

Structure and Properties of Oriented Poly(ethylene Terephthalate) Films

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Synopsis

A study was made of the structural and property changes that occur when poly(ethylene terephthalate) films are oriented, crystallized, and thermally relaxed. X-ray diffraction, infrared, density, and stress-strain measurements were used to develop information on the amount and direction of orientation of both the crystalline and amorphous regions of these films. Three structural factors influence resultant film properties: (1) the kind and perfection of crystallite orientation, (2) the amount and direction of the *trans-gauche* isomerization in the amorphous regions, and (3) the amount of crystallinity. Interactions of these factors result in substantially different film properties and relaxation behavior. Of special significance is the influence of "taut" extended amorphous regions produced by orientation which generate useful structure-property information.

The properties of polymeric fibers and films depend to a large extent on the orientation produced during processing. Oriented semicrystalline polymers, such as poly(ethylene terephthalate) are believed to consist of crystalline and amorphous regions distributed in various ways depending on the extent and kind of processing techniques used. It is convenient to depict these oriented polymer structures in accordance with a modified fringed-micelle model, having a range of degrees of order in both the crystalline and amorphous regions.

As discussed earlier,¹ a real need exists for the direct determination of the distributions of both the crystalline and amorphous regions to establish the mechanisms taking place during orientation. The requirements to accomplish this are: (1) a systematic geometrical reference system for the several types of orientation possible and (2) experimental methods for the independent determination of the distributions of each kind of structural region. The first of these requirements is satisfied by the orientation definitions that have been given. The second requirement is partially accomplished by single-crystal x-ray techniques which provide the means to measure the orientation distributions of the crystalline regions, and also by recent infrared studies which characterize the amorphous regions of the polymer. Assumed distribution functions that have appeared in the literature do not satisfactorily explain the observed orientation phenomena, nor take into account the different types of distributions found to exist in polymeric systems.

Schmidt² and others³ using polarized infrared techniques have shown the importance of a more detailed division of structure, in addition to the crystalline-amorphous division for poly(ethylene terephthalate) films. This division is based on the molecular conformations of the ethylene glycol linkage which in poly(ethylene terephthalate) may exist in either of two rotational isomeric forms (*trans* or *gauche*). The *trans* isomer is the extended form relative to the *gauche* and occurs in both the crystalline and amorphous regions of the polymer; the *gauche* isomer, however, occurs only in the amorphous regions. A film with a given amount of crystallinity may have varying amounts of *trans* isomer; likewise a film with a given amount of *trans* isomer may have varying amounts of crystallinity.

With these techniques in hand, it now appears that many of the experimental problems in measuring the complete orientation distributions of the polymer structural elements have been solved, and it is the intent of this paper to show how the results of several of these experimental techniques, i.e., x-ray, infrared, stress-strain results, etc., when viewed together, provide a comprehensive view of the structure of oriented poly(ethylene terephthalate) films. It is also an objective of this paper to demonstrate the contribution of the amorphous regions to an understanding of structural changes and how they influence the mechanical and thermal properties of oriented crystalline polymeric films.

To present this information in an orderly fashion, we will describe first the methods used to measure specific structural parameters and then define how these parameters change as a film is taken through several orientation processes. Interpretations are given which describe the structural changes that influence specific film properties.

The structural parameters studied were (1) the crystallite orientation distributions, (2) the crystallite length, (3) the long-period spacing and the amorphous length as given by low-angle x-ray diffraction, and (4) changes in the absorbance and direction of selected infrared bands (*trans-gauche* isomerism).

Since the start of the work reported here, an excellent paper has appeared⁴ which describes the molecular structure and some of the mechanical properties of poly(ethylene terephthalate) fibers. Significant structural changes, however, occur from biaxial stretching not seen by the uniaxial stretch of a film or fiber.

Terminology and Experimental Techniques

Previously,¹ orientation definitions (e.g., uniplanar, uniplanar-axial) were given to describe the kinds of structure produced in oriented films or fibers. An important attribute of these definitions is that they apply to the system as a whole, even though various kinds of experimental manipulations and orientation measurements may be required to generate the complete orientation figure.

The initially unoriented poly(ethylene terephthalate) films studied were stretched and analyzed in the sequence: (a) longitudinally stretched

(M.D.), (b) then transversely (T.D.) stretched, and (c) finally post-stretched (M.D. again).

Crystallite Orientation Distributions

In polymer structures, orientation is not perfect, and distributions of directions of crystal planes or axes will be observed. It is also possible for several orientation types to coexist within the same sample. Substantial information can be generated from the crystallite orientation distributions measured by the single crystal orienter (SCO) technique. All x-ray measurements utilized $\text{CuK}\alpha$ radiation at 50 kv. and 16 ma. As reported earlier, the crystallite orientation distributions are in fact surfaces generated from a composite of individual distribution measurements obtained from sample rotations. These surfaces provide an excellent qualitative understanding of the nature of the crystallite orientation but, as has been shown,⁵ are difficult to describe quantitatively. Our attempts to achieve a mathematical expression to fit the many kinds of orientation surfaces generated by the several process steps, involved functions with as many as seven parameters. With the additional problem of describing a large number of samples, the effort was abandoned for the following reasons: (1) the surfaces we did fit with equations added nothing to our understanding of the processes that occur; (2) even though the functions worked for a particular sample, the coefficients had no significant physical meaning; (3) it is possible to calculate an orientation parameter by using only the distribution curve at maximum orientation which correlates with other structural features. A simple and useful technique for describing the curves was suggested by Hoerl⁶ and was used to define the average orientation of either a crystallite plane or axis. Hermans et al.⁷ and Wilchinsky⁵ have used a similar approach but have incorporated into their calculations the average trigonometric functions to define an orientation factor. We feel that the method used here is just as useful and can be calculated somewhat more quickly. The numbers we generate are representative of the average position of a major crystallite plane, (100) relative to the film surface designated $\sigma_{p,p}$ and the c axis of the crystallite relative to the direction of stretching or rolling $\sigma_{a,a}$. Values obtained are in degrees, where 0° denotes perfect parallelism and 45° denotes complete randomization of the operator to reference system. The method is described in the Appendix.

