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Optical characterization of polyethylene films by refractometry

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Refractometrical measurements of polyethylene films have been obtained using a modified Abbe's refractometer that includes polarized and monochromatic light. The ordinary and extraordinary refractive index values have been obtained considering an anisotropic uniaxic model. These values are analysed in relation to the previously known degree of crystallinity in the samples of this material. The specular reflectance is derived from the Fresnel formulae and an evaluation of diffused reflectance has been made. We find that the diffuse reflectance values increase with average roughness of the polyethylene films. This question is of particular interest for the surface characterization of these materials.

1. Introduction

The use of high transparency polymeric laminates has developed progressively due to their surface structure (bright and textured) that make them adequate for a protective use. The optical industry uses them in the fabrication of commercial polaroids, phase plates, filters, protection films for ophthalmic lenses, etc. Usually, the polyethylene films are obtained by tubular expansion and they have recently been studied by reflectometry [1], finding a relation between surface roughness and reflectometrical measurements [2].

Nevertheless, an analysis of the reflectance needs to distinguish between specular and diffuse reflectance. We have considered the possibility of performing refractometrical measurements in five polyethylene film samples, with a degree of crystallinity [3], because the refractometrical measurements allow an easy derivation of the specular reflectance with Fresnel's formulae [4–6] when the values of refractive index are known. On the other hand, the refractometrical measurements can give structural information from an analysis of the refractive index values. In the last few years considerable efforts have been made in order to relate the surface roughness of several materials to their optical properties, mainly due to the increasing significance of surface characterization for the proper design of high-performance materials. In this sense we have determined the relationship between the average roughness of the polyethylene films and the corresponding diffuse reflectances for three optical geometries.

2. Experimental procedure

The refractometric measurements were made by us with an Abbe refractometer (Atago-n/302) modified by the inclusion of a goniometer in the main prism. We have also chosen a monochromatic source, a Na vapour lamp ($\lambda = 589.3$ nm, Philips SO-X, 35w); the light is incident directly on the sample; it is polarized with a visible linear polarizer (Ealing 22-9062) mounted in a rotable stage with an angular precision of $\lesssim 2°$. With this set-up we have measured the refractive indices (parallel and perpendicular to the incidence plane) of five samples of expanded polyethylene films, later stressed, on the two neutral lines for each one. The neutral lines had been previously determined with a Babinet compensator, which can also be used for measurements of birefringence. The samples were named A, B, C, D and E, and the degree of crystallinity x_c(%) was determined experimentally using an X-ray diffraction method. X-ray diffractograms were recorded with a Philips Geiger counter X-ray diffractometer. The radiation used were CuK_α of wavelength 154.2 nm and the scanning speed was 2° (2θ) min^{-1} [3]. The roughness of each surface was evaluated by the parameter R_a (average roughness) using a Taylor–Hobson Talysurf-6 surface profiler, as mentioned previously [2]. The other samples used could not be measured with this refractometrical technique because of the great number of superficial irregularities.

3. Refractometrical values

The experimental values obtained for the perpendicular ($n_\perp$) and the parallel refractive index ($n_\parallel$) are shown in Table I. The different values of the refractive indexes are due to the different crystalline orientation in the directions of neutral lines. Now, applying Fresnel's formulae for anisotropic media we have to make a special correction on one of the above-mentioned

TABLE I Values of the refractive index, degree of crystallinity and average roughness for several polyethylene films

Sample*	$n_\perp = n_o$	$n_\parallel = n'_e$	n_e	x_c	R_a (μm)
A [7]	$1.5125 \pm 9\times10^{-4}$	$1.5172 \pm 7\times10^{-4}$	$1.5235 \pm 4.8\times10^{-3}$	31.5 ± 0.6	0.40 ± 0.06
B [9]	$1.5171 \pm 4\times10^{-4}$	$1.5137 \pm 5\times10^{-4}$	$1.5095 \pm 2.6\times10^{-3}$	44.9 ± 0.9	0.20 ± 0.03
C [8]	$1.5178 \pm 6\times10^{-4}$	$1.5125 \pm 4\times10^{-4}$	$1.5058 \pm 2.8\times10^{-3}$	45.6 ± 1.1	0.29 ± 0.04
D [12]	$1.5172 \pm 6\times10^{-4}$	$1.5135 \pm 5\times10^{-4}$	$1.5089 \pm 3.1\times10^{-3}$	47.1 ± 1.2	0.17 ± 0.03
E [10]	$1.5187 \pm 4\times10^{-4}$	$1.5115 \pm 3\times10^{-4}$	$1.5024 \pm 1.9\times10^{-3}$	49.1 ± 1.3	0.17 ± 0.03

