

AMORPHOUS PHASE PROPERTIES OF ORIENTED POLYETHYLENE SOLIDS

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ABSTRACT

Solid-state deformation of polyethylene results in a preferential orientation of both crystalline and amorphous regions. Usually, one major problem in the prediction of the mechanical and thermal expansion properties of anisotropic polyethylene lies in determining values for the amorphous phase properties and, particularly, at a given level of solid-state deformation.

This paper outlines simple procedures for determining the two-dimensional amorphous orientation function and values for the mechanical and thermal expansion properties of the oriented amorphous phase. Mathematical expressions for determining the tensile and shear moduli, Poisson ratio and thermal strain of the amorphous phase for anisotropic polyethylene at any level of orientation are defined. Comparison between the predicted amorphous phase tensile modulus and the experimental measurements yields an agreement within 30%.

INTRODUCTION

Crystalline polymers usually crystallize in a spherulitic form when supercooled from the melt; spherulite also grow in concentrated solutions. They are made up of crystalline lamellae fanning out from the center and in between lies the amorphous phase. Lamellar crystallites are formed by folded molecular chains; chain folding normally occurs transverse to the growing direction. The amorphous region is comprised of molecules whose complex tacticity or branching prevents their crystallization, molecules excluded from the crystals because of their molecular weight difference, tie molecules and disordered fold regions on the crystal surface [1].

Solid-State deformation processes, either cold or hot, are commonly employed to induce plastic deformation into polyethylene [1-6]. This plastic deformation invariably produces a deep series of complex changes in the morphology of the material. For instance, when the material is drawn, deformation is localized into a 'neck' region and it is here that a discontinuous change occurs from the normal lamellar structure into a fibrillar one. The deformation of spherulites largely characterizes the material's response, for the microscopic behavior is determined by crystalline tilting, twisting, slipping, orientation distribution and sometimes recrystallization [7]. In the amorphous region, chain slippage and rubber-like deformation also occur. The resultant oriented structure is anisotropic in a number of mechanical and thermal properties with a degree of anisotropy dependent on the extent of deformation.

Many models have been proposed to describe the morphology and the mechanical and thermal properties prediction for oriented crystalline polymers [8-14]. Usually one major problem in the prediction of mechanical and expansional behavior of molecular composite systems lies in the assumed values for the amorphous (matrix) properties. Therefore, it is of prime importance to address more attention to the subtlety of the oriented amorphous phase. The objective of this paper is to elucidate how one can obtain reasonably accurate values for the mechanical and expansional properties of the amorphous phase for anisotropic polyethylene at any given state of orientation.

EFFECT OF DEFORMATION ON THE AMORPHOUS PHASE PROPERTIES

Among the contents of the amorphous phase, tie molecules seem to be the most prominent elements in altering the amorphous phase properties during the deformation process. In the fully oriented texture, tie molecules which linked different lamellae in the initial spherulitic material, now connect different microfibrils; i.e. they have become interfibrillar tie molecules and contribute to a greater extent to the mechanical properties of the highly deformed polymer [15].

For a simplified two-dimensional symmetric orientation, the extent of the amorphous phase orientation can be quantitatively represented by the following expression (16):

$$f_m = 2 \langle \cos^2 \theta_m \rangle - 1 \quad (1)$$

where θ_m represents the average orientation angle between the polymer chain axis in the amorphous phase and the reference direction of the material; $\langle \rangle$ designates the average value. At this point it is pertinent to mention that a more usual definition for the orientation function is $f_m = \frac{1}{2}(3 \langle \cos^2 \theta_m \rangle - 1)$ [16,17]; this is the widely adopted definition for three-dimensional orientation distribution. It will not be utilized in this paper, and since we are assuming two-dimensional distribution, we will rather use the definition expressed by Equation 1. In addition to being proportional to the amorphous phase stiffness, the amorphous orientation function is known to increase with drawing [17, 18]. This increase may be attributed to the presence of taut tie molecules, their quantity, orientation and degree of tautness. If one is interested in interpreting the anisotropic behavior of polyethylene, tie molecules will have to be considered. We will define the amorphous phase stiffness as:

$$E_m = E_{m, iso} (1 - f_m) + E_{m, ult} f_m \quad (2)$$

where E_m is the amorphous phase stiffness at any orientation level described by the amorphous orientation function, f_m , $E_{m, iso}$ is the amorphous phase modulus in the isotropic state and $E_{m, ult}$ is the maximum attainable value for the amorphous phase modulus. Equation 2 shows that the amorphous phase modulus increases as the orientation process proceeds and the effect of tie molecules can be implicitly accounted for in this expression (through the use of f_m). For the initial isotropic case, $f_m = 0$ and $E_m = E_{m, iso}$; on the other hand E_m is progressively approaching the upper bound imposed on the amorphous phase modulus as the deformation proceeds with f_m approaching unity. Obviously the effect of tie molecules on the mechanical properties of oriented polyethylene can now be accounted for.

The shear modulus of the amorphous phase (G_m) is also affected by solid-state deformation, and obviously, a given state of orientation will be accompanied by a particular value for G_m . Therefore, one may face the problem of determining G_m at various levels of amorphous phase orientation. Previous studies on amorphous polymers like polyvinyl chloride, polymethylmethacrylate, polystyrene and polycarbonate, have demonstrated that the shear modulus for these polymers is linearly proportional to the amorphous orientation function on a semilogarithmic plot [19-21]. Therefore, if we assume that a maximum value for the amorphous phase shear modulus is attainable at an amorphous orientation function of unity, one can interpolate the value of the shear modulus corresponding to any value for f_m . In other words, we can join the isotropic value for G_m at $f_m = 0$ to the maximum value at $f_m = 1$ with a straight line or a semi-logarithmic scale. At this point, it is pertinent to point

out that, indeed, the Poisson ratio of the amorphous phase, ν_m , is also affected by a given state of orientation. A reasonable expression to estimate it, is defined as:

$$\frac{1}{\nu_m} = \frac{1-f_m}{\nu_{m,iso}} + \frac{f_m}{\nu_{m,ult}} \quad (3)$$

where $\nu_{m,iso}$ and $\nu_{m,ult}$ are the Poisson ratios for a completely random and fully oriented amorphous phase. Obviously as f_m approaches 0, $\nu_m \approx \nu_{m,iso}$ and as f_m approaches unity, $\nu_m \approx \nu_{m,ult}$.

The thermal expansion properties are equally affected by the orientation of the amorphous region. The amorphous orientation function will be also used to weigh the amorphous thermal strain as follows:

$$\frac{1}{e_m} = \frac{1-f_m}{e_{m,iso}} + \frac{f_m}{e_{m,ult}} \quad (4)$$

where e_m is the thermal strain of the matrix at any amorphous phase orientation level defined by f_m ; $e_{m,iso}$ is that of the isotropic amorphous phase and $e_{m,ult}$ represents the thermal strain of the fully aligned amorphous region. Equation 4 shows how the isotropic thermal strain of the amorphous region gradually decreases to a value of its counterpart in the fully aligned anisotropic case, throughout the solid-state deformation as f_m approaches unity. At this point, it is pertinent to note that Equation 2 shows an increase in E_m with f_m , while Equation 4 shows a decrease in the value of e_m as f_m increases. The inverse relationship between the modulus and the thermal expansion for the amorphous region is obviously preserved; such a phenomenon is in compliance with the fact that the thermal expansivity is a stiffness-dominated property.