Infrared Studies

Infrared studies have also yielded information concerning the orientation of poly(ethylene terephthalate). Parameters characteristic of the molecular axial (Δ_a) and uniplanar (Δ_p) orientations were defined,² where

$$\Delta_a = A_z/A_y \text{ (875 cm.}^{-1}\text{)}$$

and

$$\Delta_p = A_z/A_y \text{ (875 cm.}^{-1}\text{)}$$

A_x , A_y , and A_z are the absorption intensities of the 875 cm.^{-1} infrared band along the mutually perpendicular directions, machine, transverse, and normal to the film surface.

Initially, we had expected that only the infrared technique would be needed, since the x-ray σ and infrared Δ values seemed to correlate in many of the samples investigated. However, we found that this was not a reliable correlation, because the amorphous orientation can change substantially without influencing to any great extent the crystallite orientation. Samples subjected to small amounts of stress or strain relaxation due to post heat treatments will show a greater rearrangement of direction of chain segments in the amorphous regions than in changes in the directions of the crystallites. Therefore, independent measurements of both the crystalline and amorphous structure are required.

Measurement of Crystallite Length

In poly(ethylene terephthalate), the broadening of the $(\bar{1}05)$ diffraction peak, observed in this study at $2\theta = 42.8^\circ$, is used to measure the crystallite length. The $(\bar{1}05)$ makes an angle of 88.0° with the c axis and hence can, for the purposes of crystallite length measurement, be considered normal to it. For the lattice parameters as determined by Daubeny et al.,⁸ 2θ for this plane is 46.0° . Evidence for the identity of the $(\bar{1}05)$ is as follows: (1) structure factor calculations of all the possible planes in the 2θ region from 41.8° to 47.0° indicate that the $(\bar{1}05)$ is the strongest reflecting plane, (2) other planes are not likely to be in position to diffract from the orientation produced by stretching, and (3) none of the other planes have a calculated 2θ at 46.0° . The discrepancy between the observed and calculated 2θ has not been resolved but may be due to slight differences in lattice parameters from those reported.

The theory and assumptions used for crystallite size measurements by line broadening are adequately covered elsewhere.⁹ Average crystallite lengths were calculated by using Warren's correction for the Scherrer line broadening equation. The value for instrumental broadening for our x-ray instrument was determined by using finely powdered zinc oxide scanned at $0.2^\circ/\text{min.}$ from below a 2θ angle of 30.0° to greater than 47.0° with nickel-filtered $\text{CuK}\alpha$ radiation. The broadening of the ZnO reference diffraction peaks was averaged, and a value of 0.678° for the instrumental broadening correction was obtained.

The errors in the crystallite size measurements are of the order of $\pm 3\text{ \AA}$. Increased precision of the results can be obtained by refinements in technique such as scanning slower, but the assumptions used in the line-broadening equations make the virtue of increased precision doubtful. Primary interest was not in the absolute values of crystallite size but in how size changed with orientation.

Intercrystalline Spacing

In addition to the directional arrangement and size of the crystalline regions, the influence of the intercrystalline spacing helps explain some of the properties observed in poly(ethylene terephthalate) films. The orientation distribution of the crystallites does allow one to infer to some extent what is occurring in the amorphous regions. Low-angle x-ray techniques, however, not only provide a measure of intercrystalline spacing but also help develop further insight into the amorphous character of poly(ethylene terephthalate) films.

Statton¹⁰ and others^{11,12} expanding the work of Hess and Keissig¹³ have formulated structural interpretations to explain low-angle x-ray diffractions in fibers. These interpretations have been used to explain some of the low-angle diffraction characteristics of the films studied.

The low-angle diffraction is thought to originate from a periodic spacing of the crystallites. A line lattice is formed by the crystallites over a short range, and the long-period spacing can be calculated by using the Bragg equation. The long period presumably is an average spacing of the crystallite plus the amorphous region, and the calculated values given are average values characteristic of the center-to-center spacing of the somewhat diffuse spots which occur.

The long-period spacings of poly(ethylene terephthalate) films were measured by using a sample thickness of 0.020 in., $\text{CuK}\alpha$ radiation at 50 kv. and 16 ma. with a sample-to-film distance of 17 cm. in a vacuum camera. Three types of exposures are commonly made, designated "edge" (x-ray beam normal to the M.D. axis, i.e., along the T.D. axis), "end" (x-ray beam parallel to the M.D. axis, i.e., normal to the T.D. axis), and

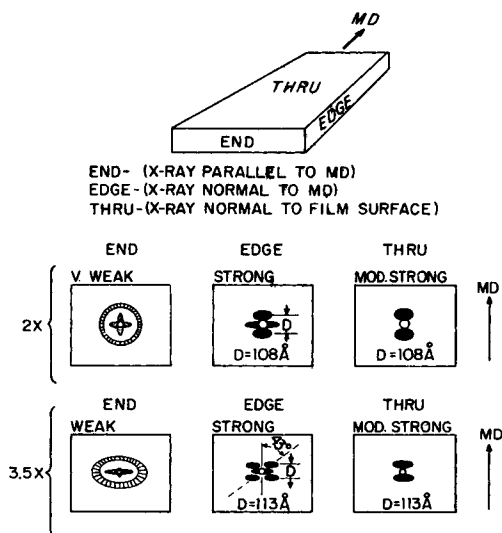


Fig. 1. Low-angle x-ray diffractions for one-way stretched films.