* The notation in brackets is that of [1].

refractive indices, based on optical and structural considerations. Taking into account the great number of measurements carried out and the subsequent verification of the axis of the uniaxic crystal, we can consider the parallel index ($n_\parallel$) as the extraordinary index (n'_e), and the perpendicular index ($n_\perp$) as the ordinary one (n_O). This can also be verified with the same refractometer. However, studies of anisotropic media have shown that the refracted extraordinary beam does not verify Snell's law, so we have to take another auxiliary direction, perpendicular to the wavefront, giving another extraordinary index n_e, different from the first n'_e. These are related by

$$n'_e = \left[n_o^2 + \left(1 - \frac{n_o^2}{n_e^2}\right)\sin^2\phi\right]^{1/2}, \qquad (1)$$

where ϕ is the angle of incidence, with respect to the normal.

In our case, the measuring mechanism of the refractometer based on the critical angle [7] implies that $\phi = 90°$. Then we obtain n_e under this hypotheses as

$$n_e = n_o[n_o^2 + 1 - (n'_e)^2]^{-1/2}. \qquad (2)$$

These corrected values of extraordinary index n_e, together with the degree of crystallinity of these polyethylene films, are shown in Table I.

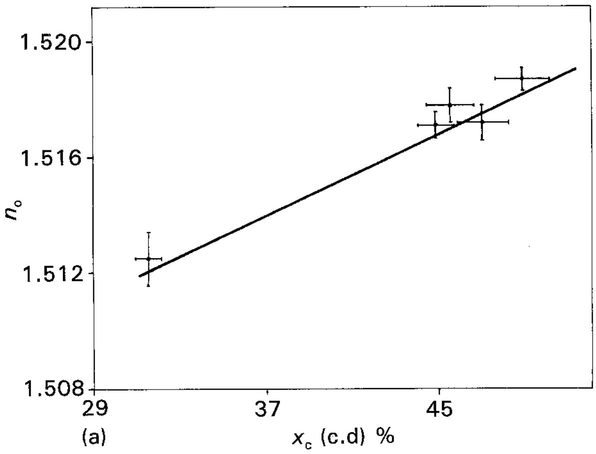
An analysis of the refractive index values, n_o and n_e, versus the degree of crystallinity gives good agreement in a linear fit, as shown in Fig. 1a and 1b. In fact, the equation

$$n_o = m_o x_c + c_o \qquad (3)$$

gives the linear fitting coefficients $m_o = 3.5319\times10^{-4}$ and $c_o = 1.5012$, and the correlation coefficient $r(n_o) = 0.9886$; and for the equation

$$n_e = m_e x_c + c_e \qquad (4)$$

gives the regression coefficients $m_e = -0.0012$ and $c_e = 1.5609$, and the correlation coefficient $r(n_e) = 0.9752$. If the n'_e values are submitted to the linear fitting analysis this gives a lower correlation coefficient $r(n'_e) = 0.9596$ than n_e values. This fact justifies the good correction given by Equation 2.



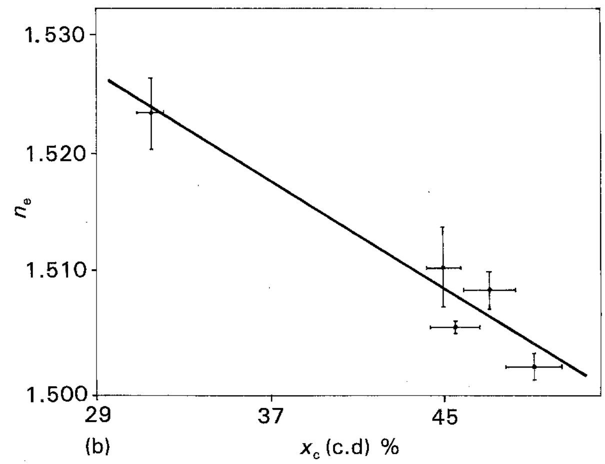


Figure 1 Ordinary (a) and extraordinary (b) refraction indices versus the degree of crystallinity. Linear fittings.

