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The degree of crystalline orientation as a function of draw ratio in semicrystalline polymers: a new model based on the geometry of the crystalline chain slip mechanism

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Abstract

The orientation behaviour of a range of high density polyethylenes (PEs) drawn to different draw ratios has been investigated by measurements of optical birefringence and wide angle X-ray diffraction (WAXS). Consistent with previous research, it can be concluded that birefringence relates to the overall degree of orientation of the amorphous and crystalline phases, and is described to a good approximation by the pseudo-affine deformation scheme.

The WAXS results show that crystalline orientation is also related uniquely to the applied strain and moreover is independent of the characteristics of the polymer concerned. It is shown that the crystalline orientation follows a new model based on the geometry of the crystalline slip mechanism where the crystalline phase deforms affinely in the longitudinal drawing direction.

Keywords

Crystalline orientation, Tensile drawing, Affine Deformation, Birefringence, WAXD

1. Introduction

The tensile deformation of polymeric materials is always accompanied by the progressive alignment of the polymeric chains along the direction of maximum extension. The degree of molecular orientation, either crystalline or amorphous, is typically related to the amount of strain experienced by the sample. When morphological characteristics (such as the molecular weight or the degree of branching) or topological characteristics (such as the degree of crystallinity or lamellar thickness) are not taken into account, the degree of molecular orientation is then a single function of the draw ratio. Two key models that express the molecular orientation as a function of draw ratio are the affine and pseudo-affine deformation schemes.

Affine deformation is one in which the deformation experienced locally by the molecules is the same as the macroscopic deformation experienced by the sample as a whole. In the context of a network of flexible amorphous chains, affine deformation means that when the polymer is stretched, the crosslink points move exactly as they would if they were pairs of points in a completely homogeneous medium deformed to the same macroscopic deformation [1]. The pseudo-affine deformation scheme assumes that the material is composed of transversely isotropic units whose symmetry axes rotate affinely on stretching, i.e. in the same manner as would lines joining pairs of points in a completely homogeneous medium deformed to the same macroscopic deformation [2,3]. The model is called pseudo-affine as opposed to affine because only the rotation of the units is considered, i.e. their increase in length is not taken into account.

The affine model has been successfully applied to predict the deformation of rubbers [1]. In amorphous polymers, the process of molecular orientation depends on whether the strain is imposed below or above Tg. Below Tg the orientation does conform to the pseudo-affine model in some cases [4,5], whereas above Tg the orientation °behaviour is better described by the affine model [4] or by an intermediate situation between the affine and the pseudo-affine schemes [5]. In the case of semicrystalline polymers, it is often found that the overall degree of orientation (average between the orientations of the amorphous and crystalline phases) conforms relatively well with the predictions of the pseudo-affine model. The first work to show this correlation in low density polyethylene between the pseudo-affine model and birefringence (technique employed to quantify the average orientation) was that of Crawford and Kolsky [2]. More recently Dirix et al. [6] demonstrated the validity of this correlation for a wide range of polyethylenes: LDPE, LLDPE, HDPE and UHMW-PE.

Surprisingly, no model has been developed to describe the evolution of the orientation of the crystalline phase with strain in semicrystalline polymers, in spite of the fact that there is strong experimental evidence in favour of crystalline orientation being a single function of strain and independent of the characteristics of the polymer considered. As long ago as 1978, Kilian and Pietralla [7] observed that the crystalline orientation data for drawn HDPE, LDPE and PVC, both stressed and relaxed, all lay on the same degree of orientation versus strain curve. More recently, this single crystalline orientation-strain relation was observed once again, this time in a series of semicrystalline polymers of crystallinities ranging from 18 to 76% [8].

In summary, the crystalline orientation mechanism appears common to all semicrystalline polymers and is, apparently, a single function of strain and independent of the long range order of the polymer considered. However, in spite of being often observed, this "universal" crystalline orientation-strain behaviour has never been characterized. The model presented in this work expresses the degree of orientation of the crystalline phase in semicrystalline polymers as a function of draw ratio only. It assumes that the crystalline phase deforms by the mechanism of chain slip. It is also considered that there is rotation of the crystalline planes as a result of the chain slip. This is not new: slip and rotation are known to be the main mechanisms by which the molecules in the crystalline phase orient towards the drawing direction. What is new is the additional assumption that this deformation is affine.

To investigate how well the proposed new model represents the orientation behaviour of semi-crystalline polymers, experiments have been conducted on a range of high-density polyethylene polymers: a homopolymer, a branched polymer, and both polymers grafted with a silane monomer.

