

Structure Characterization of Cold Drawn High Density Polyethylene Thin Film

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ABSTRACT: This work throws light to study the changes of optical birefringence for cold drawn high density polyethylene (HDPE) thin film at different stresses. A stress-strain device connected to a scattering optical system was used to investigate the dynamical behavior of opto-mechanical properties at room temperature ($27^{\circ}\text{C} \pm 1^{\circ}\text{C}$). Some structural parameters, optical and mechanical orientation factors, $f(\theta)$, $f_2(\theta)$, $f_4(\theta)$, $f_6(\theta)$, F_{av} , $P_2(\theta)$, $P_4(\theta)$, f_c , and f_m , were calculated. Also, the distribution segments at an angle (θ), the number of random links per chain (N_1), the number of chains per unit volume (N_c), and the average work per

chain W' were calculated. The average value of the maximum birefringence was evaluated. The obtained studies demonstrate changes to the molecular orientation functions and evaluated micro structural parameters as a result of the applied cold-drawing process on (HDPE) thin film. Relationships between the calculated parameters and draw ratios were presented for illustration. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 2026–2032, 2011

Key words: HDPE thin film; cold drawing; maximum birefringence; mechanical and optical orientation functions

INTRODUCTION

The subject of structure property relationships in polymers is an extremely wide one and it is therefore possible to select only a few topics for characterization in our present work. Optical methods always help in studying the mechanical, thermal, and chemical properties of synthetic thin films. The mechanical processes were the most readily available techniques for some modified polymeric structures.^{1,2}

Orientation in polymers can be produced by several processes such as hot stretching of a molten polymer followed by rapid cooling of the melt, cold drawing, or cold rolling. The drawing process gives rise to the preferred orientation of the molecular chain axis. The degree of orientation can vary significantly from one thin film to another, depending on the history during its manufacture and subsequent processing operations.^{3–5}

Optical anisotropy produced in thin films by stretching gives valuable information for characterization of these thin films on the molecular level. The molecular orientation alignment and their control becomes a key issue in many applications of polymers. An isotropic polymer has the same struc-

ture and properties in the three axes before deformation, where as the polymer becomes anisotropic due to chain alignments. So the polymer becomes oriented with respect to a particular direction, which expresses a measure of the extent of anisotropy produced by the deformation process. As the properties of an anisotropic polymer show a directional dependence, a measurement of the orientation for a polymer portrays its modification during deformation. As there were a number of different techniques for orientation determination in polymers, the use of the optical technique was one of considerable importance to provide valuable information for the degree of orientation.⁶ By the drawing process, the isotropic starting material is transformed into anisotropic thin film. The molecular chains are oriented along the drawing direction, and the crystal lamellae are stacked roughly normal to the drawn direction.⁷

The effects of orientation on the physical properties of polymers are profound, generally in the expected direction of increased stretching and stiffness with increasing orientation. As orientation is increases, anisotropy of the mechanical properties becomes evident. At the same time, the physical properties of the sample change significantly. Thermo mechanical histories, such as annealing, influences the ability of materials to undergo plastic deformation on (HDPE) thin films as previously reported in several studies.^{5,7–10} Annealing at high temperatures renders a polymer stiffer and more brittle. On the

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microstructural level, an irreversible reorganization sometimes occurs leading to shrinkage.

The opto-mechanical properties throw light on the end use of films, sheets, bottles and containers, pipes and tubes, and as well as wire insulation and cables.¹¹ The characteristics of polyethylene foam make it a versatile material. Uses include floatation applications in water sports equipment, padding for baseball, wrestling, and other sports. It is also used in cushion packaging, weather stripping and gaskets, and construction joints in buildings.¹²

This work focuses attention on the use of the principal birefringence parameter obtained by scattering and mechanical parameters for determining some essential indicative industrial parameters. Also the orientation of thin film and other opto-mechanical parameters were evaluated.

THEORETICAL

The scattering techniques attached with the mechanical device were used for determining the principle opto-mechanical parameters.¹³ These parameters were used to characterize the changes in the structure of HDPE thin film.