1. Amorphous Phase Moduli

Three different teams of investigators [22-24] have recorded experimental data for the dynamic shear modulus for polyethylene with different levels of crystallinity over a wide range of temperature. Extrapolation of these data to zero volume fraction crystallinity at room temperature leads to the determination of the amorphous phase shear modulus for isotropic polyethylene. The work of Gray and McCrum [22] is not challenging since dual extrapolation is required because the temperature range covered in their work does not include room temperature. On the other hand, the work of Mandelkern et al. [23] and Illers [24], covers the temperature range -200°C to 100°C, and only extrapolation to zero volume fraction crystallinity is required

in order to obtain a value for the amorphous phase shear modulus. The work of Mandelkern et al. gives an amorphous phase shear modulus ($G_{m,iso}$) of 0.0317 GPa, while that of Illers gives the value of 0.057 GPa. With an amorphous phase Poisson ratio, $\nu_{m,iso}$, of 0.45 [25, 26], the values for the corresponding tensile moduli, $E_{m,iso}$, will be 0.09215 and 0.1653 GPa, respectively. It is pertinent to note that Holliday [27] discussed various models from the literature to predict the amorphous phase tensile modulus ($E_{m,iso}$) and he set out a plausible picture of how the overall stiffness of an isotropic polyethylene is built up in which $E_{m,iso}$, ranged from 0.1 to 0.5 GPa. Accordingly, it was decided to use an average value for the extrapolated results mentioned earlier, and the values for $G_{m,iso}$ and $E_{m,iso}$ were taken as 0.044 GPa and 0.128 GPa, respectively. On the other hand, the ultimate value for the amorphous phase tensile modulus, $E_{m,ult}$, needed in Equation 2 was obtained from the work of Holliday [27] who used a simple crystalline-amorphous series arrangement and estimated the value of 1.6 GPa for the amorphous phase tensile modulus for a completely aligned chain-extended polyethylene texture.

It was mentioned earlier that the shear modulus of the amorphous phase is linearly proportional to the amorphous phase orientation function on a semi-logarithmic plot. Accordingly, a further problem arises: the determination of the maximum value of the amorphous phase shear modulus, $G_{m,ult}$. Obviously, an entirely amorphous phase having completely random order can easily be assumed in a relaxed state. On the other hand, an unrelaxed amorphous phase is a state where the molecular chains in this phase are highly restricted in their mobility due to the extremely low temperature environment or high molecular orientation. Therefore, the unrelaxed (below -140°C) amorphous phase shear modulus was assigned to the maximum attainable shear modulus for a highly oriented amorphous phase. Using the work of Mandelkern et al. [23] and Illers [24], an average value for the shear modulus in the temperature range -140 to -180°C was found to be 1.42 GPa. Having obtained the upper limit on the amorphous phase shear modulus, one can join it to the lower bound of 0.044 GPa (value for the isotropic shear modulus) with a straight line, as shown in Figure 1. This figure may be utilized to interpolate values for the amorphous phase shear modulus at any level of orientation. The relationship may be mathematically expressed as:

$$G_m = 0.044 \exp(3.474 f_m) \quad (5)$$

Finally, in order to obtain the Poisson ratio for the amorphous phase at a given level of orientation one may use Equation 3. It was difficult to find experimental work on values of Poisson ratio for a fully aligned amorphous

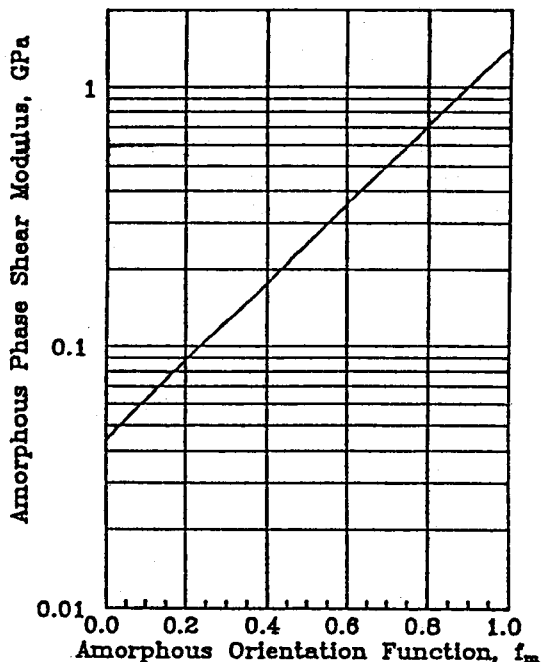


Figure 1: Plot of the amorphous phase shear modulus vs. the amorphous orientation function

