Macromolecules **1990,** *23,* 2365–2370

From this the average depolarization takes the form

$$\Delta \sim (w^2/t_\mathrm{h})(t_\mathrm{h}) \sim w^2 t_\mathrm{h} \sim t^2 t_\mathrm{h} \qquad (11)$$

and therefore the nucleation parameter, n, is clearly 2 (not 3).

A similar analysis would be applicable to athermally activated plates growing in 2-D in almost any orientation. The only requirement is that the crystallite growth directions do not lie *exactly* parallel to the light beam. For any other orientation the thickness of any given crystallite parallel to the light beam is invariant with the time of growth so that the depolarization would be proportional to t^2. Only when one of the crystal growth directions is *exactly* parallel to the light beam (and thus the thickness of the crystallite is increasing) will the depolarization go as t^3 (i.e., $n = n + 1$). Such a crystallite orientation is highly improbable if its initial placement and orientation in the sample is random. On the basis of this reasoning it follows that the number of crystallites growing parallel to the light beam is extremely small compared with those in other orientations. Consequently an average Avrami n of 2 should dominate the DLI results obtained for 2-D crystallites.

In Binsbergen's final analysis the time dependence of the thickness is not removed when making the assumption that an athermally activated 2-D spherulite (and by inference any 2-D crystallite) would result in a nucleation parameter of 3 (i.e., $n + 1$) instead of 2. We have shown that this is not the case and, by analogy, proved that in general, for 2-D crystallites with neither growth direction oriented *exactly* parallel to the light beam, an n of 2 should be expected. Thus the results presented in our papers, parts 2 and 3, are thoroughly consistent with platelets growing in two dimensions in which neither growth direction is parallel to the light beam.

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The Theoretical Modulus of Biaxially Oriented Polymer Films

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ABSTRACT: Young's moduli of balanced, biaxially oriented polymer films composed of single crystal elements are calculated for several hypothetical structures, in the ideal case of 100% crystallinity. The numerical data used in the computations are the mechanical properties of the single-crystal unit, in the form of the modulus or compliance tensor. Structural characteristics of equibiaxially oriented polyethylene samples indicate that the appropriate model is an aggregate of single crystals, for which the tensile modulus is calculated by Reuss-averaging the properties of the structural unit over all directions. It is predicted, in accordance with experimental observations, that the modulus of such equibiaxially oriented films is low in comparison with the axial theoretical modulus of single crystals, due to the large contribution of the shear compliance of the crystals. By contrast, calculations presented in this study indicate that structures in which a uniform distribution of strain is achieved may exhibit a very high modulus. Such materials include laminates and certain composites.

1. Introduction

Numerous studies have been devoted to the theoretical modulus of polymeric crystals in the direction of the macromolecular chains.[1–6] It has been shown that, in general, the axial crystal modulus is high (40–320 GPa) in comparison with that of isotropic materials (1–3 GPa). These results have triggered major experimental efforts to develop routes toward uniaxially oriented materials from both flexible and rigid macromolecules.[7–11] Nowadays, oriented fibers and films are manufactured that exhibit extraordinarily high Young's moduli that approach the theoretical estimates.

Little attention has been paid to the theoretical limits of the stiffness of biaxially oriented structures, despite

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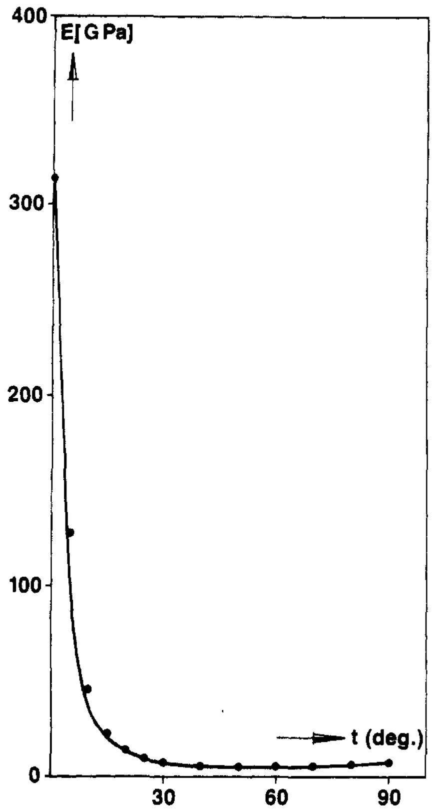