"thru" (x-ray beam normal to the film surface). These are identified in Figure 1. The values from the edge exposures were used for the long-period measurements and for the calculations of a so-called amorphous length. The amorphous length is calculated by subtracting the average crystallite length obtained from line broadening from the long-period spacing.

Stress-Strain Character of Film Samples

The tensile properties, modulus, strength, elongation, and others are useful in determining the results of orientation introduced in films or fibers. Typical stress-strain curves for one-way, two-way, and post-stretched films are as shown in Figure 2. Experimental procedures for the measurements of the tensile properties of poly(ethylene terephthalate) films have been described by Amborski and Flierl.¹⁴ The curve shapes obtained during tensile testing in several directions reflect orientation differences quite dramatically.

Tensile modulus at 1% elongation is a measure of the stiffness of the film and tensile break strength is indicative of the perfection of orientation. Elongation can be considered as a measure of the mobility of the chains

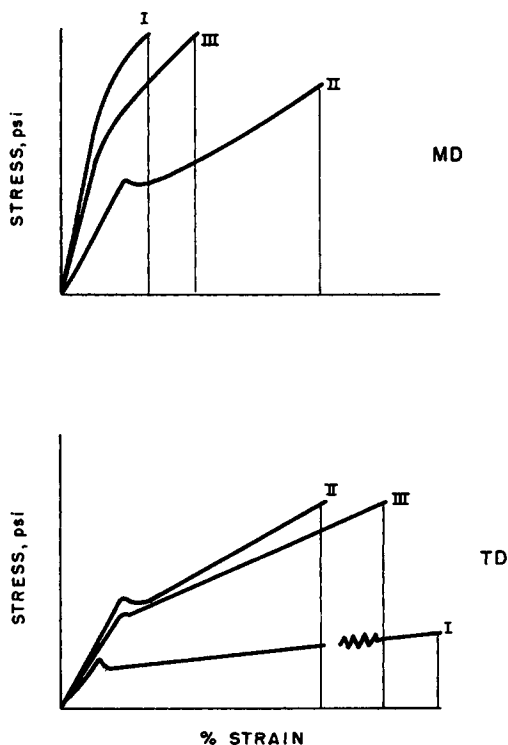


Fig. 2. Stress vs. strain for films: (I) one-way stretched, not heat-set; (II) two-way stretched, balanced heat-set; (III) post-stretched, heat-set.

TABLE I
One-Way Stretched Films (Structure)

Stretch ratio	$\sigma_{(a,a)}$, °	$\sigma_{(p,p)}$, °	Δ_a	Δ_p	Long period, A.	Crystallite length, A.		Total <i>trans</i> , %	Crystalline <i>trans</i> , %	Amorphous <i>trans</i> , %
						—	—			
As cast	45.0	45.0	1.00	1.00	—	—	—	13	0	13
2.0	27.7	37.1	1.41	1.05	107	44	63	21	7	14
3.0	21.3	30.9	1.74	1.22	113	52	61	34	14	20
3.5	18.0	25.9	1.97	1.39	113	58	55	41	17	24
4.0	14.5	21.4	2.21	1.70	113	60	53	56	25	31
4.5	11.8	18.1	2.47	1.77	113	63	50	65	27	38
5.0	12.2	17.4	2.68	1.86	113	65	48	78	30	48

TABLE II
Two-Way Stretched Films (Structure), Heat-Set

Stretch ratio	$\sigma_{(a,a)}$, °	$\sigma_{(p,p)}$, °	Δ_a	Δ_p	Long period, A.	Crystallite length, A.		Total <i>trans</i> , %	Crystalline <i>trans</i> , %	Amorphous <i>trans</i> , %
						—	—			
2.5 × 2.5	47.3	16.7	0.90	1.45	119	48	64	59	48	11
3.0	21.3	30.9	1.74	1.22	113	52	61	73	48	25
3.0 × 3.0	42.3	14.7	0.99	1.88	120	57	63	73	48	25
3.5	18.0	25.9	1.97	1.39	113	58	55	74	48	26
3.5 × 3.5	36.1	11.9	1.13	1.85	120	64	56	74	48	26

TABLE III
 Post-Stretched Films (Structure)

Stretch ratio	$\sigma_{(a,a)}$, °	$\sigma_{(c,c)}$, °	Δ_a	Δ_p	Long period, A.		Crystal-lite length, A.		Amorphous length, A.		Total <i>trans</i> , %	Crystal-line <i>trans</i> , %	Amorphous <i>trans</i> , %
					A.		A.		A.				
1.30	37.5	16.0	1.23	1.72	131	60	71	79	44	35			
1.45	36.5	15.9	1.30	1.78	132	57	75	88	48	40			
1.68	36.2	16.2	1.46	1.65	141	56	85	88	42	46			

 TABLE IV
 One-Way Stretched Film (Properties)

Stretch ratio	Modulus, psi		Tensile strength, psi		F_5 , psi ^a		Elongation, %	
	M.D.	T.D.	M.D.	T.D.	M.D.	T.D.	M.D.	T.D.
2.0	460,000	328,000	16,900	6,470	9,000	7,000	214	497
3.0	883,000	299,000	26,000	6,540	16,000	5,870	92	490
3.5	1,018,000	265,000	31,800	7,090	19,300	5,660	68	400
4.0	1,276,000	253,000	40,800	6,520	24,500	7,800	48	474
4.5	1,546,000	303,000	47,318	7,410	33,350	7,563		
5.0	1,772,000	331,000	57,744	7,290	40,700	8,138	19	492

^a F_5 = tensile stress at 5% elongation.