Optical orientation function

Hermans represented the orientation function $f(\theta)$ by a series of spherical harmonics^{14,15} (Fourier series) as follows:

$$f(\theta) = \sum_{n=0}^{\infty} \left(n + \frac{1}{2} \right) \langle f_n \rangle f_n(\theta) \quad (1)$$

where the odd components are all zero and the first three even components are given by $f_2(\theta)$, $f_4(\theta)$, and $f_6(\theta)$.

Average optical orientation

The overall orientation F_{av} was calculated using birefringence measurements. Optical birefringence gives the average of crystalline and amorphous orientation. The term "orientation" frequently means orientation of ordered phases. It is strongly emphasized, however, that both crystalline and amorphous materials can exist in both oriented and nonoriented states. The average orientation F_{av} was calculated according to the following equation¹⁶

$$F_{av} = 2\Delta n / (\Delta n_c^\circ + \Delta n_a^\circ) \quad (2)$$

where Δn is the measured birefringence for high density polyethylene (HDPE) thin film, and crystalline and amorphous birefringence where: $\Delta n_c^\circ = 0.0585$, and $\Delta n_a^\circ = 0.20$.

Mechanical orientation

In the aggregate model, the small values of the strain mechanical anisotropy are related to the orientation functions $\langle P_2(\cos\theta) \rangle$ and $\langle P_4(\cos\theta) \rangle$. These functions provide fair understanding for the mechanism of deformation. So by considering the network of freely jointed chains for identical links called random links, $\langle P_2(\cos\theta) \rangle$ was given by¹⁷

$$\langle P_2(\theta) \rangle = \frac{1}{2} \left[\frac{2 + U^2}{1 - U^2} - \frac{3U \cos^{-1} U}{(1 - U^2)^{3/2}} \right] \quad (3)$$

where $U = D^{-3/2}$ and D is the draw ratio (final fiber length/starting length). Using the Treloar expression for the inverse Langevin function to obtain $\langle P_4(\cos\theta) \rangle$

$$\langle P_4(\theta) \rangle = \frac{1}{8} \left\{ \frac{35}{(1 - U^2)^2} \left[1 + \frac{U^2}{2} - \frac{3U \cos^{-1} U}{2(1 - U^2)^{1/2}} \right] - \frac{30}{1 - U^2} \left[1 - \frac{U \cos^{-1} U}{(1 - U^2)^{1/2}} \right] + 3 \right\} \quad (4)$$

and the shrinkage stress δ_r is related to the draw ratio by the following relation

$$\delta_r = (D - 1)/D \quad (5)$$

Shrinkage stress is generated through an entropic retraction. When the internal energy of an oriented polymer is elevated by an increase in ambient temperature, polymer molecules tend to relax the orientation by retracting from an ordered extended conformation to a disordered random coil. This eventually produced a change of length or contraction force.

Crystalline orientation

The orientation for the crystalline phase has been calculated from theoretical analysis¹⁸ of stress induced crystallization in Gaussian networks whose results have been shown to be in good agreement with various experimental data.^{19,21} This analysis results in the following expression for f_c as a function of draw ratio

$$f_c = \frac{1}{2} \left(\frac{3D^3}{2 + D^3} - 1 \right) \quad (6)$$

Models for deformation of amorphous and partially ordered polymers

In the amorphous state, polymer chains are visualized as interpenetrating each other as they meander along what may be regarded as essentially random

paths. Such interpenetrating paths create topographical entanglements that can only be eliminated by the repetition of chains along their paths to allow a chain end to slip through the entanglement. Two contrasting schemes have been proposed to account for the development of orientation during deformation. The first approximates the entangled polymer to a crosslinked rubber network where each chain between crosslink can be represented by freely joint rigid links and where the crosslink deforms in an affine manner along with the change of deforming body. Roe and Krigbaum^{19,20} derived an expression for the distribution of segments at an angle θ with respect to the draw direction:

$$\omega(\cos \theta) = \frac{1}{2} + \frac{1}{4N_1} (3 \cos^2 \theta - 1)(D^2 - D^{-1}) \quad (7)$$

where N_1 is defined as the number of random links per chain. The second scheme considers the polymer only in terms of an aggregate of the segments that make up the chains. Before orientation, the segments will be randomly oriented at an angle θ with respect to the draw direction. After drawing, the segments will be constrained at an angle β according to the pseudoaffine scheme, given by

$$\tan \beta = D^{-3/2} \tan \theta \quad (8)$$

Subsequent work⁴ has demonstrated the applicability of these models to polymer deformation, respectively, above and below the T_g .