Figure 1. Theoretical modulus of polyethylene versus the angle (*t*) between test and chain direction.

the fact that biaxial orientation of polymeric films, in the molten or in the solid state, is widely used to enhance mechanical properties.[12] It is the aim of this study to provide theoretical estimates of the maximum modulus of equibiaxially drawn polymer films.

2. Theory

First, we will briefly review some of the literature on modeling of small-strain mechanical properties of polymers pertinent to the present work.

Kardos et al. proposed a model to estimate the theoretical modulus of isotropic crystalline polymers, based on the mechanics of composite materials.[14,15] In their approach a two-dimensional orientation is assumed in isotropic polymers, which appears to result in an overestimation of the theoretical modulus. Ward and coworkers proposed a useful model in which polymers are regarded as aggregates of anisotropic elastic units.[9,17] The mechanical properties of the units are considered to be those of a highly oriented polymer and are obtained from experimental data. Although this aggregate model has been applied successfully to some semicrystalline polymers,[18-21] it is essentially a one-phase model and, consequently, more applicable to amorphous polymers. Ward's aggregate model was extended to two-phase systems (semicrystalline polymers) by Samuels, Seferis, and their coworkers.[22-26] In their studies the mechanical properties of the amorphous and crystalline phases were considered explicity and small-strain mechanical properties were calculated as a function of crystallinity and amorphous/crystalline orientation. Subsequently, detailed morphological characteristics of semicrystalline polymers, such as spherulitic structures in isotropic polymers, were introduced into this model by Boyd et al.[27,28]

The aforementioned models have been used primarily to describe the properties of isotropic and uniaxially drawn polymers. In this study we will use similar models to estimate the theoretical modulus of biaxially oriented films. In the following paragraphs the calculations will be presented, employing polyethylene as an illustrative example.

2.1. Polyethylene Single Crystals.

First we will address the mechanical properties of single crystals, which are the basic structural units of the biaxially oriented films discussed below.

The small-strain mechanical properties of homogeneous, isotropic elastic solids can be calculated by using the generalized Hooke's law:[29]

$$\epsilon_{ij} = S_{ijkl}\sigma_{kl} \qquad (1)$$

$$\sigma_{ij} = C_{ijkl}\epsilon_{kl} \qquad (2)$$

Here ϵ_{ij} and σ_{ij} denote the strain and stress tensor components, respectively, and S_{ijkl} and C_{ijkl} the compliance and elastic constants, respectively. Generally, the so-called contracted notation of eq 1 and 2 is used:

$$\epsilon_p = S_{pq}\sigma_q \qquad (3)$$

$$\sigma_p = C_{pq}\epsilon_q \qquad (4)$$

In eqs 3 and 4 ϵ_p and σ_p are the strain and stress components, respectively, and S_{pq} and C_{pq} are the compliance and elastic constants, respectively. The theoretical elastic and compliance constants of polyethylene single crystals are[30]

$$C_{pq} = \begin{vmatrix} 7.99 & 3.28 & 1.13 & 0 & 0 & 0 \\ 3.28 & 9.92 & 2.14 & 0 & 0 & 0 \\ 1.13 & 2.14 & 316 & 0 & 0 & 0 \\ 0 & 0 & 0 & 3.19 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1.62 & 0 \\ 0 & 0 & 0 & 0 & 0 & 3.62 \end{vmatrix} \text{ GPa} \qquad (5)$$