Measurements of crystal orientation were combined with measurements of optical birefringence on a range of drawn samples.

2. Equations for the overall degree of molecular orientation and for the degree of crystalline orientation

In this section the proposed new "crystalline chain slip model" that describes the evolution with draw ratio of the degree of crystalline orientation will be presented. The derivation is similar to that of the pseudo-affine model mentioned above: the method is exactly the same and only the starting point (i.e. the starting equation) differs. The method follows that adopted in Ref. [3] and consists of first defining the final orientation θ of a single molecular segment as a function of its initial orientation θ_0 and the draw ratio λ

The average orientation of the aggregate of molecular segments is expressed as an integral function of the orientation of the individual segments. Assuming that the undeformed state is isotropic and that there is transverse isotropy in the deformed state, this is given by:

$$\langle\cos^2\theta\rangle = \int_0^{\frac{\pi}{2}} \cos^2\theta \sin\theta_0 \,\mathrm{d}\theta_0 \qquad (1)$$

where $\langle \cos^2 \theta \rangle$ is the average cosine square of the angles between the oriented molecular segments and the stretching (drawing) direction.

The Hermans orientation function $\langle \mathrm{P}_2 \rangle$ is then:

$$\langle \mathrm{P}_2 \rangle = \frac{3\langle \cos^2 \theta \rangle - 1}{2} \tag{2}$$

2.1 The pseudo-affine model

The pseudo-affine model makes no distinction between the amorphous and crystalline phases; it assumes that the material is made of transversely isotropic units whose properties are those of the completely oriented polymer. In the isotropic state the axes of the units are distributed randomly in space. On drawing, each unit rotates in the same manner as lines joining pairs of points in the bulk material, i.e. the units rotate in an affine manner. The units do not change in length or properties on drawing [2,3]. As unrealistic as these assumptions may seem, the birefringence in oriented polyethylene agrees quite well with the predictions of this model, as mentioned in the Introduction. This agreement suggests that the pseudo-affine deformation scheme is suited to model the evolution of the overall degree of molecular orientation (average of crystalline and amorphous orientations) with draw ratio.

The change in orientation of a line joining a pair of points in a completely homogeneous medium deformed to a macroscopic draw ratio λ is given by (3), in which θ_0 and θ are the initial and final inclinations, respectively, of the line in relation to the draw direction.

$$\tan(\theta) = \lambda^{-\frac{3}{2}} \tan(\theta_0) \tag{3}$$

Equation (3) is easily derived from observation of Fig. 1, that represents deformation at constant volume of a cylinder that fully encloses the line joining the arbitrary pair of points.

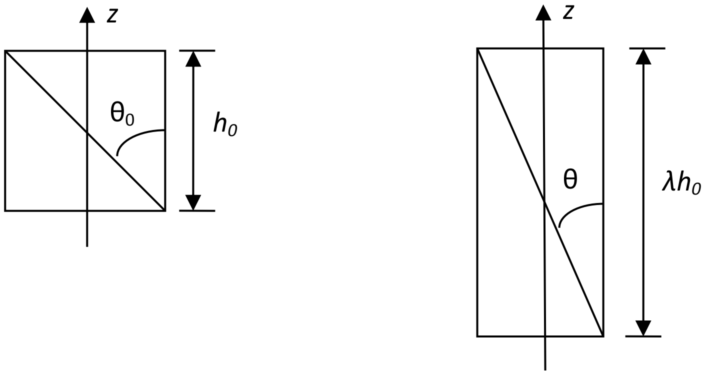


Fig. 1. Change of orientation of a line joining a pair of points in a sample as a result of drawing. z - draw direction, λ - draw ratio, θ_0 *and* θ - initial and final inclinations (taken from [9])

The transversely isotropic units of the pseudo-affine model are assumed to rotate affinely and therefore their orientation is described by (3). They do not change in length and therefore the increase in length of that line joining the arbitrary pair of points is simply ignored. Because there is not one single unit, but an aggregate of units, the average orientation of this aggregate, given by (1), must be considered. Combining (1) and (3):

$$\langle \cos^2\theta \rangle = \int_0^{\frac{\pi}{2}} \frac{\lambda^3 \sin\theta_0}{\lambda^3 + \tan^2\theta_0} \mathrm{d}\theta_0 \qquad (4)$$

After performing the integration and converting the average cosine square to the Hermans orientation function through (2), the following is obtained:

$$\langle \mathrm{P}_2 \rangle = \frac{3}{2}\left[\frac{\lambda^3}{\lambda^3 - 1} - \frac{\lambda^3}{\sqrt{\left(\lambda^3 - 1\right)^3}} \arctan\left(\sqrt{\lambda^3 - 1}\right) \right] - \frac{1}{2} \qquad (5)$$

Equation (5) represents $\langle \mathrm{P}_2 \rangle$, as a function of draw ratio only, for the case of the pseudo-affine model and has been presented in previous literature on this topic, see for example Dirix et al. [6].