phase in the literature. Therefore, we assumed that $\nu_{m,ult}$ is 0.3. With $\nu_{m,iso} = 0.45$ [25,26], Equation 3 shows that the Poisson ratio of the amorphous phase decreases with increasing the degree of orientation. Such a result makes sense, since, by definition the Poisson ratio is the ratio between lateral and longitudinal extension. Obviously, stretching will impose more constraint on the amorphous phase extension, therefore, its Poisson ratio will be reduced.

2. Thermal Expansion of the Amorphous Phase

The thermal strains of the isotropic amorphous state, $\epsilon_{m,iso}$, at different temperature levels were found by extrapolating polyethylene data from various levels of crystallinity to zero volume fraction crystallinity using the work of Buckley and McCrum [4], who provided the temperature dependence of the linear thermal strain for isotropic polyethylene, covering a crystallinity range from 0.494 to 0.775. Smoothing the data using a second degree polynomial one can obtain the following expression:

$$e_{m, iso} = -3.269 \times 10^{-4} + 2.2034 \times 10^{-4} T + 3.696 \times 10^{-7} T^2 \quad (6)$$

where T is the temperature in $^{\circ}\text{C}$, and the reference temperature is 0°C . At this point it is important to mention that the thermal expansion coefficient (obtained from the first derivative of Equation 6) of the isotropic amorphous region is in good agreement with the work of Stehling and Mandelkern [23] and Engeln et al. [28] over a wide temperature range of -150°C to room temperature.

Now, $e_{m, ult}$, used in Equation 4 deserves the final attention. This thermal strain is assumed to be the lowest attainable strain by the amorphous phase in an extremely oriented polyethylene texture. The values for this thermal strain were also obtained from the work of Buckley and McCrum [4]. They prepared a single-crystal sample of polyethylene and provided experimental data for the thermal strain in the deformation (draw) direction. They made the approximation that all the c -axes were parallel to this direction and accordingly, they have postulated a simple crystalline-amorphous series arrangement in the draw direction. This approximation is similar to the one adopted by Holliday [27] to obtain $E_{m, ult}$. Furthermore, this approximation is also equivalent to the assumption made by Sakurada et al. [29] in connection with the calculation of the Young's modulus in the chain direction in the crystalline phase of polyethylene using X-ray measurement of strain. Knowing the thermal strain in the draw direction and that of the c -axis (the chain axis), $e_{m, ult}$ was obtained from the following expression:

$$e_z = V_r e_c + V_m e_{m, ult} \quad (7)$$

which is the relation proposed by Buckley and McCrum [4] to express the thermal strain in the draw direction, e_z . Values for e_c were determined from the work of Davis et al. [30]. V_r and V_m are the volume fraction of the crystalline phase and the amorphous phase, respectively. Obviously, Equation 7 is the familiar rule of mixtures expression and its use in this particular case is in the spirit of the idea introduced by Schapery [31], that whenever a state of uniform stress is implied (crystalline-amorphous series arrangement), the expansivity is obtained by the rule of mixtures expression. Therefore, the expression developed for $e_{m, ult}$ may be expressed as:

$$e_{m,ult} = 5.0485 \times 10^{-6} + 8.556 \times 10^{-7} T - 1.7754 \times 10^{-9} T^2 \quad (8)$$

Again, T is in $^{\circ}\text{C}$ and the reference temperature is 0°C . Now, at any given temperature, knowing $e_{m,iso}$ and $e_{m,ult}$, one should be able to calculate the thermal strain of the amorphous phase for polyethylene at any orientation level using Equation 4.

