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Anisotropy of optical and mechanical properties of stretched low density polyethylene

C. Fonseca [1], M. L. Cerrada [2], J. M. Pereña [2]

[1] Departamento de Química Industrial y Polímeros, EUITI (UPM), Ronda de Valencia 3,
E-28012 Madrid, Spain
[2] Instituto de Ciencia y Tecnología de Polímeros (CSIC), Juan de la Cierva 3,
E-28006 Madrid, Spain

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Summary

Parallel measurements of IR dichroism, birefringence and microhardness anisotropy of drawn low density polyethylene films have been carried out. The angle a between the dipole moment vector of the IR band at 1367 cm^{-1} and the chain axis has a value of 50°. The longitudinal and transverse moduli of the drawn samples, measured by microhardness indentations, increase as the draw ratio increases after passing through a minimum for a draw ratio of around 1.5.

Introduction

Stretching processes develop orientation in polymer chains, whose determination can be obtained by using different techniques: X-ray diffraction, sonic modulus, birefringence, polarized fluorescence, broad-line NMR, polarized Raman spectroscopy, ultraviolet and infrared dichroism and anisotropy of different mechanical properties (1-5).

The measurement of chain orientations by infrared spectroscopy takes into account the differences on the orientation of the transition moment vector of the molecular group interacting with the infrared electromagnetic radiation, with respect to the direction of stretching. The angle of the transition vector of the specific vibration with respect to the chain axis, α, can be calculated by determination of the dichroic ratio, R. This ratio is obtained by dividing the infrared absorbances at parallel ($A_{||}$) and perpendicular ($A_{\perp}$) directions relative to the stretching axis. Since specific absorption bands on polyethylene are related to either crystalline or amorphous components, infrared dichroism determinations can provide information on both types of structures. Depending on the specific band considered (associated to amorphus, crystalline or both phases), R values can increase, decrease or remain practically constant as the draw ratio, λ, increases.

The second moment of the orientation function, $<P_2\cos\Theta>$, can be calculated as a function of either the dichroic ratio, R, or the birefringence, Δn, of the stretched polymer, through the equation (6-8):

$$<P_2(\cos\theta)> = (3\cos^2\theta - 1)/2 = (R-1/R+2) / (R_0+2/R_0-1) = \Delta n / \Delta n_{max} \qquad [1]$$

where $R_0 = 2\cot^2\alpha$, α being the angle between the dipole moment vector of the vibration and the chain axis, and Δn_{max}. is the maximum birefringence attainable for the polymer.

Moreover, the Vickers microhardness (MH) test measures the resistance of a material to the plastic deformation produced by the impact of a square-based diamond pyramidal indenter. MH results of polymers can be related either to macroscopic mechanical parameters such as elastic modulus and yield stress (9, 10), or to structural characteristics (glass transition (11, 12) and physical ageing (13)). In the last years there has been an upsurge of interest about microindentation (and recently, nanoindentation) studies, considered as an adequate and non destructive technique to analyse the structure-dependent properties of polymers. Uniaxially stretched polymers display anisotropic microindentations and an evaluation of this anisotropy can be correlated to the orientation of the polymer (14).

Drawn polymers display two different microhardness values, corresponding to parallel ($MH_{||}$) and perpendicular ($MH_{\perp}$) directions with respect to the stretching direction. As the Vickers indenter imposes almost symmetrical strain on the sample, the higher microhardness (lower diagonal) along the draw direction of the stretched polymer must be attributed to the greater instantaneous elastic recovery of the impression, due to the greater elastic modulus of the material along that direction.

In the present work infrared dichroism, birefringence and microhardness anisotropy are used for studying the influence of the draw ratio on the overall orientation of a low density polyethylene fastly cooled from the melt. Moreover, the results obtained from those techniques are compared and discussed.