2.2 The proposed new crystalline chain slip model

The proposed new model, shown in Fig. 2, is based on the illustration of Ritchie [9]. It is assumed that only chain slip (i.e. slip along directions parallel to the direction of the chains) operates in the process of crystalline deformation/orientation. The other known modes of deformation - transverse slip (perpendicular to the chain direction), twinning and martensitic transformation - are ignored.

Crystalline blocks in the material slide over one another along slip planes so that they are rotated and displaced, but the macroscopic material (tape or fibre) remains parallel to the loading axis. The crystalline blocks are therefore rotated so that their c-axes are progressively aligned with the loading direction.

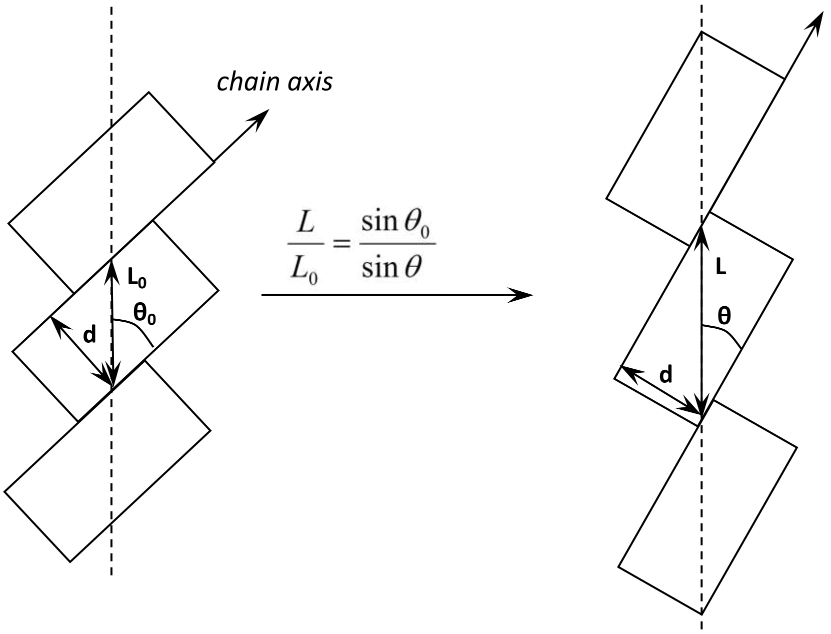


Fig. 2. Change of orientation of crystalline planes as a result of the mechanisms of chain slip and rotation, λ - draw ratio, θ_0 *and* θ - initial and final inclinations of the crystalline chain segments (based on the illustration of Ritchie [9])

It follows that the increase in length experienced by the crystal is related to the change in orientation of the chain segments in the crystal by the following equation:

$$\frac{\mathrm{L}}{\mathrm{L}_0} = \frac{\sin\theta_0}{\sin\theta} \tag{6}$$

in which L_0 and L are the initial and final distances in the direction of the fiber/loading axis between slip planes; θ_0 and θ are the initial and final angles, respectively, that the molecular segments in the crystal make with the fiber/loading direction.

The additional assumption added to the previous assumptions is that the increase in length experienced locally by the crystal in the longitudinal direction matches the increase in length of the fiber itself, i.e. it matches the macroscopic draw ratio λ; in this sense we are assuming that the deformation of the crystals is affine in the longitudinal direction:

$$\frac{\mathrm{L}}{\mathrm{L}_0} = \lambda \tag{7}$$

Combining (6) and (7), we arrive at an equation that represents the final orientation θ of a crystalline chain segment in relation to the drawing direction as a function of its initial orientation θ_0 and the draw ratio λ (note the parallel with (3)):

$$\sin\theta = \frac{\sin\theta_0}{\lambda} \tag{8}$$

It must be emphasized that in this model the distance "d" between slip planes does not need to be specified, therefore the model contemplates both fine and coarse slip; in other words "d" may represent the distance between two adjacent crystalline planes, or it may be a multiple of the distance between two adjacent planes. The type of chain slip does not need to be specified either; but given that the easiest chain slip systems in PE are (100)[001] and (010)[001][10], these are expected to dominate the orientation process.