Obviously, to determine any of the properties expressed by Equation 2 to 5, values for f_m should be known. The following is an attempt to clarify how one can readily determine the amorphous phase orientation function for anisotropic polyethylene.

3. Amorphous-Phase Orientation Function

Samuels [32] realized the identity of crystalline polymers as two-phase systems, and expressed the sonic modulus (Young's modulus measured using the ultrasonic technique) measured in the direction of solid state deformation as:

$$\frac{1}{E} = \frac{V_c}{E_{t,c}^{\circ}} (1 - \langle \cos^2 \theta_c \rangle) + \frac{V_m}{E_{t,m}^{\circ}} (1 - \langle \cos^2 \theta_m \rangle) \quad (9)$$

where $E_{t,c}^{\circ}$ and $E_{t,m}^{\circ}$ are the intrinsic lateral moduli of the perfectly oriented crystalline phase chains and amorphous phase chains, respectively. The angle θ_c is the average orientation angle between the c -axis of the crystallites and the deformation direction. For a simplified two-dimensional orientation distribution, the crystalline orientation function is defined as [33]:

$$f_c = 2 \langle \cos^2 \theta_c \rangle - 1 \quad (10)$$

For two-dimensional, randomly oriented, isotropic polyethylene both f_m and f_c vanish and from Equations 1 and 10:

$$\langle \cos^2 \theta_c \rangle = \langle \cos^2 \theta_m \rangle = 1/2 \quad (11)$$

Therefore, for isotropic polyethylene Equation 9 reduces to:

$$\frac{2}{E_{iso}} = \frac{V_r}{E_{t,c}^{\circ}} + \frac{V_m}{E_{t,m}^{\circ}} \quad (12)$$

From the definition of the orientation functions and the combination of Equations 9 and 12, we obtain the following expression:

$$2 \left[\frac{1}{E_{iso}} - \frac{1}{E} \right] = \frac{V_r f_c}{E_{t,c}^{\circ}} + \frac{V_m f_m}{E_{t,m}^{\circ}} \quad (13)$$

In this equation E_{iso} and E are the sonic moduli of the isotropic sample and the oriented sample, respectively $E_{t,c}^{\circ}$ is the inter-molecular transverse tensile modulus of the crystalline chain, for polyethylene its value is 3.6 GPa [29, 34]. Therefore, for polyethylene of known volume fraction crystallinity and isotropic sonic modulus, the intrinsic transverse modulus of the amorphous region, $E_{t,m}^{\circ}$, can be readily obtained using Equation 12. Polyethylene samples of different thermal histories were prepared and fully characterized; the experimental details and methodology are outlined elsewhere [35]. Using experimentally determined values for E_{iso} , E and the corresponding volume fraction crystallinities and crystalline orientation functions, $E_{t,m}^{\circ}$ was found to be 0.4433 GPa. Therefore, for an oriented sample of known crystalline orientation function, f_c , and sonic modulus, E , one may use Equation 13 to obtain f_m , and a set of corresponding values for the amorphous orientation function can be readily obtained. Consequently, for any orientation level described by a given value for f_m , one may use Equation 2 and 5 to estimate the amorphous phase tensile and shear moduli, while Equation 3 may be utilized to estimate the Poisson ratio of the amorphous region and Equation 4 may be used to estimate the thermal strain of the amorphous phase. Table 1 summarizes the values for the amorphous properties along with the predictive relations to estimate the mechanical and expansional properties of the amorphous phase at any orientation level described by a given value for f_m .

COMPARISON BETWEEN PREDICTION AND MEASUREMENT

One may argue about the validity of Equation 2 in estimating the amorphous phase modulus at any given level of orientation. Therefore, it was found necessary to compare theoretical prediction with experimental findings.