TABLE V
Two-Way Stretched Films (Properties)

Stretch ratio	Modulus, psi		Tensile strength, psi		F_6 , psi		Elongation, %	
	M.D.	T.D.	M.D.	T.D.	M.D.	T.D.	M.D.	T.D.
2.5 × 2.5	624,000	700,000	19,500	23,200	13,500	14,000	128	140
3.0 × 3.0	655,000	641,000	26,500	22,400	14,600	14,400	114	135
3.5 × 3.5	759,000	674,000	30,500	24,300	15,500	14,700	78	100

TABLE VI
Post-Stretched Films (Properties)

Stretch ratio	Modulus, psi		Tensile strength, psi		F_3 , psi		Elongation, %	
	M.D.	T.D.	M.D.	T.D.	M.D.	T.D.	M.D.	T.D.
1.30	921,000	564,000	37,000	21,000	20,100	12,000	40	150
1.45	994,000	463,000	38,200	17,000	26,600	10,800	52	250
1.68	1,050,000	530,000	42,100	18,310	27,100	11,800	27	133

under stress while the F_5 (the force required to elongate the sample 5%) is a measure of the tautness of the polymer chains. Each of these characteristics provides a qualitative idea of what the sample was structurally, prior to testing.

On the basis of the kinds of measurements discussed, made on many samples, we shall describe now what we believe to occur during the stretching of poly(ethylene terephthalate) films. Our conclusions are based on the combinations of the changes in the structural parameters we have been able to measure. In this discussion we hope to convey to the reader the significance of the interaction between crystallite orientation and of an extended "taut" amorphous structure on the useful properties of a polymeric film.

TABLE VII
One-Way Stretched Films (Structure)

Stretch ratio	Δ_a	Δ_p	Total <i>trans</i> , %	Amorphous <i>trans</i> , %	Crystalline <i>trans</i> , %
Not Heat-Set					
4.0	2.21	1.70	56	31	25
4.5	2.43	1.77	65	38	27
5.0	2.68	1.86	78	47	31
5.5	2.96	1.91	89	55	34
Heat-Set					
4.0	1.78	1.50	67	19	48
4.5	1.98	1.55	74	26	48
5.0	1.90	1.65	77	29	48
5.5	2.36	1.83	82	34	48

TABLE VIII
Two-Way Stretched Films (Structure)

Stretch ratio	Δ_a	Δ_p	Total <i>trans</i> , %	Amorphous <i>trans</i> , %	Crystalline <i>trans</i> , %
Not Heat-Set					
2.0 × 3.5	0.828	1.60	41	24	17
3.0 × 2.5	1.02	1.60	42	24	17
3.0 × 3.0	0.973	1.76	52	35	17
3.5 × 3.0	1.14	1.69	51	35	17
3.5 × 3.5	1.02	1.63	51	35	17
Heat-Set					
2.0 × 3.5	0.712	1.84	63	16	47
3.0 × 2.5	1.15	1.92	63	15	48
3.0 × 3.0	0.991	1.88	73	25	48
3.5 × 3.0	1.12	1.82	77	29	48
3.5 × 3.5	1.13	1.85	74	26	48

TABLE IX
One-Way Stretched Films (Structure)

Stretch ratio	Δ_a	Δ_p	Total <i>trans</i> , %	Crystalline <i>trans</i> , %	Amorphous <i>trans</i> , %
Not Heat-Relaxed					
3.5	1.97	1.39	41	17	24
4.0	2.21	1.70	56	25	31
4.5	2.47	1.77	65	27	38
5.0	2.68	1.86	78	31	47
5.5	2.96	1.91	89	34	55
Heat-Relaxed					
	1.41	1.39	28	17	11
	1.62	1.66	38	25	13
	1.84	1.68	48	27	21
	2.22	1.58	58	31	27
	2.10	1.60	61	34	27

TABLE X
Strain Relaxation of One-Way, Two-Way, and Post-Stretched Films

Sample	M.D. relaxation, %	Density g./cc.	MD F_b , psi	MD elongation, %	Long period, A.	Crystalline length, A.	Amorphous length, A.
Sample 1, post-stretched	0.0	1.3799	23,200	26.4	132	64	68
	0.6	1.3809	21,548	23.5			
	4.4	1.3814	17,855	41.8			
	7.6	1.3850	16,582	52.0	120	64	56
	10.8	1.3878	15,735	42.5			
Sample 2, one-way stretched	14.8	1.3942	15,029	46.9	115	63	52
	0.0	1.3839	32,761	24	115	57	58
	3.2	1.3843	22,718	31	114	61	53
	10.5	1.3924	19,100	36			
Sample 3, two-way stretched, 3.5 × 3.5	15.5	1.4011	16,529	45	110	62	58
	0.0	1.3932	15,468	80.8	120	58	62
	10.7	1.3999	14,750	99.7	120	57	63

The structural changes that take place in an initially amorphous unoriented film as it is taken through several stretching procedures are described below. Experimental results are presented in Tables I-X. The values given are average results of duplicate samples.

One-Way Stretched Films

Quenched amorphous poly(ethylene terephthalate) film with $\bar{M}_n \cong 15,000$ is a mixture of molecular chains of varying lengths having no unique directivity. In this state the chains are most likely coiled, folded, or both, and extremely tangled. The orientation of this structure is called random.