For random links, the orientation function $f_{\Delta}(\theta)$ as previously calculated²² and was given by

$$f_{\Delta}(\theta) = (D^2 - D^{-1})/5N_1 \quad (9)$$

from which N_1 can be obtained.

The number of chains per unit volume

The Kuhen-Treloar theory gives²²

$$f_{\Delta}(\theta) = (2/5)N_c(D^2 - D^{-1}) \quad (10)$$

where N_c is the number of chains per unit volume and depends upon the number of crystallites in the polymer material.

The average work per chain W' could be given by of the following equation²³

$$W' = \frac{3KT}{2} \left[\frac{1}{3}(D^2 - D^{-1}) + (D^{-1} - 1) \right] \quad (11)$$

The Poisson's ratio μ for very small radius contraction by loading and on the base of the assump-

tion of constant volume can be obtained by the following equation

$$\mu = 1/2D \quad (12)$$

Average mechanical orientation

The deformations of a semi crystalline polymer can be described by the Kratky model.¹⁵ Based on this model; Zbinden²⁴ has derived an expression for the distribution of function with draw ratios. From this expression the mechanical orientation function f_m can be calculated as

$$f_m = 1 - \frac{3}{2} \left[1 - \frac{D^3}{D^3 - 1} + \frac{D^3}{(D^3 - 1)^{3/2}} \cos^{-1} \left(\frac{1}{D^{3/2}} \right) \right] \quad (13)$$

EXPERIMENTAL RESULTS AND DISCUSSION

Material

In this study, we used high-density polyethylene (HDPE) sheets 500- μm thick provided by Shin-Kobe Electric, Japan. All polymer sheets were cut in dimple shape of different lengths to be suitable for the required draw ratio from our sample to be drawn. In the present work, polyethylene sheets were drawn at room temperature (cold drawn). All drawn samples were annealed for 2.5 h at temperature 55°C which is enough to relax all stored strains without serious changes for the structural elements of the polymer.

Drawing process

The dynamic birefringence technique was the first one to be developed. The early static light scattering studies on polymer films were carried out using a mercury lamp source and photographic recording. Dynamic studies only became possible with the development of the continuous wave gas laser. High speed studies were accomplished through taking light scattering interpretation of the obtained patterns.¹³ Drawing of macromolecular samples represents one of the most extensive changes in orientation of the polymer chains. In most instances the chain orients parallel to the draw direction. Our present results clarify that new orientations occur as a result of cold drawing at various draw ratios.

A local designed drawing machine was previously constructed and used in the present work.¹³ Figure 1 shows the main structure of this machine that was designed to allow the user, select the needed required draw ratio, temperature, and speed for drawing process. The sample S is clamped by the clamps $C1$ and $C2$. From the control panel, the

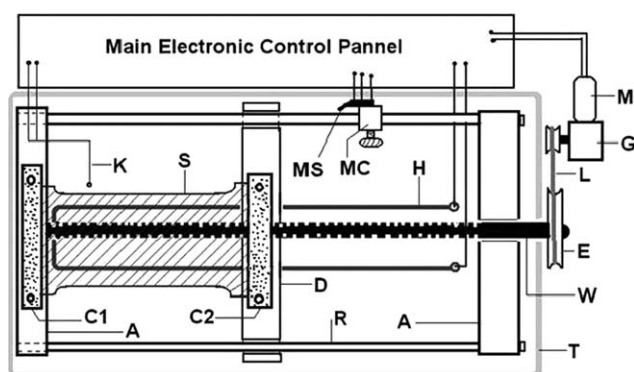


Figure 1 Shows the schematic diagram for the used drawing machine where, *A* are 1 sq. in iron rods, *D* is driving iron rod, *C1* and *C2* are clamps, *R* is a smooth steel bar of 12 mm diameter, *H* is a heater, *K* is a *K*-type thermocouple, *S* is the sample, *MC* is a movable clamp, *MS* is a two way micro switch, *T* is a thermostatic chamber, *W* is a long 12 mm diameter screw, *E* is a wheel, *L* is a rubber belt, *G* is a gearbox, and *M* is a DC powerful motor.