Table 1 Mechanical* and thermal expansion properties for the amorphous phase of polyethylene**

Amorphous phase moduli			Moduli for predicitive Calculations		
(Randomly aligned)		(Completely aligned)			
$E_{m,iso}$	$G_{m,iso}$	$E_{m,ult}$	$E_{t,m}$	$G_{m,ult}$	$E_m = 1.6f_m + 0.128(1-f_m)$
0.128	0.044	1.6	0.4433	1.42	$G_m = 0.044 \exp(3.474f_m)$

Amorphous phase Poisson ratio

Randomly aligned	Completely aligned	Poisson ratio for predicitive calculations
$\nu_{m,iso} = 0.45$	$\nu_{m,ult} = 0.30$	$\frac{1}{\nu_m} = \frac{f_m}{0.30} + \frac{1-f_m}{0.45}$

Thermal strains

Randomly aligned:	$e_{m,iso} = -3.269 \times 10^{-4} + 2.234 \times 10^{-4}T + 3.696 \times 10^{-7}T^2$
Completely aligned:	$e_{m,ult} = 5.0485 \times 10^{-6} + 8.556 \times 10^{-7}T - 1.7754 \times 10^{-9}T^2$

Thermal strain for predicitive calculations

$$\frac{1}{e_m} = \frac{f_m}{e_{m,ult}} + \frac{1-f_m}{e_{m,iso}}$$

* All moduli are in GPa

** Temperature is in °C and the reference temperature is 0°C

An effective value for the tensile modulus of the amorphous phase, E_{θ_m} , can be estimated from [36]:

$$\frac{1}{E_{\theta_m}} + \frac{\sin^4 \theta_m}{E_{t,m}^{\circ}} + \frac{\cos^4 \theta_m}{E_{1,m}^{\circ}} + \cos^2 \theta_m \sin^2 \theta_m \left[\frac{1}{G_m} - \frac{2\nu_m}{E_{1,m}^{\circ}} \right] \quad (14)$$

$E_{1,m}^{\circ}$ is the intrinsic longitudinal modulus of the polymer chain constituting the amorphous phase in a perfectly oriented polyethylene texture; this modulus is nothing but $E_{m,ult}$. The effective angle, θ_m , between the polymer chains in the amorphous region and the deformation direction can be obtained from the following approximation:

$$\cos^2 \theta_m = \langle \cos^2 \theta_m \rangle \quad (15)$$

where from Equation 1, $\langle \cos^2 \theta_m \rangle = (f_m + 1)/2$. Therefore, a set of values for E_{θ_m} can be obtained for given degrees of orientation described by different value for f_m and corresponding values for G_m and ν_m . Figure 2 shows that Equation 2 predicts E_m for anisotropic polyethylene sheets at various levels of

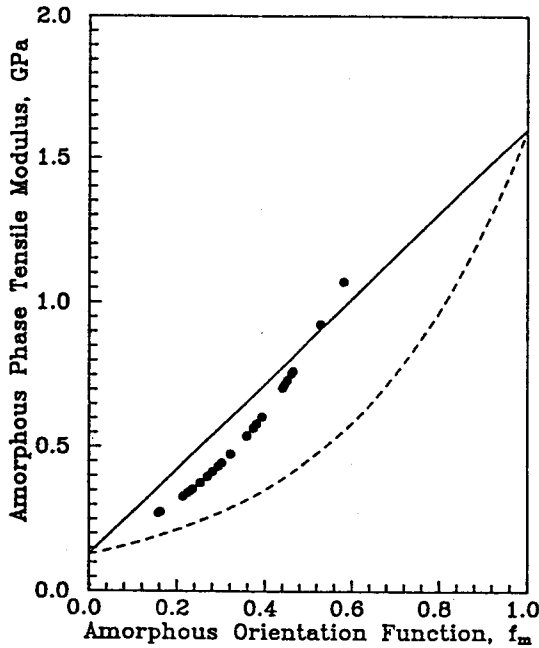


Figure 2: Comparison between experimentally determined amorphous phase tensile modulus (●) and theoretical prediction: (—) Equation 2; (---) Equation 16.

orientation with an agreement between 2% and 30%. This agreement may be considered quite good if one accounts for the procedure followed for the determination of the modulus which involved many assumptions and approximations.