and

$$S_{pq} = \begin{vmatrix} 14.5 & -4.78 & -0.019 & 0 & 0 & 0 \\ -4.78 & 11.7 & -0.062 & 0 & 0 & 0 \\ -0.019 & -0.062 & 0.317 & 0 & 0 & 0 \\ 0 & 0 & 0 & 31.4 & 0 & 0 \\ 0 & 0 & 0 & 0 & 61.7 & 0 \\ 0 & 0 & 0 & 0 & 0 & 27.6 \end{vmatrix} \times 10^{-2}\ \text{GPa}^{-1} \qquad (6)$$

By transforming coordinate systems, the small-strain mechanical properties of polyethylene crystals in any given direction can be calculated.[29]

For the derivations of the moduli of biaxially oriented films, the Young's modulus of polyethylene crystals as a function the angle (t) between the test and chain direction is of particular importance; for the b axis orientation perpendicular to the plane of the film it is given by

$$E(t) = S_{33}^{-1}(t) = (S_{11}\sin^4 t + 2S_{13}\cos^2 t\sin^2 t + S_{33}\cos^4 t - 2S_{35}\cos^3 t\sin t - 2S_{15}\cos t\sin^3 t + S_{55}\cos^2 t\sin^2 t)^{-1} \qquad (7)$$

The Young's modulus of polyethylene single crystals as a function of the angle between test and chain direction is plotted in Figure 1. This figure illustrates that the mechanical properties indeed are highly anisotropic; this is mainly caused by the low shear modulus/high shear compliance.[29] Similar transformations can be applied to calculate all elastic and compliance constants.

Having discussed the mechanical properties of single crystals, we will now calculate the theoretical moduli of equibiaxially oriented polyethylene films for several hypothetical structures.

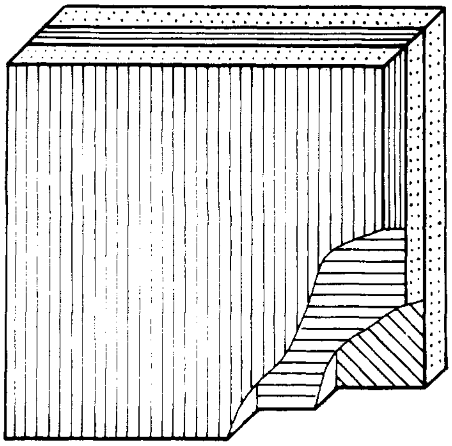

Figure 2. Laminate of single crystals.

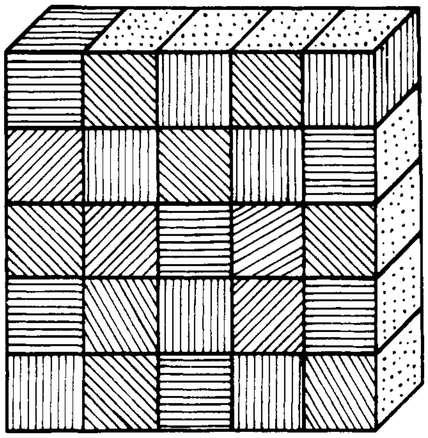

Figure 3. Schematic drawing of an aggregate of single crystals.

2.2. Polyethylene Single-Crystal Laminate. Figure 2 displays a schematic laminate of polyethylene single crystals. In this figure the chain axis (*c* axis) of the crystals is represented by solid lines. The following assumptions are made: the chain (*c*) axis is randomly oriented, on macroscopic scale, in the plane of the film (i.e. planar orientation is assumed); the crystallinity is 100%; the single crystals have infinite dimensions in the plane of the film; the film contains no defects of any kind; the laminate consists of an infinite number of layers. The unit cell of polyethylene single crystals is orthorhombic and is therefore characterized by three mutually perpendicular axes, which are conventionally termed the *a*, *b*, and *c* axes.[31] In the case of a—macroscopically—random *c* axis orientation several options are left with respect to orientation of the *a* and *b* axes. We will limit ourselves to the following cases: the *a* axis of all crystals perpendicular to the plane of the film; the *b* axis of all crystals perpendicular to the plane of the film; the *a* and *b* axes random in the plane perpendicular to the *c* axis.