drawing temperature and drawing speed are set. By the movable clamp *MC* the user can set the draw ratio. When starting the drawing process, the powerful DC motor *M* runs causing the wheel *E* to rotate through the gear box *G* and the belt *L*. Rotation of *E* causes a similar rotation for the long screw *W* (70-cm long and 12 mm in diameter). Because of the nut groove in the driving bar *D*, this bar moves and stretches the sample until it arrives at the stopper *MC* and presses the micro switch *MS*, then the whole system turns off. To determine the exact draw ratio, marks of 1 cm separation were written on one edge of the sample, then the separation of marks were measured again after finishing the drawing process, it was then easy to estimate the exact draw ratio. This machine can draw polymer sheets either at room temperature (cold drawing) or at selected fixed temperature (hot drawing).

Birefringence measurements

Measurement changes for birefringence were an excellent choice when caring for orientation in a molecular system. The higher birefringence along a certain direction,²⁵ the higher mechanical strength along the same direction. Different optical methods can be followed for the determination of the birefringence (Δn) of solid polymers, either films or fibers. The optical technique was the most accurate and sensitive technique, where one can measure the refractive indices and birefringence.

More recently, Beekmans and Posthuma de Boer²⁶ described a spectrographic method to measure the birefringence online. The characteristic of this

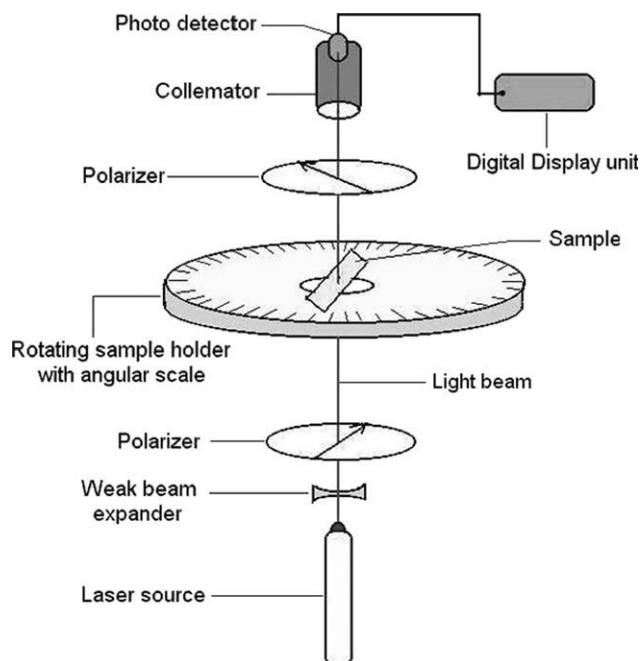


Figure 2 Shows the schematic diagram for the optical set up used for photo-metric measurement of film birefringence and the angular light intensity distribution.

method used white light as a source to get the order number of retardation automatically. In the current work, a laser source was used as to measure the birefringence of samples at single wavelength ($\lambda = 633 \text{ nm}$). The set-up of the used optical arrangement is shown in Figure 2. The polymer film was placed perpendicular to the propagation direction of the light beam between two parallel or crossed polarizers, the directions of polarization were set at $\pm 45^\circ$ with respect to the machine direction (MD) of drawing the sample. Transmitted light intensities through the system for parallel and crossed polarizers were

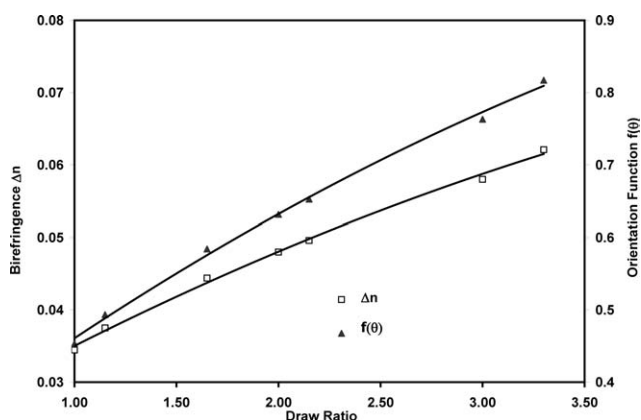


Figure 3 Shows the relationship between the mean birefringence and optical orientation functions $f(\theta)$ at different draw ratio for (HDPE) thin film.