At this point one may also argue that the amorphous phase tensile modulus may follow a trend similar to the one followed by the shear modulus (see Equation 5). In other words one may postulate that it could be obtained through the expression:

$$E_m = 0.128 \exp (2.5257 f_m) \quad (16)$$

The constants 0.128 and 2.5257 were obtained through the bounds on E_m when $f_m = 0.0$ and $f_m = 1.0$, respectively. Figure 2 also shows that either Equation 2 or 16 predicts E_m within 30%, but up to an amorphous orientation function of 0.26, above which Equation 2 shows better agreement. Therefore, Equation 2 is more suitable than Equation 16 in estimating reasonable values for the amorphous phase tensile modulus.

CONCLUSION

The subtlety of the micromorphological behavior of the amorphous phase in anisotropic polyethylene has been highlighted and the potential of the amorphous phase contribution to the behavior of anisotropic polyethylene has been emphasized.

A simple algorithm for determining the amorphous orientation function of anisotropic polyethylene has been outlined. Procedures for determining numerical values for the mechanical and thermal expansion properties of the amorphous phase for isotropic and fully oriented polyethylene have been demonstrated. Mathematical expressions for determining the tensile and shear moduli, Poisson ratio and thermal strain of the amorphous phase at a given two-dimensional orientation level have been defined. Comparison between theoretically predicted and experimentally determined tensile modulus of the amorphous phase for anisotropic polyethylene shows a reasonable correlation, within 30%.

REFERENCES

1. **Ward I.M., 1985**, The Preparation, Structure and Properties of Ultra-High Modulus Flexible Polymers, *Adv. Polym. Sci.*, 70, 3.
2. **Choy C.L., Chen F.C. and Ong E.L., 1979**, Anisotropic Thermal Expansion of Oriented Crystalline Polymers, *Polymer*, 20, 1191.
3. **Choy C.L., Chen F.C. and Young K., 1981**, Negative Thermal Expansion in Oriented Crystalline Polymers, *J. Polym. Sci; Phys.*, 19, 335.
4. **Buckley C.P. and McCrum N.G., 1973**, The Thermal Expansion of Single-Crystal Texture Linear Polyethylene between 0 and 190°C, *J. Mater.Sci.*, 8, 1123.
5. **Gibson A., Davis G. and Ward I.M., 1978**, Dynamic Mechanical Behavior and Longitudinal Crystal Thickness Measurements on Ultra-High Modulus Linear Polyethylene: a Quantitative Model for the Elastic Modulus, *Polymer*, 19, 683.
6. **Tager A., 1978**, *Physical Chemistry of Polymer: second edition*, Mir, Moscow.
7. **Magil J.H., 1977**, Morphogenesis of Solid Polymer Microstructures, in *Treatise on Materials Science and Technology*, J.M. Schultz Ed., 10.
8. **Peterlin A., 1969**, Folded Chain Model of Highly Drawn Polyethylene, *Polym. Eng. Sci.*, 9, 172.
9. **Peterlin A., 1971**, Molecular Model of Drawing Polyethylene and Polypropylene, *J. Mater. Sci.*, 6, 490.
10. **Peterlin A., 1975**, Plastic Deformation of Polymers with Fibrous Structure, *Coll. Polym. Sci.*, 253, 809.
11. **Fischer E. and Goddar H., 1969**, Electron Microscopic Examination of Cold Drawn Polyethylene, *J. Polym. Sci.*, C16, 4405.