The relation between the characteristics of a single crystal and the properties of a material composed of an assembly of single crystal units has been investigated extensively. Voigt calculated the stiffness of an aggregate by averaging the elastic constants of the crystals, which, in fact, in equivalent with the assumption of uniform strain in the material.[32] Reuss, on the other hand, calculated the stiffness of an aggregate by averaging compliance constants. This corresponds to the assumption that the stress is uniform, not the strain.[33] Hill demonstrated theoretically that the Voigt moduli are higher than the Reuss moduli and that actual moduli are always between these two extremes.[34] Moreover, it was shown by Hill that both methods are approximations, since in the Voigt limit the forces are not in equilibrium and in the Reuss model the deformed crystals do not fit together.

In the case of a laminate the stress and strain distribution in the material is highly dependent on the "adhesion" between the single-crystal layers. The following two extreme cases can be distinguished:

(a) No Adhesion. The layers of the laminate are separated and experience uniform strains in one dimension, i.e. the test direction. In all other directions, each layer deforms according to the orientation of its principal axes with respect to the test direction. The modulus of a polyethylene laminate with a random *c*-axis distribution and the *b* axis oriented perpendicular to the plane of the film is given by

$$E_1 = (2\pi)^{-1}\int_{-\pi}^{\pi}E(t)\,\mathrm{d}t = (2\pi)^{-1}\int_{-\pi}^{\pi}(S_{11}\sin^4 t + 2S_{13}\cos^2 t\sin^2 t - 2S_{15}\cos t\sin^3 t + S_{33}\cos^4 t - 2S_{35}\cos^3 t\sin t + S_{55}\cos^2 t\sin^2 t)^{-1}\,\mathrm{d}t \quad (8)$$

The modulus of the laminate for this particular case was calculated numerically. The stress/strain state in these laminates is between the Reuss average (uniform stresses in three dimensions) and the Voigt average (uniform strains).

(b) Adhesion. In this limiting case, the distribution of strains is forced upon the separate layers through adhesion, and the single-crystal layers experience uniform strains in three dimensions. This particular strain distribution corresponds to the previously discussed Voigt average. In this case the elastic constants of the laminate with the *c* axis parallel and the *b* axis oriented perpendicular to the plane of the film is

$$\begin{gathered}\bar{C}_{11} = \bar{C}_{33} = 0.125(3C_{11} + 2C_{13} + 3C_{33} + 4C_{55})\\ \bar{C}_{13} = 0.125(C_{11} + 6C_{13} + C_{33} - 4C_{55})\\ \bar{C}_{55} = 0.125(C_{11} - 2C_{13} + C_{33} + 4C_{55})\\ \bar{C}_{12} = \bar{C}_{23} = 0.5(C_{12} + C_{23})\\ \bar{C}_{44} = \bar{C}_{66} = 0.5(C_{44} + C_{66})\\ \bar{C}_{22} = C_{22}\end{gathered} \quad (9)$$

The Young's modulus of the laminate is

$$E_3 = \bar{C}_{33} + (\bar{C}_{23}{}^2\bar{C}_{11} + \bar{C}_{22}\bar{C}_{13}{}^2 - 2\bar{C}_{23}\bar{C}_{13}\bar{C}_{12})/(\bar{C}_{12}{}^2 - \bar{C}_{11}\bar{C}_{22}) \quad (10)$$

2.3. Polyethylene Single-Crystal Aggregate. In this paragraph the theoretical modulus of an aggregate of single crystals is computed. The structure of interest is schematically depicted in Figure 3. The modulus of the aggregate shown is calculated assuming the following: the *c* axis is —macroscopically—randomly oriented in the plane of the film; the crystallinity is 100%; single crystals have finite size. The upper and lower limits of the theoretical modulus of the aggregate in Figure 3 are respectively the Reuss and Voigt averages of the mechanical properties of the constituting elements.