TABLE I
Comparison Between Experimentally Determined and Literature Values of Δn_{\max} for HDPE Thin Film

Sample	B_1	B_2	B_3	D_m	Δn_{\max} calculated	Δn_{\max} literature
HDPE	0.0197	0.0165	-0.0012	6.875	0.076	0.064

measured by a sensitive photodiode and digital display unit. Mueller matrix analysis of the optical train, neglecting any dichorism, yields the following equation for the light intensity transmitted through a pair of crossed (\perp) or parallel (\parallel) polarizer and the sample:

$$I^\perp = \frac{I_o}{2} e^{-2a} \left[\sin^2 \left(\frac{\pi d \Delta n}{\lambda} \right) \right] \quad (14)$$

$$I^\parallel = \frac{I_o}{2} e^{-2a} \left[1 - \sin^2 \left(\frac{\pi d \Delta n}{\lambda} \right) \right] \quad (15)$$

where I_o is the intensity of the incident beam with wavelength λ , Δn is the birefringence, d is the sample thickness and e^{-2a} is a term that accounts for the attenuation of light due to isotropic absorption or scattering. Normalized, these equations give:

$$N^\perp = \frac{I^\perp}{I^\perp + I^\parallel} = \sin^2 \left(\frac{\pi d \Delta n}{\lambda} \right) \quad (16)$$

$$N^\parallel = \frac{I^\parallel}{I^\perp + I^\parallel} = \cos^2 \left(\frac{\pi d \Delta n}{\lambda} \right) \quad (17)$$

$$N^\parallel - N^\perp = \cos \left(\frac{2\pi d \Delta n}{\lambda} \right) \quad (18)$$

Equations (16)–(18) are independent of I_o and the attenuation term e^{-2a} . Thus, by the accurate measurement of $I[\text{dbar}]$ and I^\perp the value of Δn for given λ and d is achieved.

Part of the modern trend in thin film research is to alter its properties. One of the methods used for

property modification involves the effects of stretching process under different conditions. Several studies have been reported on the effects of mechanical processes on the structure of synthetic thin films. The birefringence and orientation elasticity are some of the properties that affect the film quality for the main end use. Figure 3 shows the birefringence as a function of draw ratio of cold drawn HDPE. The experimental points show best fit with a second order polynomial function in the form:

$$\Delta n = B_1 + B_2 D + B_3 D^2 \quad (19)$$

Differentiating this empirical relation with respect to D and equating the result to zero leads to the value of D_m which gave the draw ratio at maximum birefringence Δn_{\max} , and B_1 , B_2 , and B_3 were known as numerical constants. At D_m one expects most of extendable chains in the amorphous region aligned to be parallel to the drawing direction. Further drawing may cause defolding for some crystallites, the defolded chain segments are not temporarily extended parallel to the drawing direction and hence birefringence may be reduced. So,

$$\frac{d(\Delta n)}{dD} = B_2 + 2B_3 D_m = 0 \quad D_m = -\frac{1}{2} \frac{B_2}{B_3} \quad (20)$$

introducing D_m into eq. (19) Δn_{\max} is determined the results were given in Table I. Figure 3 shows also the dependence of the orientation function $f(\theta)$ and Δn on the draw ratio for HDPE. It is shown that increasing the draw ratio the birefringence increases,