When this amorphous film is M.D. stretched, the molecular chains become partially aligned along the stretch direction and some crystallization occurs. The crystallites formed, in general, have their *c* axes, i.e., the long axis of the poly(ethylene terephthalate) crystallite, parallel to the direction of stretch, and some fraction of the (100) crystallite planes are aligned parallel to the surface of the film. As the amount of stretch is increased, the alignment of the *c* axes relative to the direction of stretch is improved, as are also the alignment of the (100) planes relative to the film surface (Table I). The resulting structure is classified as uniplanar-axial orientation. Since the molecular chains were most likely initially tangled and randomly oriented, many chain segments probably remain entangled after the M.D. stretch. In fact, a fibrillar type structure is presumed to have been formed. Under the stretching conditions we used here, at stretch ratios greater than about $3.5 \times$ (3.5 times or 250% of the initial length) the chains are believed to be so strained that there are many "taut" oriented amorphous regions between the crystallites. In other words, many chain segments are extended, and rather limited, by entanglements with other taut chains or crystallites in how far they can be further stretched. As a result, the slope of the initial portion of the stress-strain curve is steep, and F_5 values above 20,000 psi are produced (Table IV). The transverse direction properties remain essentially unchanged. X-ray measurements tell us that the distance between crystallite centers is about 112–114 Å for one-way stretched films, and that the distance between crystallite "edges" (the amorphous length) decreases with increased orientation (Table I). The crystallite length produced is dependent upon the extent to which the film is stretched, i.e., the higher the stretch ratio, the longer the crystallite length, since the crystalline regions can grow more easily as the alignment of chains in this direction is improved (Table I).

Infrared studies show the cast amorphous poly(ethylene terephthalate) films to be randomly oriented and to contain a fixed amount of *trans-gauche* structure. In these films, there is approximately 13% *trans* structure and 87% *gauche* structure. Since the *trans* structure is an extended form, this indicates that the majority of molecules are in a relaxed, unextended state. When the cast film is M.D. stretched and the molecules become aligned along the stretch direction, the individual chain segments become extended; that is, some *gauche* poly(ethylene terephthalate) is converted into *trans* poly(ethylene terephthalate) (Table I). The *trans* isomer is the only one that exists in the crystalline regions, and some crystallization will occur as the *trans* isomers are brought into proximity while being aligned along the stretch axis (Table I). For stretch ratios below $3.5 \times$, there is only a small amount of preferred orientation of the phenyl rings relative to the plane of the films. As the stretch ratio approaches $3.5 \times$, a significant fraction of the chain segments have been aligned and placed in the taut extended *trans* configuration; further stretching puts additional stress on the *trans* segments and twists them into a position which will facilitate greater crystalline growth. At this point, the planes of the phenyl rings are approxi-

mately parallel to the plane of the film (Table I). As stretching is continued beyond 3.5X, the *trans* content of the film increases, the *gauche* content decreases, the amount of amorphous *trans* increasing at a rate more rapid than the amount of *trans* from crystallization (Table I). The alignment of the molecular chains to the stretch direction and the alignment of phenyl rings to the plane of the film also increase (Table I). Since the *trans* isomer of poly(ethylene terephthalate) is extended relative to the *gauche* isomer, the amount of *trans* structure at a given level of crystallinity is a measure of the "tautness" of the amorphous regions of the polymer and it is directly related to the modulus, strength, elongation, and F_5 values of the film (Table IV).

Two-Way Stretching

Subsequent stretching of the one-way M.D. stretched film in the transverse direction causes the chain segments in the amorphous regions and the crystallites to be shifted from the machine direction toward the transverse direction, the amount of this movement being dependent upon stretch ratio, temperature, and other process conditions. From this treatment, some of the crystallite *c* axes move from the M.D. toward the T.D., the amount of this movement measured by the crystallite orientation distribution parameter $\sigma_{(a,a)}$. In addition, the (100) planes of the crystallites are forced into better parallelism with the surface of the film, as measured by the crystallite orientation parameter $\sigma_{(p,p)}$ (Table II). Values for the one-way stretched film are included in Table II for comparison. It is believed that during the second direction stretch some chain disentanglements occur, since the long period (the distance between crystallite centers in the M.D.) increases to 119-120 Å. (Table II). The crystallite length, however, increases slightly over that produced by the first direction stretch and, therefore, the average amorphous length is essentially unchanged. The structural changes that take place during the second direction stretch are primarily associated with the reapportionment of the structure that has been produced by the first direction stretch. The amorphous regions of this film are not as highly strained in either the M.D. or T.D. and as a consequence the initial part of the force-elongation tensile curves have a lower slope and resultant lowered modulus and F_5 (Table V) than one-way stretched films. The shifting of some of the orientation from M.D. toward the T.D. has now generated comparable properties in the two directions. At balance the orientation is uniplanar. During the second direction stretch a slight increase in the amorphous *trans* content occurs (compare Tables I and VIII). Additional changes occur due to crystallinity.

Crystallization

The production of dimensionally stable films requires that the structure introduced by these orientation steps be immobilized through crystallization. This process has become known as heat setting. Only the *trans* isomers are capable of crystallizing. Crystallization may be induced in

either of two ways: by polymer stretching or by heat setting at temperatures substantially higher than the glass transition: As noted before, *gauche* poly(ethylene terephthalate) is transformed into *trans* poly(ethylene terephthalate) during the stretching process (Tables I and VIII). Here many *trans* isomers are brought into proximity of one another; hence crystallization occurs. Crystallization induced by the heat-setting process may come about by either the movement of amorphous *trans* molecules into the necessary proximity or by the thermal isomerization of *gauche* near neighbors with a subsequent crystallization of the newly formed *trans* material. The latter explanation is more plausible, since the amorphous *trans* content changes only about one-third that of the *trans* crystalline change during the crystallization of two-way stretched films (Table VIII).