4. Specular reflectance evaluation

For normal incidence ($\phi = 0$), since the incident beam is parallel to the optical axis, it behaves isotropically (so $n_e = n_o$). Thus the specular reflectance R^0 can be calculated by use of the linear fitting (Equation 3) from the simplified Fresnel formula

$$R^0(x_c) = R^0_\parallel(x_c) = R^0_\perp(x_c) = \left[\frac{n_O(x_c) - 1}{n_O(x_c) + 1}\right]^2 \qquad (5)$$

A linear fitting shows a correlation coefficient equal to 1. On the other hand, we can calculate the values of the reflectance $R^0_\parallel(x_c) = R^0_\perp(x_c) = R^0$ using the experimental values of n_O in Table I, and these are shown in Fig. 2. Now, if we want to calculate the values of the mean parallel and perpendicular reflectance for the other angles of incidence, it is necessary to take into account the modified Fresnel expressions of [8]. These equations are valid for an anisotropic uniaxic film with the optical axis perpendicular to the surface, and contained in the incidence plane, in agreement with our optical and structural results. Thus we obtain

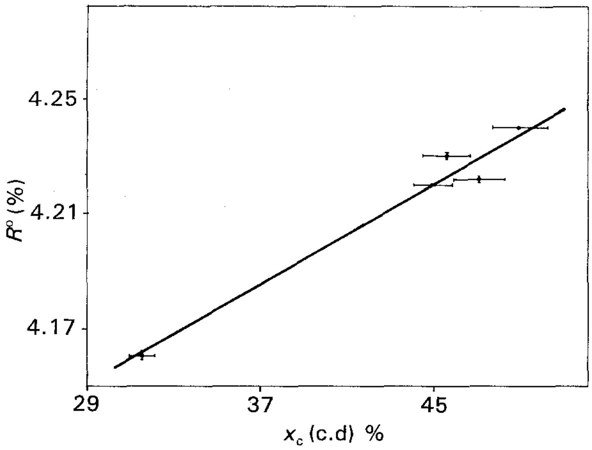


Figure 2 Values of specular reflectance for normal incidence ($\phi = 0°$) as a function of crystallinity degree. Linear fittings.

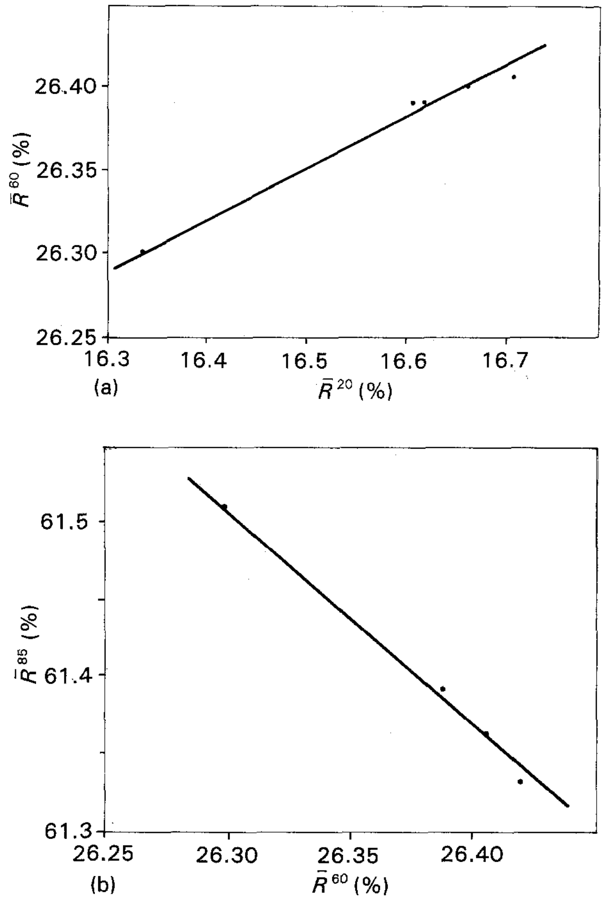


Figure 3 Values of average reflectance with incidence angle $\phi = 60°$ versus the values obtained with incidence angle $\phi = 20°$ (a), and average reflectance with incidence angle $\phi = 85°$ versus the values obtained with incidence angle $\phi = 60°$ (b). Both linear fittings are shown.