Now that we have the equation that represents the final orientation θ of a crystalline chain segment in relation to the drawing direction as a function of its initial orientation θ_0 and the draw ratio λ (Equation (8)), we can proceed to the integration of the equation over an aggregate of chain segments. Combining (1) and (8):

$$< \cos^2\theta >= \int_0^{\frac{\pi}{2}} \left(1 - \frac{\sin^2\theta_0}{\lambda^2}\right) \sin\theta_0 \, \mathrm{d}\theta_0 \tag{9}$$

After performing the integration and converting $< cos^2\theta >$ to $< P_2 >$ making use of (2), the following is obtained:

$$< \mathrm{P}_2 >= \frac{\lambda^2 - 1}{\lambda^2} \tag{10}$$

Equation (10) represents $\langle \mathrm{P}_2 \rangle$, as a function of draw ratio only, for the proposed new crystalline chain slip model.

3. Experimental

3.1 Materials and sample preparation

Two grades of HDPE were used for this study: a homopolymer and a copolymer, supplied by BP Chemicals Limited under the trade names of Rigidex® HD6007EA and Rigidex® HD5502S respectively. “H6007-U” and “C5502-U” is how these materials will be referred to throughout this work and Table 1 summarizes their most relevant characteristics.

Table 1
Characteristics of the polyethylenes used in this study.“H”- homopolymer, “C”- copolymer, “U”- ungrafted

sample name	number of branches [per 1000 C]	M_w	M_w/M_n	density [kg/m^3]	Tensile Stress at Yield [MPa]
H6007 - U	< 0.1	131 000	6.9	955	30.5
C5502 - U	1.2 (butyl)	156 000	9.2	949	26

Silane monomers were subsequently grafted onto the chains of these two grades of PE. A detailed description of the grafting trials and the chemistry involved in these operations can be found in Ref. [11].

There were then 5 different materials: the ungrafted PEs H6007-U (homopolymer) and C5502-U (copolymer) and their silane grafted versions H6007-G2, H6007-G3 and C5502-G2, in which G2 stands for "grafted with 2 % silane" and G3 for "grafted with 3 % silane". These 5 materials were first extruded into tapes of dimensions of approximately 6.7 × 0.45 mm and then drawn in a drawing frame, using several different nominal draw ratios (DR). They were drawn in water at 75 °C, and drew at a pronounced neck, implying high strain rates of about 8 to 14 s^{-1}. Table 2 summarizes the samples prepared for this study. The nominal DRs here were calculated from the roller speed ratio of the drawing frame.

Table 2
Samples prepared for this study

	Nominal draw ratios
H6007-U	DR7, DR10
H6007-G2	DR7, DR8, DR9
H6007-G3	DR7, DR8, DR9
C5502-U	DR7, DR7.75, DR9, DR10.6
C5502-G2	DR7, DR8.15

3.2 Characterization

3.2.1 DSC (Differential Scanning Calorimetry)

DSC scans were performed between 30 and 180 °C at a heating rate of 10 °C/min, in a Perkin-Elmer DSC-7 calorimeter. The weight fraction crystallinity X_{weight} was calculated from the heat of sample melting Δh from:

$$X_{weight} = \frac{\Delta h}{\Delta h_c} \qquad (11)$$

in which Δh_c for PE was taken to be 293 J/cm^3 [12].

The volume fraction crystallinity (X_{volume}) was calculated from X_{weight} according to the equation:

$$X_{volume} = \frac{X_{weight}}{\left(\rho_c / \rho_a\right)\left(1 - X_{weight}\right) + X_{weight}} \qquad (12)$$

in which ρ_c=1000 kg/m^3 (density of the crystalline phase) and ρ_a=850 kg/m^3 (density of the amorphous phase) [12].

3.2.2 Birefringence

The refractive indices n_1 and n_3 (electric vector parallel to the transverse and draw directions respectively) of all tapes were measured using a Zeiss 'Interphako' image-splitting interference microscope. This measures the optical path difference between the sample and an identical thickness of one of a series of liquids (under a cover slip), each of known refractive index. This difference shows up as a fringe shift, and the refractive index is found by using a suitable series of liquids and interpolating to zero fringe shift. A range of R.P.Cargille standard refractive-index liquids was used, at 22°C, and their refractive indices at that temperature were checked by an Abbe refractometer (a Bellingham & Stanley 'Degree Scale' model 60/ED) at the 589.3nm of Na D light.

The Abbe refractometer was also used to confirm the transverse isotropy of the tapes.