Tension on the film samples during crystallization plays an important role in the development of structure. Generally, if a one-way stretched film is heat-set under tension to try to maintain the orientation produced by stretching, the total *trans* content of the film increases (Table VII) as the crystallinity increases. The larger the initial *trans* content, the smaller will be the subsequent increase, since the remaining *gauche* content that can be converted to *trans* will be small. The degree of molecular orientation of this film, however, will decrease (Table VII). Evidently the orientation stresses are so great that they cannot be completely restrained by tension on the film during crystallization so that stress decay, localized melting, and recrystallization occur. The parameters characteristic of both the molecular axial and uniplanar orientation decrease in value. We will refer to this process as structural relaxation as contrasted to strain relaxation.

During the restrained crystallization of a two-way stretched film of near balanced orientation, the total *trans* content increases in value, this change reflecting the increase in the crystalline *trans* content (Table VIII). In contrast to the one-way stretched, highly strained structures, the molecular axial order Δ_a of these films remains essentially unchanged while the amount of molecular uniplanar structure, Δ_p increases (Table VIII). It is felt that the greater mobility of the biaxially stretched structure is such that the near-neighbor *gauche* segments, having acquired sufficient thermal energy to isomerize, easily shift into *trans* segments, which crystallize. Subsequent crystallite growth produces a volume decrease which exerts additional tensile forces on the *trans* segments and forces them into a uniplanar configuration, i.e., Δ_p increases. During the nonrestrained crystallization of two-way stretched films, the amorphous *trans* content decreases appreciably, the crystalline *trans* content increases, and Δ_p decreases. The amorphous regions are relaxed.

Post-Stretching

If the essentially balanced, crystallized, two-way stretched film is subsequently given an additional M.D. stretch, i.e., by post-stretching, the

molecular chain segments are once again shifted toward the machine direction but are now more constrained in their motion by the additional crystallinity present (Table III). As a result, the molecular chain segments in the amorphous regions are drawn taut. Infrared measurements show that the amount of *trans* crystalline structure remains essentially unchanged, but that the amount of *trans* amorphous structure has increased

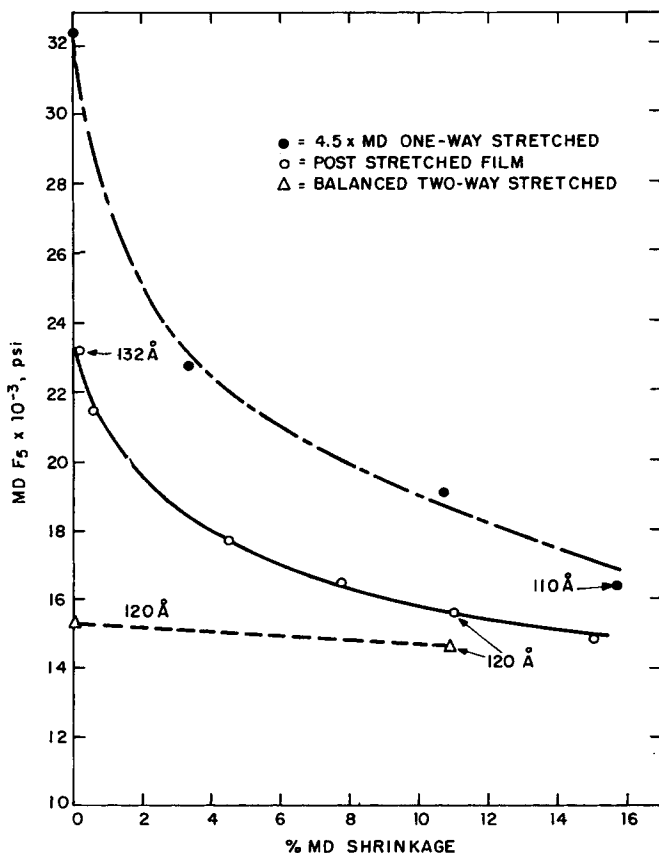


Fig. 3. Tensile F_5 vs. shrinkage, long period vs. shrinkage.

(Table III). X-ray measurements show that the crystallite lengths remain essentially unchanged, but that the long-period spacings have increased (to beyond 125 Å), so that the distance between crystallites (the amorphous length) has increased (Table III). This very taut structure is difficult to deform further, since the chain segments in the amorphous regions are already extended in a variety of directions, thereby limiting the freedom that can occur during additional stretching, e.g., during tensile testing. Low elongations, high modulus, and high F_5 values are, therefore, produced (Table VI).

Strain Relaxation

One of the most significant features exhibited by these taut extended amorphous structures is the ability to relax easily and generate new structural and property features. For example, if a one-way stretched film is heated to a temperature of 100°C. for a short time without the application of tension, there is a large decrease in the amorphous *trans* content, little or no change in the crystalline *trans* content, along with a decrease in the