(a) In the Reuss approximation, the 11 component of the compliance tensor of the aggregate is

$$S_{11} = (2\pi)^{-1}\left(S_{11}\int_{-\pi}^{\pi}\cos^4 t\,\mathrm{d}t + 2S_{13}\int_{-\pi}^{\pi}\cos^2 t\sin^2 t\,\mathrm{d}t - 2S_{15}\int_{-\pi}^{\pi}\cos^3 t\sin t\,\mathrm{d}t + S_{33}\int_{-\pi}^{\pi}\sin^4 t\,\mathrm{d}t - 2S_{35}\int_{-\pi}^{\pi}\cos t\sin^3 t\,\mathrm{d}t + S_{55}\int_{-\pi}^{\pi}\cos^2 t\sin^2 t\,\mathrm{d}t\right) \quad (11)$$

The nonzero components of the compliance tensor of a

Table I
Young's Moduli of Equibiaxially Oriented Polyethylene Single-Crystal Laminate (Figure 2)

E_{th}, GPa	*a*-axis normal	*b*-axis normal	*a*-axis random
uniform strain in one dimension	34.9	25.0	29.0
Voight average	111	109	110

Table II
Young's Moduli of Equibiaxially Oriented Polyethylene Single-Crystal Aggregate (Figure 3)

E_{th}, GPA	*a*-axis normal	*b*-axis normal	*a*-axis random
Reuss average	11.9	7.5	9.6
Voight average	111	109	110

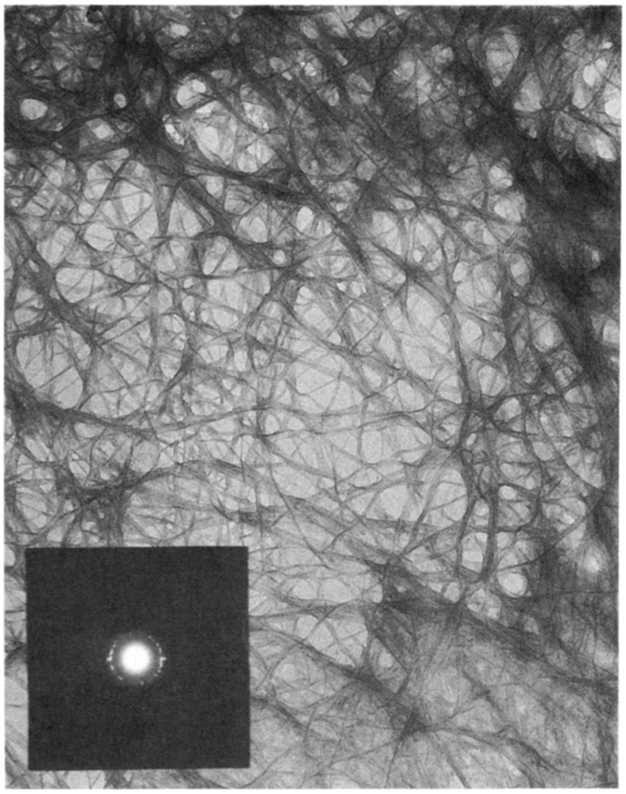

Figure 4. Transmission electron micrograph of 15 × 15 times drawn UHMW PE film (35 000×). Insert: selected area electron diffraction pattern.

