Sample 6, highly oriented; Sample 8, isothermally crystallized, unoriented.*

5. Other Viscoelastic Functions

It can be seen from figure 4 that G'' is not strongly dependent upon morphological factors, and that except in the β and α' regions all the samples are nearly the same. It has been pointed out [1] however that the relationship of extent of relaxation to density and other morphological factors depends upon whether the various samples are compared at constant macroscopic stress or macroscopic strain. This comes about because crystalline polymers are mechanically composite systems consisting of a reasonably well-ordered crystalline phase and less well-defined interlamellar regions which may partake of some of the characteristics of an amorphous phase. In the case of polypropylene [1], for instance, one can come to opposite conclusions about the site, if not the nature, of the relaxation process depending upon whether one compares samples of different morphologies at constant strain by considering the behavior of G'', or at constant stress by considering J'', the shear loss compliance.

We have, therefore, shown in figures 8 and 9 J'' and J' for samples 1, 6, and 8. All the other samples fall within the two extremes represented by samples 1 and 8. It is to be noted that whereas on the G'' plot (fig. 4) the curves were nearly coinsident in the α and γ regions but separated in the β region, the opposite is now true. The curves are more nearly coincident in the β region but separated in the α and γ regions. Moreover, whereas on the G'' plot the curve for sample 8 was higher in the α region but lower in the γ than for sample 1, it is now lower throughout the whole temperature range.

Finally, it should be mentioned that, although not shown, an effect due to orientation is also reflected in J'' if the data for all the samples are considered. Unfortunately however, J'' does not show a definite peak in the region of the α process as in the case of G'', and the relaxation appears only as a small shoulder on a rapidly increasing background. Consequently, no conclusions can be drawn from the J'' data as to how the relaxation peak varies with variations in the degree of lamella orientation.

It is clear that if one were to consider this behavior on a simple two-phase model, one could again come to quite different conclusions regarding the site of the relaxation process. In actual fact Illers [10] has shown that no "amorphous phase" is necessary for the presence of α and γ relaxations and any explanation of the behavior of the curves in figures 4 and 8 must await the solution of the complex mechanical problem involved in the deformation of a crystalline polymer.

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