The birefringence Δn is then obtained by subtracting the refractive indices,

$$\Delta \mathrm{n} = \mathrm{n}_3 - \mathrm{n}_1 \tag{13}$$

and the Hermans orientation function is then calculated by dividing the birefringence Δn by the maximum birefringence Δn_{max}, i.e. the birefringence at full molecular orientation:

$$< \mathrm{P}_2 >_{\mathrm{c+a}} = \frac{\Delta \mathrm{n}}{\Delta \mathrm{n}_{\mathrm{max}}} \tag{14}$$

In this work the value chosen for Δn_{max} was that reported in Bunn and Daubeny [13] for crystalline PE, i.e. Δn_{max}=0.0585.

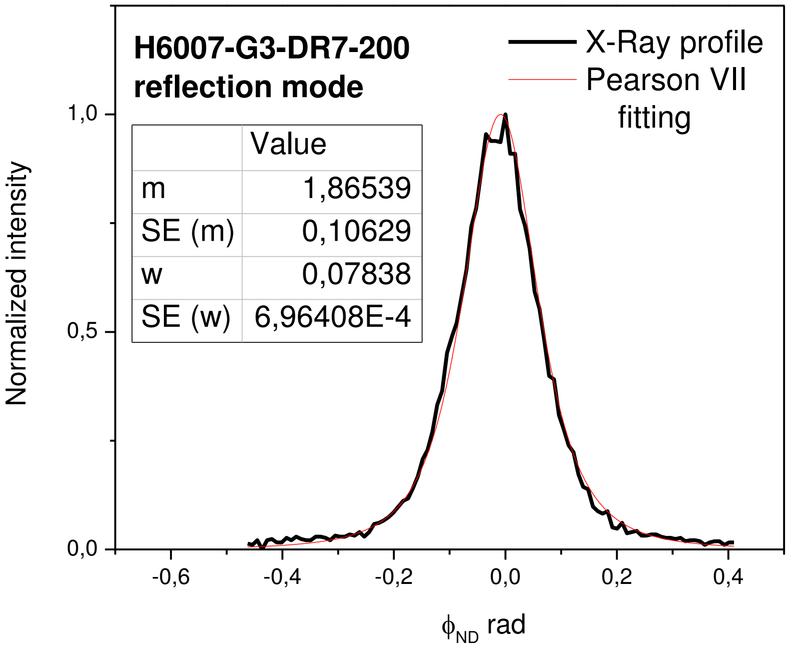
As mentioned above, this particular orientation function is considered to describe the overall degree of molecular orientation (average of crystalline and amorphous orientations), and therefore it is called $< P_2 >_{c+a}$ in the present work.

3.2.3 WAXD (Wide-Angle X-Ray Diffraction)

A computer-controlled Huber 4020 four-circle texture goniometer with crystal-monochromated CuKα radiation at 1.5418Å was used for the WAXD scans. The exact positions of the equatorial 110 and 200 reflections were found by $\theta/2\theta$ scans; then each reflection was scanned at its 2θ angle in a circumferential sense in both reflection and transmission modes. An intensity profile was obtained for each scan. Parasitic scattering was also measured, then subtracted from the measured intensity. It was found that the intensity profiles were symmetrical with respect to the plane normal to the draw direction. After normalizing each intensity curve (by dividing the curve by the value at its peak) a Pearson VII distribution was fitted onto each normalized curve:

$$I_{\mathrm{normalized}} = \frac{w^{2m}}{\left[w^2 + \left(2^{\frac{1}{m}} - 1\right)\phi_{\mathrm{ND}}{}^2\right]^m} \tag{15}$$

in which ϕ_{ND} is the angle between the X-Ray reflection plane normal and the plane normal to the draw direction, and w and m are the parameters that characterize the Pearson VII distribution. No attempt was made in order to isolate the amorphous contribution from the total scattering, which means that it is being assumed that the intensity profile is due entirely to scattering from the crystalline regions. Fig. 3 shows that the fit was very good to the entire X-ray curve.