film with the *b* axis perpendicular to the plane of the film are

$$\begin{aligned} \bar{S}_{11} = \bar{S}_{33} &= 0.125(3S_{11} + 2S_{13} + 3S_{33} + S_{55}) \\ \bar{S}_{13} &= 0.125(S_{11} + 6S_{13} + S_{33} - S_{55}) \\ \bar{S}_{15} &= 0.5(S_{11} - 2S_{13} + S_{33} + S_{55}) \\ \bar{S}_{12} = \bar{S}_{23} &= 0.5(S_{12} + S_{23}) \\ \bar{S}_{44} = \bar{S}_{66} &= 0.5(S_{44} + S_{66}) \\ \bar{S}_{22} &= S_{22} \end{aligned} \tag{12}$$

The Young's modulus in the case of a *b*-axis orientation perpendicular to the plane of the film is

$$E = S_{33}^{-1} = S_{11}^{-1} \tag{13}$$

(b) If uniform strain (Voigt) is imposed, the Young's modulus in the case of a *b*-axis orientation perpendicular to the plane of the film is identical with the previously discussed Voigt average of laminates; i.e., it is given by eq 10.

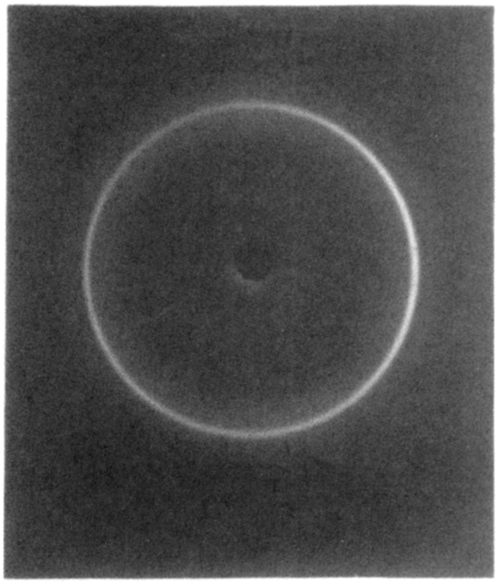

Figure 5. WAXS patterns of UHMW PE film normal to the plane of the film.

2.4. Results. The moduli of planar oriented polyethylene can now be calculated from the theoretical elastic constants and compliance tensors of the single-crystal units (eqs 5 and 6) and relations 7–13. The results of these calculations are listed in Tables I and II. These data illustrate that the theoretical moduli of balanced, biaxially oriented films are highly dependent on the assumed structure, stress/strain distribution, and, to a lesser extent, the orientation of the *a* and *b* axes. As a result, a rather wide range of structure-dependent theoretical moduli is obtained (8–111 GPa) which is, of course, an unsatisfactory result. Accordingly, we turned to experimental data to guide us in the selection of the relevant structure.

3. Balanced Biaxially Oriented Films

3.1. Polyethylene. Biaxially oriented films were prepared from ultra-high molecular weight polyethylene (UHMW PE, Hifax 1900, Himont, $M_w = 5 \times 10^6$ g/mol) by casting from solution, following standard techniques.[13] The nominal polymer concentration in solution was 5% w/w. Dried gel films were simultaneously drawn in two mutually perpendicular directions to a draw ratio of 15 × 15, at a temperature of 120 °C. Balanced films with isotropic properties in the plane of the film were obtained. The Young's modulus of the drawn films was approximately 5 GPa.

Figure 4 displays a transmission electron micrograph (TEM) of the biaxially drawn UHMW PE film. This micrograph indicates that the film consists of long, interconnected fibrils (see also ref 35 and 37). The insert shows a selected-area electron diffraction pattern. This diffractogram reveals that the macromolecules in the individual fibrils are highly oriented along the fibril axis. Figure 5 displays a wide-angle X-ray pattern (WAXS) taken with the incident beam normal to the film plane. In accordance with other studies,[35,37] it was found that the films possess a macrosopically random *c*-axis orientation in the plane of the film. Figures 4 and 5 clearly reveal that the biaxially oriented films consist of highly anisotropic fibrils that are randomly oriented in the plane of the film. In the following it is assumed that a similar structure is always observed in biaxially drawn UHMW PE films even at high draw ratios (> 15 × 15). Consequently, the structure relevant for the estimation of the theoretical modulus is the hypothetical structure drawn in Figure 3.