12. **Clark E.S. and Scott L.S., 1984, Superdrawn Crystalline Polymers: A New Class of High-Strength Fiber, Polym. Eng. Sci., 14, 682.**
13. **Harrison I. and Juska T., 1982, A Criterion for Craze Formation, Polym. Eng. Sci., 22, 766.**
14. **Takayanagi M., Imada K. and Kajiyama T., 1966, Mechanical Properties and Fine Structure of Drawn Polymers, J. Polym. Sci., C15, 263.**
15. **Choy C.L. and Leung W., 1985, Elastic Moduli of Ultra-Drawn Polyethylene, J. Polym., Sci: Phys., 23, 1759.**
16. **Yuann J.K., and Kardos J.L., 1981, Prediction and Measurement of Orientation Distribution Effects on the Stiffness and Strength of Short Fiber and Molecular Composites, Proc. 2nd World Congress of Chem. Eng. and World Chem. Expo, Montreal.**
17. **Pezzutti J. and Porter R., 1985, Uniaxial Orientation in Linear Low Density Polyethylene, J. Appl. Polym. Sci., 30, 4251.**
18. **Samuels R., 1985, Polymer Structure, the Key to Process-Property Control, Polym.Eng.Sci., 25, 864.**
19. **Robertson R. and Buenker R., 1964, Some Elastic Moduli of Bisphenol A Polycarbonate, J. Polym. Sci., A2, 4889.**
20. **Wright H., Faraday C., White E. and Treloar L., 1971, The Elastic Constants of Oriented Glassy Polymers, J. Phy. D; Appl. Phys., 4, 2002.**
21. **Rawson F. and Rider J., 1974, The Elastic Constants of Oriented Polyvinyl Chloride, J. Phys. D; Appl. Phys., 7, 41.**
22. **Gray R. and McCrum M., 1969, γ -Relaxations in LPE and PTFE, J. Polym. Sci., A-27, 37.**
23. **Stehling F. and Mandelkern L., 1970, The Glass Temperature of Linear Polyethylene, Macrom., 3, 242.**

24. **Illers K., 1973**, The Dependence of the Dynamic Mechanical Properties of Linear Polyethylene on its Crystallinity, *Coll. Polym. Sci.*, 251, 394.
25. **Kardos J.L., Rasoni J. and Piccarolo S., 1979**, Prediction and Measurement of the Thermal Expansion Coefficient of Crystalline Polymers, *Polym. Eng. Sci.*, 19, 1000.
26. **Kardos J.L. and Rasoni J., 1975**, The Potential Mechanical Response of Macromolecular Systems-A Composite Analogy, *Polym. Eng. Sci.*, 15, 183.
27. **Holliday L., 1975**, The Stiffness of Polymers in Relation to their Structure, in *Structure and Properties of Oriented Polymers*, I.M. Ward, Ed., John Wiley and Sons, NY.
28. **Engeln I., 1985**, Thermal Expansion and Gruneisen Parameter of Polyethylene between 5 and 320 K, *Polymer*, 26, 364.
29. **Sakaruda I., Ito T. and Nakamae K., 1966**, Elastic Moduli of the Crystal Lattices of Polymers, *J. Polym. Sci.*, C-15, 75.
30. **Davis G., Eby R. and Coulson J., 1970**, Thermal Expansion of Polyethylene Unit Cell: Effect of Lamella Thickness, *J. Appl. Phys.*, 41, 4316.
31. **Schapery R.A., 1968**, Thermal Expansion Coefficients of Composite Materials Based on Energy Principles, *J. Comp. Mater.*, 2, 380.
32. **Samuels J.R., 1974**, *Structured Polymer Properties*, John Wiley and Sons, NY.
33. **Fakirov S. and Fakirova C., 1985**, Direct Determination of the Orientation of Short Glass Fibers in an Injection-Modeled Poly(ethylene-terephthalate)System, *Polym. Comp.*, 6, 41.
34. **Odajima A. and Maeda T., 1966**, Calculation of the Elastic Constants and the Lattice Energy of the Polyethylene Crystal, *J. Polym. Sci.*, C-15, 55.