	Value
m	1,86539
SE (m)	0,10629
w	0,07838
SE (w)	6,96408E-4

Fig. 3. Pearson VII fit to a WAXD scan (SE - standard error)

All the tapes appeared to be uniaxial from the fact that the normalized intensity profiles obtained in reflection and transmission modes were almost identical. The degree of orientation of the normals to the (110) and (200) planes with respect to the draw direction (machine direction, MD) was expressed in terms of “average cosine square”, according to the following equation [14]:

$$< \cos^2 \phi_{\mathrm{MD}} >= \frac{\int_0^{\frac{\pi}{2}} \mathrm{I}_{\mathrm{normalized}} \cos^2 \phi_{\mathrm{MD}} \sin \phi_{\mathrm{MD}} \mathrm{d}\phi_{\mathrm{MD}}}{\int_0^{\frac{\pi}{2}} \mathrm{I}_{\mathrm{normalized}} \sin \phi_{\mathrm{MD}} \mathrm{d}\phi_{\mathrm{MD}}} \tag{16}$$

in which $\phi_{MD} = \frac{\pi}{2} - \phi_{ND}$

The degree of orientation of the chain axis ((002) planes) along MD was then computed according to Wilchinsky’s method. For polyethylene this was calculated to give [15]:

$$< \cos^2 \phi_{002,\mathrm{MD}} >= 1 - 0.565 < \cos^2 \phi_{200,\mathrm{MD}} > -1.435 < \cos^2 \phi_{110,\mathrm{MD}} > \tag{17}$$

$< cos^2\phi_{002,MD} >$ is more conveniently represented by $< cos^2\theta >$, in accordance with the notation adopted throughout the present paper.

Finally, the Hermans orientation function is computed from $< cos^2\theta >$, making use of (2). In this case the orientation function is considered to describe the degree of orientation of the crystalline phase only, and therefore it is called $< P_2 >_c$.

4. Experimental results and discussion

DSC and the degree of crystallinity

Fig. 4 presents the degree of crystallinity by volume for all the samples analysed in this study, plotted as a function of the nominal draw ratio (roller speed ratio).

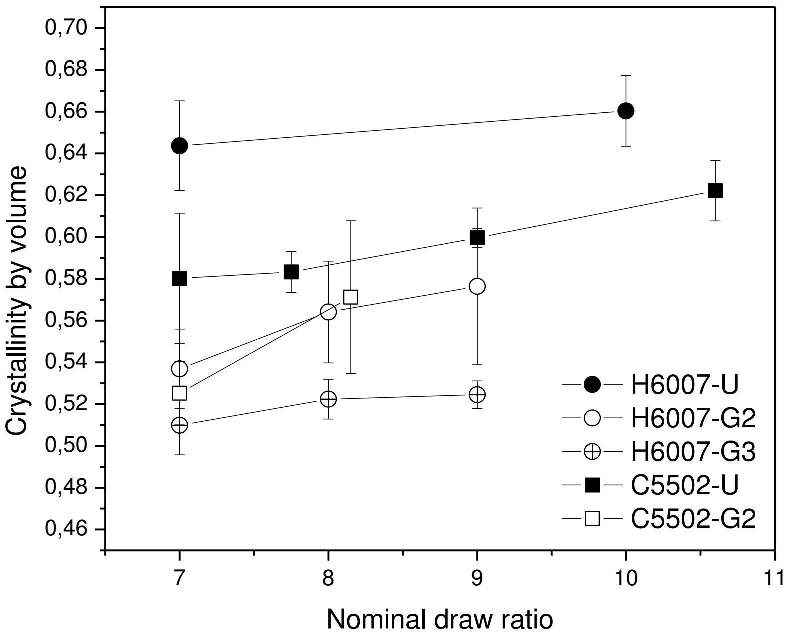


Fig. 4. Volume fraction crystallinity as a function of draw ratio

Small increases in the degree of crystallinity with draw ratio were observed in all materials. This has been reported many times (see, for example, Butler et al. [16]), and it is generally attributed to the stress-induced crystallization of amorphous material which becomes stretched and aligned by the drawing process. As expected, Fig. 4 shows that the homopolymer (H6007-U) is the most crystalline, followed by the copolymer (C5502-U), and then silane grafting leading to a greater proportion of amorphous material.

Birefringence and the pseudo-affine model

Fig. 5 shows the results for crystal orientation (WAXD) and overall orientation (birefringence), together with their theoretical estimates (crystalline chain slip and pseudo-affine models respectively).