Table III
Young's Moduli of Equibiaxially Oriented Polymers Films

E_{th}, GPA	a-axis normal	b-axis normal	a-axis random
poly(vinyl alcohol)	18.7	9.7	12.6
nylon 6 (α)	7.1	5.0	5.9
nylon 6 (β)	17.2	7.2	9.7

The fibrils in balanced, biaxially oriented UHMW-PE contain crystallites of limited size and are inevitably interconnected by an amorphous phase which probably has a certain degree of planar orientation. The modulus of the amorphous phase will nevertheless be low. Therefore, the amorphous phase cannot impose additional deformation to the crystals, which implies that the strain in a crystal depends only on its modulus in the test direction and, therefore, on its orientation with respect to the test direction. This is equivalent with uniform stress in the film. The theoretical modulus of balanced, biaxially oriented films thus should be calculated by using the stress distribution in semicrystalline films as a starting point and extrapolating to 100% crystallinity. This, in fact, corresponds to the previously calculated Reuss average of the theoretical modulus of the aggregate of Figure 3.

The results in Table II indicate that the crystallographic a and b axis orientation in polyethylene films significantly affects the theoretical moduli of the films. Detailed X-ray diffraction studies indicate that several preferred a and b axis orientations are present in biaxially oriented films.[35,37] Consequently, the exact theoretical moduli of these films cannot be accurately predicted on the basis of the calculations presented. However, the above calculations combined with the structural data on UHMW-PE films indicate that the theoretical maximum modulus of such films is approximately 8–12 GPa.

3.2. Other Polymers. The maximum attainable modulus of biaxially oriented polymer films can be calculated with the previously presented model if it is assumed that these films possess a similar structure and provided that the elastic and/or compliance constants of the crystals are known. The elastic/compliance constants of poly(vinyl alcohol) and nylon 6 crystals have been calculated by Tadokoro et al.[30,38] The results of the calculations of the theoretical modulus of biaxially oriented films of these two materials are listed in Table III.

4. Discussion and Conclusions

The calculated maximum attainable modulus of balanced, biaxially drawn polyethylene films is low in comparison with that of uniaxially oriented structures. This low value is a result of the uniform distribution of stress within the films and of the low shear moduli/high shear compliances of polyethylene. The uniform distribution of stress in biaxially oriented films is a direct consequence of the structure of these films (section 3.1). The strong influence of the shear compliances on the theoretical moduli of biaxially oriented films is very apparent from eqs 11 and 12. The shear compliance (S_{55}) of polyethylene is large in comparison with the other components of the tensor, and consequently the theoretical modulus is dominated by this compliance. The low shear modulus/high shear compliance of polyethylene crystals originates, of course, from the weak interaction (van der Waals forces) between the macromolecules.

The chain interactions in poly(vinyl alcohol) crystals are strong compared to those in polyethylene because of hydrogen bonding between the macromolecules and monomer segments. Consequently, the shear moduli are substantially higher, which results in an increased maximum modulus of biaxially oriented films (Table III). The theoretical moduli of biaxially oriented nylon 6 films are predicted to be low, despite the presence of hydrogen bridges (Table III). One should bear in mind, however, that nylon 6 crystals are built up of sheets in which the macromolecules are connected through hydrogen bridges. These sheets, by contrast, interact only through van der Waals, forces, which results in low shear moduli.[38]