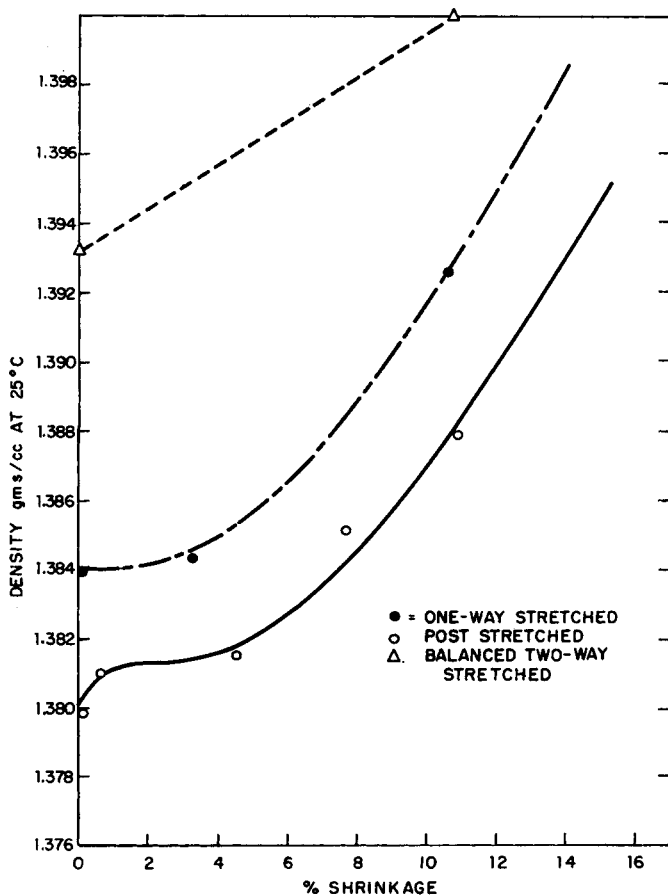


Fig. 4. Density vs. shrinkage.

amount of molecular alignment, Δ_x and Δ_p (Table IX). Evidence for the strained or taut amorphous structure which accounts for the high tensile properties in one-way and post-stretched films is found in the thermal relaxation results given in Tables IX and X. Figure 3 shows the degeneration of the F_s and long period as the film is thermally relaxed. If this strain relief is caused by a change in the tautness of the segments in the amorphous regions, it should be reflected in several ways. For example,

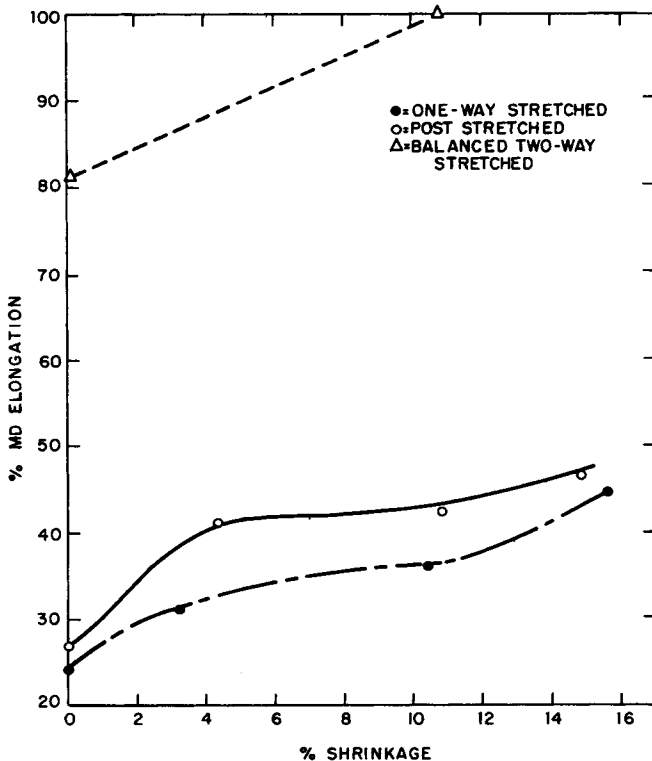


Fig. 5. M.D. elongation vs. shrinkage.

the amorphous length should become smaller and the chain segments should coil or fold into a more compact structure. As a consequence, lower long-period values and higher elongations and density should be observed. Each of these effects does occur, as shown in Figures 4 and 5. Balanced, two-way stretched heat-set films with a less taut amorphous structure do not exhibit these effects to the same magnitude. One further structural change deserves mention, since it is indicative of the interdependence of crystallite orientation and highly strained amorphous regions. Relaxation of the strained amorphous structure causes very little change in the alignment of crystallite c axes, i.e., the change in $\sigma_{(a,a)}$ is small, but the crystallites do rotate out the plane of the film, i.e., increasing $\sigma_{(p,p)}$. This again emphasizes the necessity of having independent measurements of both the crystalline and amorphous structural parameters. Apparently, the high uniplanarity of the crystalline structure produced in stretched films is at least partially due to coplanar tensile forces applied by means of the connecting segments in the amorphous region.

Discussion

We have attempted to present a comprehensive view of the structural changes taking place in poly(ethylene terephthalate) films resulting from

stretching, crystallization and thermal relaxation using several measurement techniques. Basically the system is an initially amorphous un-oriented polymer which develops strain-induced crystallinity during stretching and then undergoes a secondary crystallization upon subsequent thermal treatment. Three structural factors influence resultant film properties: (1) the kind and perfection of crystallite orientation, (2) the amount and direction of the *trans-gauche* isomerization in the amorphous regions, and (3) the amount of crystallinity. The degree of interaction of these factors results in substantially different film properties and relaxation behavior. It is not our intent here to discuss the various models of polymer morphology that have been proposed. However, we feel that our results are plausible in the context of a crystalline and amorphous system having a broad degree of order between these extremes.

Most studies of crystalline polymers have been almost exclusively concerned with crystal morphology and the amount of crystallinity. The thesis we have tried to present here is that the so-called amorphous region is an often neglected area for work, since it contributes substantially to an understanding of the structural changes that occur.