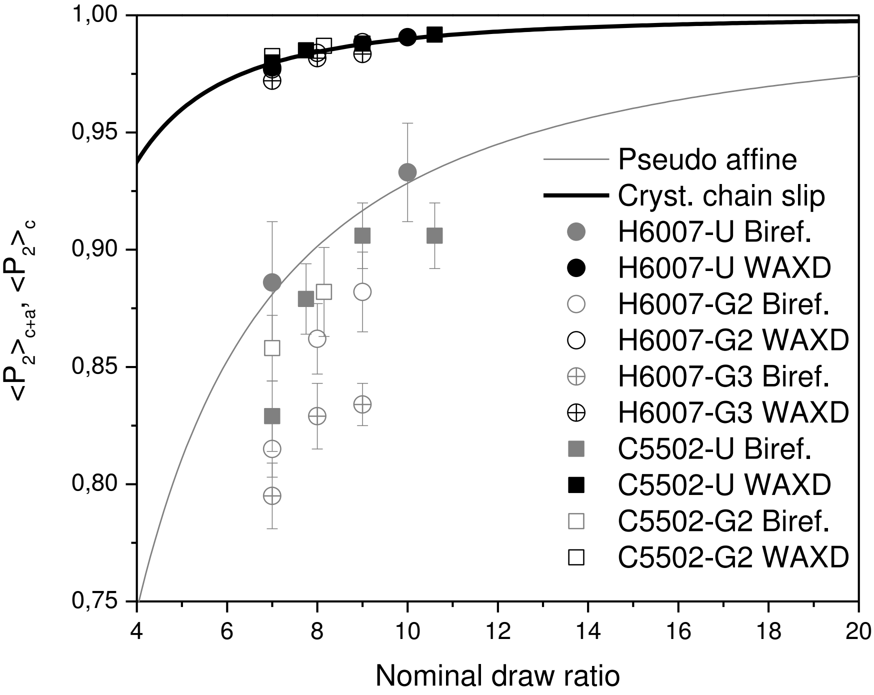


Fig. 5. Orientation as a function of draw ratio for pseudo-affine and crystalline chain slip models compared with experimental data (birefringence and WAXD)

It is clear that the crystal orientation data for all five materials tend to lie on a single curve. In other words, the observation reported by previous authors [7,8] of a single crystalline orientation-strain relation, irrespective of the polymer considered, is also verified in our case. Moreover, that single curve is represented well by the crystalline chain slip model, and this will be explored in more detail.

The birefringence data show lower orientation, which is very reasonable, as the orientation function includes not only crystalline material but also less well-oriented non-crystalline material. Close inspection of the results proves to be worthwhile. Unlike the crystalline orientation, there is considerable variation among the samples in terms of overall orientation for a given draw ratio. First, the homopolymer H6007-U results are close to the predicted curve, followed by the copolymers C5502-U and C5502-G2. The silane grafted homopolymer, grades H6007-G2 and H6007-G3, show even lower orientation in the birefringence data. With the exception of the C5502-G2 grade, these results parallel the crystallinity degree results presented in Fig. 4 in the sense that both $< P_2 >_{c+a}$ and degree of crystallinity decrease in the same order:

H6007-U > C5502-U > H6007-G2 > H6007-G3

Consideration of Fig. 4 and Fig. 5 together suggests that the lower values of orientation shown by the birefringence data in Fig. 5 might be a combination of a progressive reduction in the proportion of crystalline material in progressing from the homopolymer first to the copolymer and then to the silane grafted materials, as well as the lower orientation of the non-crystalline material in the latter samples.

It should be stressed that $< P_2 >_{c+a}$ reflects the relation between the actual measured birefringence and that of a perfectly oriented polymer with a similar morphology, generally called "intrinsic birefringence" $\Delta n_{\max}$ (see (14)). The correct procedure for $\Delta n_{\max}$ determination would be, for each sample, to imagine inserting a number of fully oriented chains into the amorphous and crystalline regions and compute the birefringence of that fully oriented sample. Because of the impossibility of doing that, a constant value was assumed, $\Delta n_{\max}$=0.0585, which was the birefringence measured by Bunn and Daubeny in paraffin n-$C_{36}H_{74}$ single crystals [13]. Since $< P_2 >_{c+a}$ depends on the value chosen for the intrinsic birefringence, the degree of orientation will be overestimated if the assumed 0.0585 is lower than the actual intrinsic birefringence (and vice-versa). The effect the presence of silane groups may have on the polarizability, and therefore birefringence, of the silane grafted samples, has also been neglected.

Wide-Angle X-Ray Diffraction and the crystalline chain slip model

Although the plot of $< P_2 >_c$ shows a remarkable fit to the theoretical curve in Fig. 5, it is necessary to explore the fit more closely, because the $< P_2 >_c$ values are so close to unity, so that this plot cannot be expected to define the relationship of $< P_2 >_c$ to draw ratio very precisely. For this reason, the actual numerical values for the crystalline orientation are given in Table 3.