A few critical remarks are in order with respect to comparison of the predicted maximum moduli of equibiaxially oriented films and reported maximum experimental values. First, in contrast to the aggregate drawn in Figure 3, balanced, biaxially oriented films possess a fibrillar structure (Figure 4). However, in the rigorous calculation of the theoretical limits of the modulus of such films the dimensions of the crystals/fibrils appeared to be irrelevant. These dimensions will be of importance only in states between uniform stress and strain distribution, which will be commented upon below. More importantly, the modulus of balanced, biaxially oriented films was calculated on the basis of an aggregate of perfect single crystals, i.e. in the limit of 100% crystallinity. Actual samples of biaxially drawn polyethylene invariably display the presence of a significant amorphous fraction.[35–37] Accordingly, the experimental maximum achieved modulus will always be lower than the theoretical modulus. In the case of polyethylene the reported maximum experimental modulus is approximately 50% of the theoretical modulus.[35–37]

As discussed above, the stiffness of equibiaxially oriented polymer films appears to be disappointingly low, which is a direct consequence of the aggregate-like structure and the poor stress transfer in the amorphous "matrix". The question arises, of course, what structural or physical requirements should be met for the films to approach a state of equal strain, which would result in significantly higher moduli (Table III). From the above considerations as well as from standard composite theories, it is evident that major improvement, even for aggregate structures, is to be expected when the adhesion between the structural elements is enhanced through, e.g., drastically increasing their aspect ratio or increasing the stiffness of the connecting matrix, i.e. the amorphous interphase (for example, by raising its glass transition temperature through chemical modification). Following that argument, it is predicted that films consisting of equibiaxially oriented crystals of high aspect ratio embedded in a high modulus matrix material are potentially very stiff. As a matter of fact, high modulus films (~80 GPa) possessing such a structure were indeed recently described by Krause et al.[40] Alternatively, and more effectively, the stiffness of biaxially oriented films can be dramatically improved when the formation of an aggregate-like morphology is circumvented altogether and a laminate structure is produced (cf. Table I). It appears unlikely that such structures can be produced through a simple biaxial tensile drawing technique, but the desirable laminate morphologies can, in principle, be manufactured by laying down successive layers of uniaxially oriented macromolecules. It seems that a "paint-brushing" scheme, employing liquid crystalline polymers, may yield the appropriate structure.

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Solubilities and Diffusivities of Permanent Gases in Poly(phenolphthalein terephthalate)

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ABSTRACT: Solubility and diffusivity of pure carbon dioxide, methane, ethane, oxygen, argon, and nitrogen in solution-polymerized poly(phenolphthalein terephthalate) [PPha-tere] were determined from independent sorption and permeation measurements. PPha-tere absorbs ~8 wt % carbon dioxide at 35 °C (20 atm), roughly 80% more than polycarbonate or polysulfone does. The carbon dioxide permeability of PPha at 35 °C exceeds 20 Barrers. The permselectivities, defined as the ratio of pure-gas permeabilities, for CO_2/CH_4 and CO_2/C_2H_6, respectively, are greater than 28 and 59 at 35 °C. The dual-mode model formalism was adopted to analyze the sorption and permeation data. Inference regarding the physical state of absorbed gas molecules is made. The equilibrium sorption parameters and the diffusion coefficients are correlated with the critical temperature of the gas and the dimension of the gas, respectively.

Introduction

Recent intensified searches for better gas-separation membrane and permeation barrier materials has led to the discovery of many polymers exhibiting extraordinary transport properties.[1-4] Our interest has been in the relationship between molecular features (including packing density, local chain mobility, and functional groups of the polymer and dimensions and the donor–acceptor nature of the penetrants) and transport parameters (including the diffusion and solubility coefficients of penetrants in the polymer). One of the polymers which we found to exhibit transport properties superior to commercial materials is the polyester of phenolphthalein and phthalic acid chloride. The effects of the nature of the phthalate (tere-, iso-, or a mixture of them) on the various properties of the polymer have been reported in a previous paper.[5] It was found that the para linkage in poly(phenolphthalein terephthalate) (to be called PPha-tere in this paper) resulted in a lower mass density of the polymer relative to its isophthalate counterpart (PPha-iso). The lower mass density of PPha-tere was considered equivalent to poorer packing since PPha-tere and PPha-iso are essentially isomers made of the same constituent atoms.

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