APPENDIX

Method of Calculating the Crystallite Orientation Distribution Parameters $\sigma_{(a,a)}$ and $\sigma_{(p,p)}$

The x-ray intensity distribution curves obtained from specific sample rotations on the single crystal orienter can be considered as a distribution of mass, with the x-ray intensity at a given angle, a measure of the number of mass elements occupying that position. The problem then is to determine the center of gravity of the curve. This was the procedure used to define the crystallite orientation distributions by a single number. The x-ray intensities at 5° intervals in the range 0–90° were measured and coded f_0 to f_{18} and the distance from 0°, $X_n = 0.5$ to 18.5. Other arithmetic scales could have been used for X_n but these were found to be convenient. $\sigma_{(p,p)}$ and $\sigma_{(a,a)}$ were calculated by numerical integration as follows:

$$\sigma = \frac{\sum f_n X_n}{\sum f_n} \quad (1)$$

where

$$\begin{aligned} \sum f_n &= f_0 + f_1 + \dots + f_{18} \\ \sum f_n X_n &= f_0 (0.5) + f_1 (1.5) + f_2 (2.5) + \dots + f_{18} (18.5) \end{aligned}$$

It is often more convenient to discuss the curves in terms of the angle of orientation. This is done by multiplying eq. (1) by the size of the angular increment, 5°, and subtracting one-half the increment, i.e.,

$$\sigma^\circ = [(\sum f_n X_n)/(\sum f_n)] (5^\circ) - 2.5^\circ \quad (2)$$

Perfect orientation now equals 0° and a random distribution, 45° . Equation (2) was used for the values given in the tables.

Several minor errors influence the values of $\sigma_{(p,p)}$ and $\sigma_{(a,a)}$. Among these are differences in sample density, sample volume, and the total x-ray intensity used to make the measurements. To point out the magnitude of one of these errors, that due to gross changes in the x-ray intensity, a sample was measured with an old x-ray tube (>2000 hr.) and a new one. The $\sigma_{(p,p)}$ and $\sigma_{(a,a)}$ values differ in the two cases by less than 1° for a difference in total intensity of greater than 2.5 times (Table XI).

TABLE XI

Total intensity maximum of the (100) plane	Old tube (9200 counts/sec.)	New tube (24,500 counts/sec.)	Change in distribution index
$\sigma_{(p,p)}$	11.73°	10.76°	$\Delta\sigma_{(p,p)} = 0.97^\circ$
$\sigma_{(a,a)}$	39.28°	38.81°	$\Delta\sigma_{(a,a)} = 0.47^\circ$

Small differences in sample volume and density likewise introduce only small errors. Absorption differences are shown to be negligible by rotating the sample parallelepiped¹ through 360° , during which the diffracted intensity fluctuations are within the counting error.

The similarity between methods used by two other authors to calculate the orientation angle are given below in eqs. (3-5) with the use of similar notation:

Hermans:⁷

$$\langle \sin^2 \phi \rangle = \int_0^{\pi/2} \sin^2 \phi I_{(\phi)} \sin \phi d\phi / \int_0^{\pi/2} I_{(\phi)} \sin \phi d\phi$$

Wilchinsky:⁵

$$\langle \cos^2 \phi \rangle = \int_0^{\pi/2} \cos^2 \phi I_{(\phi)} \sin \phi d\phi / \int_0^{\pi/2} I_{(\phi)} \sin \phi d\phi$$

This work:

$$\sigma_{(p,p)} = \langle \phi \rangle = \int_0^{\pi/2} I_{(\phi)} \phi d\phi / \int_0^{\pi/2} I_{(\phi)} d\phi$$

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Résumé

Une étude a été effectuée sur les changements de structure et de propriétés qui ont lieu lorsque des films de téréphtalate de polyéthylène sont orientés, cristallisés et dé-tendus thermiquement. Des mesures de diffraction aux rayons X, à l'infrarouge, de densité et de tension-élongation ont été employées pour obtenir des informations concernant la quantité et la direction d'orientation des régions cristalline et amorphe de ces films. Trois facteurs de structure influencent les propriétés finales du film: (1) la sorte et la perfection de l'orientation cristalline, (2) la quantité et la direction de l'isomérisation *trans-gauche* dans les régions amorphes et (3) la quantité de cristallinité. Les interactions de ces facteurs proviennent des propriétés pratiquement différentes du film et du comportement à la relaxation. Une importance spéciale est à attribuer à l'influence des régions amorphes étendues produites par une orientation qui procure une information utile sur la relation structure-propriété.

Zusammenfassung

Eine Untersuchung der Struktur- und Eigenschaftänderungen, welche während der Orientierung, Kristallisation und thermischen Relaxation von Polyäthylenterephthalat-filmen auftreten, wurde durchgeführt. Röntgenbeugungs-, Infrarot-, Dichte- und Span-nungs-Dehnungsmessungen wurden verwendet, um eine Information über den Betrag und die Richtung der Orientierung in den kristallinen und den amorphen Bereichen dieser Filme zu erhalten. Drei Struktur-faktoren beeinflussen die resultierenden Filmeigen-schaften: (1) Art und Vollkommenheit der Kristallitorientierung, (2) Betrag und Rich-tung der *trans-gauche*-Isomerisierung in den amorphen Bereichen und (3) der Betrag an Kristallinität. Wechselwirkungen zwischen diesen Faktoren führen zu wesentlich ver-schiedenen Filmeigenschaften und unterschiedlichem Relaxationsverhalten. Besonders bemerkenswert ist der Einfluss von "straff" gespannten, durch Orientierung erzeugten amorphen Bereichen, welche brauchbare Struktur- und Eigenschaftsinformationen liefern.

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