The birefringence results have also been added to this table, to make the comparison between WAXD and birefringence easier. The comparison is important in order to stress that the more highly crystalline samples, shown in the previous section to have higher $< P_2 >_{c+a}$, also have, in general, higher $< P_2 >_c$. In other words, those samples for which the overall degree of molecular orientation is higher, also tend to have a higher degree of crystalline orientation. Moreover, it is shown that, in spite of the differences being very small, the copolymers (both grafted and ungrafted) do seem to attain higher degrees of crystalline orientation than the homopolymers. C5502-G2 does have a degree of orientation (both crystalline and overall) that is exceptionally high given its relatively low crystallinity. Possible reasons for this grade's atypical behaviour can be found in Ref. [11].

Table 3

Orientation functions <P_2> from WAXD and birefringence for all the samples

	<P_2> birefringence (Δn_{max} =0.0585)	<P_2> WAXD
H6007-U-DR7	0.886±0.026	0.978
H6007-U-DR10	0.933±0.021	0.991
H6007-G2-DR7	0.815±0.012	0.977
H6007-G2-DR8	0.862±0.015	0.984
H6007-G2-DR9	0.882±0.017	0.989
H6007-G3-DR7	0.795±0.014	0.972
H6007-G3-DR8	0.829±0.014	0.982
H6007-G3-DR9	0.834±0.009	0.984
C5502-U-DR7	0.829±0.015	0.980
C5502-U-DR7.75	0.879±0.015	0.985
C5502-U-DR9	0.906±0.014	0.988
C5502-U-DR10.6	0.906±0.014	0.992
C5502-G2-DR7	0.858±0.014	0.983
C5502-G2-DR8.15	0.882±0.019	0.987

The differences in crystalline orientation among samples are, nonetheless, small, and the most impressive fact when looking at Fig. 5 and Table 3 is the agreement between the WAXD results and the proposed new crystalline chain slip model, especially for the ungrafted grades. This agreement has the implication that the mechanism responsible for the "universal" orientation-strain behaviour in semicrystalline polymers mentioned in the Introduction is the affine deformation of the crystalline phase. In other words, the crystalline phase must deform affinely irrespective of the long range order and of the degree of crystallinity of the polymer, even in the presence of slight crosslinking such as in the case of the silane grafted grades. And this is what gives the crystalline phase a simple orientation behaviour that is to a good approximation a single function of strain.

The agreement between crystalline orientation and the new model also supports the idea that the post-drawing recovery does not affect significantly the degree of crystalline orientation attained during the drawing stage, i.e. crystalline orientation is, to a large extent, retained while recovery takes place. This explains why crystalline orientation relates to the roller speed ratio (nominal draw ratio) and not to the "true" draw ratio (ratio between initial and final cross-sections of the sample). The irreversibility of the crystalline deformation had already been implied in the work of Kilian and Pietralla [7] in which the crystalline orientation data for both stressed and relaxed HDPE and LDPE all lie on the same master orientation-strain curve. Hiss et al. [8] made a similar observation and stated that "...there exists a one-to-one correspondence between the [crystalline] orientational order and the strain, independent of (...) whether the sample is stressed or unloaded."

5. Conclusions

The experimental results show that, for the different grades of oriented polyethylene considered in this paper, the degree of crystalline orientation is to a very good approximation uniquely defined by the draw ratio, independent of the characteristics of the polymer such as degree of crystallinity or lamellar structure. This observation agrees with similar results reported by other authors. In our case the single orientation-strain relation is also verified in PEs onto which silane groups have been grafted that also happen to be slightly crosslinked [11], which further demonstrates the universality of the relation.

It is proposed that this crystalline orientation-strain relation can be described by the equation:

$$< \mathrm{P}_2 >= \frac{\lambda^2 - 1}{\lambda^2}$$

which implies that the crystalline deformation is affine in the longitudinal direction. This means that at each stage of the deformation the average orientation over all the crystallites is such as that the overall increase in length of the aggregate of crystals matches the macroscopic draw ratio λ.

It is believed that it is precisely because the crystalline phase must always deform affinely that the orientation-strain curve is universal, i.e. independent of the degree of crystallinity or lamellar structure of the polymer, as well as independent of the conditions under which drawing takes place such as temperature and strain rate (for independence in relation to strain rate and temperature as shown previously by Hobeika et al. [17] and Lezak and Bartczak [18]). An immediate corollary is that the crystal orientation does not depend directly on the deformation of the non-crystalline material, so that it is as if the crystals were embedded in a matrix whose deformation can accommodate the crystal slip processes. What makes this simple behaviour possible may be the block-like nature of the crystalline lamellae [19] as has been suggested by Hiss et al. [8]. (The block-like nature follows from the fact that crystallization is a two-step process, with formation of blocks first, and then their fusion into lamellae).

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