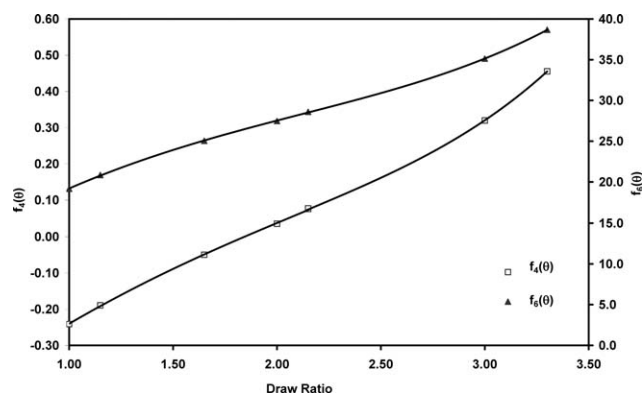


Figure 4 Shows the relationship between the optical orientation functions $f_4(\theta)$ and $f_6(\theta)$ with draw ratios for (HDPE) thin film.

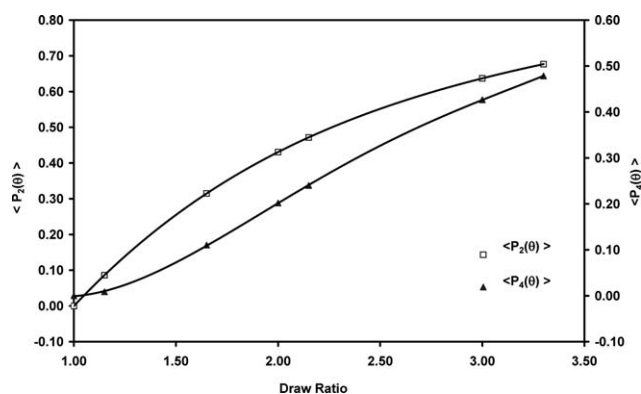


Figure 5 Shows the mechanical orientation factors $\langle P_2(\theta) \rangle$ and $\langle P_4(\theta) \rangle$ as a function of the draw ratios for (HDPE) thin film.

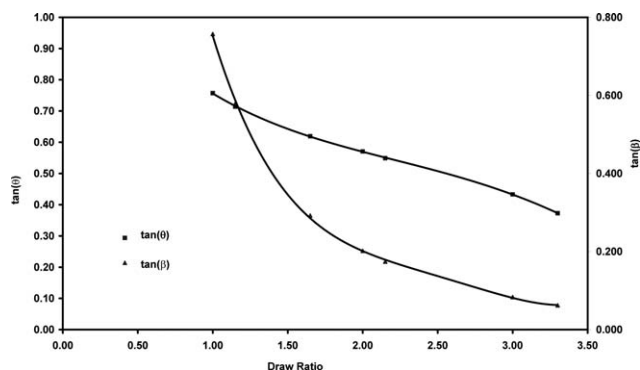


Figure 6 Shows the relationship between $\tan \theta$ and $\tan \beta$ for (HDPE) thin film.

which means that more orientation occurs involving chain arrangements in amorphous regions, as well as the crystallite redistribution of the crystalline phase.

Figure 4 shows the relationship between the optical orientation functions $f_4(\theta)$ and $f_6(\theta)$ with different draw ratios for (HDPE) thin film.

Under a given external force, different materials will exhibit different types of deformation response. In the mechanical vein, elastomers must stretch rapidly under tension with little loss of energy as heat, which could be felt as results of the change in entropy. When stress is released, they recover their original dimension with rebound. Therefore, the recovery achieved is indicated by shrinkage parameters. Finally, there is the importance of molecular orientations in determining physical properties, especially mechanical properties. The deformation scheme that describes the results obtained assumes that the polymer consists of aggregate of transversely isotropic units whose symmetry axes rotate on drawing in the same manner as lines joining pairs of points in the bulk material, which deforms at constant volume. Hence, the mechanical anisotropy for crystalline polymer and glassy polymer, deformed by cold drawing, enables the factor $P_2(\theta)$ together with $P_4(\theta)$ to be calculated as a function of draw ratio shown in Figure 5. Also, Figure 6 shows the relationship between $\tan \theta$ and $\tan \beta$.