Experimental

Materials and drawing

Low density polyethylene, LDPE, samples were moulded as films in a Collin press, at a temperature of 140 °C and a pressure of 25 MPa for 10 min. Then the pressure was decreased to 10 MPa and the press plates were cooled to room temperature with running water. Rectangular specimens were cut from the moulded sheets and stretched using an automated materials testing Instron machine at room temperature and a crosshead speed of 1 cm min^{-1}. Different samples were uniaxially deformed at several strain rates and draw ratios, λ, without reaching the rupture point. Draw ratios were determined as the ratio between the final distance between equally separated ink marks and the initial ones, considering only the portion of the specimen homogeneously deformed.

Dichroism

The polarized spectra of several samples of polyethylene, previously stretched at different draw ratios, were performed on a Nicolet 520 Fourier transform infrared spectrometer. The polarization of the infrared beam was obtained by using a Specac gold wire-grid polarizer. The effects of the machine polarization were eliminated by placing the sample axis at-45° position with respect to the spectrometer slit and orienting the polarizer axis successively at -45° and +45°. Dichroic ratio values were calculated from the respective absorbances ($A_{||}$ and $A_{\perp}$) at the absorption maximum of each band.

Birefringence

Birefringence was measured with a rotary Ehringhaus compensator attached to an Amplival Pol D polarizing microscope. The thickness of the drawn sample was measured at the same place of the microscopic observation.

Microhardness

Microhardness measurements were carried out at room temperature with a Leitz microhardness apparatus using a Vickers pyramidal diamond. In this way, the contact pressure of the indenter is independent of the indent size and the delayed elastic recovery is minimized by measuring the final permanent deformation immediately after the load release. A series of 5 to 8 indentations were made on each one of the drawn anisotropic specimens, which were placed perfectly aligned with respect to the stage of the microhardness apparatus in order to get the short diagonal placed either parallel or perpendicular to the direction of the deformation. A loading cycle of 25 s and a contact load of 0.98 N were used for all the measurements.

The hardness value (in MPa) was calculated by dividing the contact load (in N), by the square of the value of the indentation diagonal (in mm), according to the relationship:

$$MH = 2 \sin 68^{\circ} P/d^2 \qquad [2]$$

Depending on the alignment of the drawn sample, two different diagonal values (|| and ⊥) were obtained.

Results and discussion

Fig. 1 displays the variation of the dichroic ratio with the draw ratio for the low density polyethylene samples, in relation to some of the most significative LDPE infrared bands.

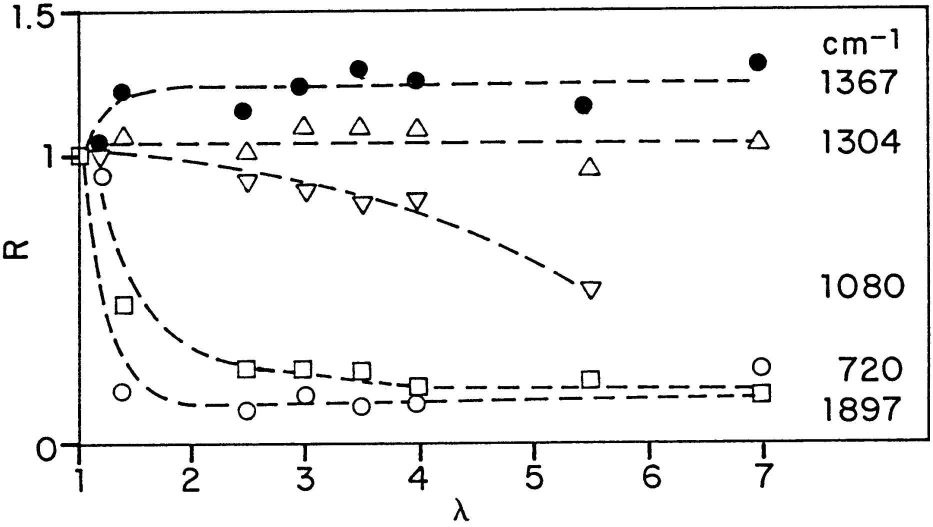

Figure 1 Dichroic ratio as a function of draw ratio for drawn LDPE samples, corresponding to several infrared bands (wavenumbers inserted).

In this figure a perpendicular dichroism for 1080 cm^{-1} (skeletal C-C stretching), 1897 cm^{-1} (combination of CH_2 rock) and 720 cm^{-1} (out of plane CH_2 rocking) is shown. However, infrared bands at 1367 and 1304 cm^{-1} (all of them CH_2 wagging) show a parallel dichroism. The dichroic ratio remains practically constant after a draw ratio of 2.5 for all the bands analysed, with the exception of the 1080 cm^{-1} band that diminishes continuously with the increasing of draw ratio.

As reported for other polymers and dichroic bands (3,15), when a series of birefringence and dichroic ratio values are compared according to eqn. [1], a straight line is obtained from the plot $<P_2(\cos \theta)>$ *vs* (R-1)(R+2), where the ordinate and abscissa points are derived from birefringence and dichroic ratio values, respectively. That plotting confirms that the orientation function can be deduced by using jointly different techniques, as occurs in the present results for the 1367 cm^{-1} band (wagging of the CH_2 groups) which lead to a straight line (correlation coefficient = .991). The slope of the line allows to obtain the magnitude of the angle α, 50°.

The variation of the longitudinal and transverse moduli with draw ratio has been studied for different polymers. For example, the longitudinal and transverse microhardnesses of poly(ethylene terephtalate), which can be easily correlated with the corresponding macroscopic Young moduli, increases and decreases respectively when the draw ratio increases. This variation parallels the dependence of the refractive indices on the birefringence, for the same polymer (14). In the case of high density polyethylene, the longitudinal Young modulus increases as draw ratio does, while the transverse modulus remains almost constant. On the other hand, low-density polyethylene displays significant increases of both the longitudinal Young modulus and the transverse modulus as the draw ratio increases (16). The results presented in this paper (Fig. 2) are similar to the above mentioned, including the minimum values of the moduli for draw ratios around 1.5. The initial decrease of the microhardness at low draw ratios could indicate a prevailing contribution of the amorphous chains, which line up along the drawing direction as draw ratio and microhardness of the stretched sample increase. This leading role of the amorphous part in

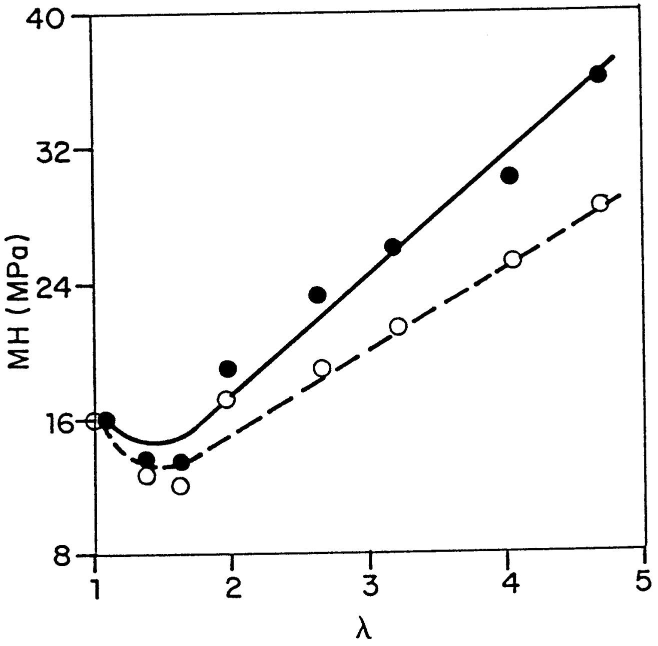

Figure 2 Dependence of microhardness with draw ratio for drawn LDPE samples. Filled and blank points correspond to longitudinal and transverse directions, respectively.

the initial stage of the drawing is confirmed by the results presented in Figure 1, corresponding to the dichroic ratio for the 1367 cm^{-1} band that arises from methylene vibrations in the amorphous part of LDPE. Therefore, the present results confirm that the transverse modulus of drawn polyethylene displays a different variation with the draw ratio depending on its grade. Moreover, the results corroborate that microhardness measurements are an easy and non destructive technique to follow the trend of the changes produced by drawing in the macroscopic mechanical properties.

Acknowledgement

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