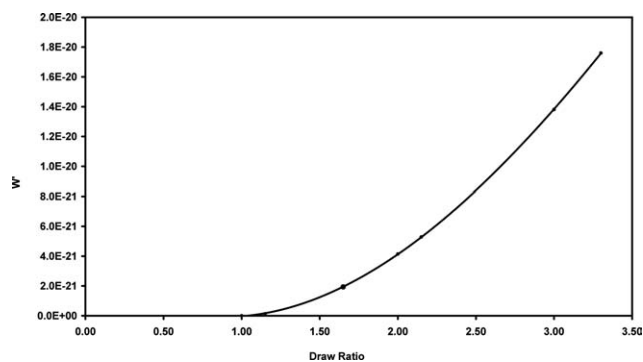


Figure 7 Shows the average work per chain W' with draw ratio for (HDPE) thin film.

The average work per chain W' for (HDPE) film was calculated and represented at different draw ratios as given in Figure 7. There was a gradual increase in the average work per chain with different draw ratios, which may be attributing to the increase of the work done on the film and increase of the amount due to associated deformation. By calculating the shrinkage stress, Poisson's ratio, crystalline orientation, mechanical orientation, average optical orientation, the number of random links per chain, the number of chains per unit volume, the distribution of segments at different draw ratios were given in Table II. The degree of orientation and other structural parameters, such as: Δn_{\max} , δ_r , N_1 , N_c , W' for instance, are correlated to the end use of the final film. The change in thin film volume is an indication of a change in density attributed to the mass redistribution associated with the annealing and drawing processes. This change in volume affects some other parameters. This may be due to changes of the free volume area spaces, which can be represented by mobile voids moving freely about in the structure by stretching. An alternative view is that the change in obtained optical birefringence results from the polymer material having two or more separate phases Δn_a and Δn_c . The birefringence of a crystalline polymer is made up of contributions from the crystalline and amorphous regions.

TABLE II

The Shrinkage Stress, Poisson's Ratio, Crystalline Orientation, Average Mechanical Orientation, Average Optical Orientation, the Number of Random Links Per Chain, the Number of Chains Per Unit Volume, the Distribution of Segments at Different Draw Ratios for HDPE Thin Film

Draw ratio	δ_r	μ	f_c	f_m	F_{av}	N_1	N_c	$\omega(\cos\theta)$
1.00	0.0000	0.500	0.0000	0.0000	0.2665	0.0000	0.0000	0.0000
1.15	0.1304	0.435	0.1479	0.0860	0.2901	0.1836	2.7235	1.1087
1.65	0.3939	0.303	0.5379	0.3150	0.3435	0.7245	0.6901	1.3533
2.00	0.5000	0.250	0.7000	0.4307	0.3714	1.1083	0.4511	1.4972
2.15	0.5349	0.233	0.7487	0.4716	0.3838	1.2740	0.3925	1.5648
3.00	0.6667	0.167	0.8966	0.6370	0.4487	2.2713	0.2201	1.9560
3.30	0.6970	0.152	0.9209	0.6767	0.4805	2.5913	0.1930	2.1692

CONCLUSIONS

From the above-mentioned measurements and calculations of the various optical and mechanical parameters which annealed for 2.5 h at temperature 55°C which was enough to relax all stored strains without serious changes for the structural elements of the polymer, the following conclusions can be drawn:

1. The average value of the maximum birefringence evaluated in the partially oriented HDPE thin film, was equal to 0.076 using wavelength ($\lambda = 633$ nm), and this value was nearly approximated according to Ref. 6.
2. Optical and mechanical orientations are different techniques that are suitable for predicting molecular orientation in HDPE thin films. Every technique has its own contribution, and both increase as the draw ratio increases.
3. The factor $P_4(\theta)$ is always comparatively small, so the mechanical method could be used for evaluating the orientation parameters.
4. Both the shrinkage stress and the distribution function of segments increase as the draw ratio increases. Changes of $\omega(\cos\theta)$ give indication for mass redistribution within thin film chains and new reorientations were given. The number N_1 of random links was between the network junction points per unit volume and the average work per chain (W') increases as the draw ratio increases.

From the above results we can confirm that the used scattering and mechanical techniques in the present work are promising techniques and their applications give observable changes in various parameters and functions for high density polyethylene.

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