the expressions for the mean parallel and perpendicular reflectances

$$R_{pp} = \frac{r_{01pp} + r_{12pp}\exp(-i2\beta_p)}{1 + r_{01pp}r_{12pp}\exp(-i2\beta_p)},$$
$$R_{ss} = \frac{r_{01ss} + r_{12ss}\exp(-i2\beta_s)}{1 + r_{01ss}r_{12ss}\exp(-i2\beta_s)}, \quad (6)$$

where $r_{01pp/ss}$ and $r_{12pp/ss}$ are the reflection coefficients, (parallel or perpendicular) for the air–film interface and film–air interface, β_p and β_s being the corresponding phase shifts. Assuming that both external and internal reflected beams are reflected out in any random direction as diffuse light, we have to consider the average value of the phase as 1. Starting from the second reflection, if we calculate the mean reflectances for incidence angles of 20°, 60° and 85° in order to compare with the reflectometric values of [1], after transforming them into reflectances

$$R^{20}_{[1]} = 0.049\,R'_{20}, \quad (7)$$

$$R^{60}_{[1]} = 0.10\,R'_{60}, \quad (8)$$

$$R^{85}_{[1]} = 0.62\,R'_{85}, \quad (9)$$

where R'_{20}, R'_{60} and R'_{85} are the refractometrical values given in [1].

Now if we take the linear fitting of $\bar{R}^{60}$ versus $\bar{R}^{20}$ and $\bar{R}^{85}$ versus $\bar{R}^{60}$ we obtain

$$\bar{R}^{60} = q\bar{R}^{20} + b, \quad (10)$$

where $q = 0.3416$, $b = 20.7123$ and correlation coefficient $r(\bar{R}^{60}, \bar{R}^{20}) = 0.9985$; together with

$$\bar{R}^{85} = p\bar{R}^{60} + c, \quad (11)$$

where $p = -1.4651$, $c = 100.0458$ and correlation coefficient $r(\bar{R}^{85}, \bar{R}^{60}) = 0.9930$, as shown in Fig. 3a and 3b.

5. Diffuse reflectance evaluation

In order to calculate the average diffuse reflectance values [9] for an incidence angle of 20°, we subtract from our $\bar{R}^{20}$ the corresponding values given in Equation 9, since this angle has the lowest specular reflectance.

To obtain the relationship between $\bar{R}^{60}_{dif}$ and $\bar{R}^{20}_{dif}$, we have considered the following result, related to Equations 7 and 10, to transform them into reflectances

$$R'_{60} = 6.3 + 23\ln(R'_{20}) = 6.3 + 23\ln(20.37\,R^{20}_{[1]}), \quad (12)$$

where R'_{60} and R'_{20} are the reflectometrical values. For this angle (60°), after subtracting from the linear fitting given by Equation 10 the results of Equation 12 and expanding in a series, we obtain the expression

$$\bar{R}^{60}_{dif} = 0.34\,\bar{R}^{20} + \frac{4.60}{R^{20}_{[1]}} - \frac{1.15}{[R^{20}_{[1]}]^2} + 9.70. \quad (13)$$

Such values are fitted to a parabolic function

$$\bar{R}^{60}_{dif} = 0.28\,[\bar{R}^{20}_{dif}]^2 - 7.27\,\bar{R}^{20}_{dif} + 63.33, \quad (14)$$

with the correlation coefficient $r(\bar{R}^{60}_{dif}) = 0.9976$, that is shown in Fig. 4.

However, in order to fit in a similar way $\bar{R}^{85}_{dif}$ versus $\bar{R}^{60}_{dif}$, we have considered the following result of Equation 11, to transform them into reflectances by Equation 8

$$R'_{85} = -4 + 24.7\ln(10R^{60}_{[1]}), \quad (15)$$

where R'_{85} are the reflectometrical values. For this angle (85°), after subtracting from the linear fitting given by Equation 11 the expression given by Equation 15 and expanding in a series, we obtain the

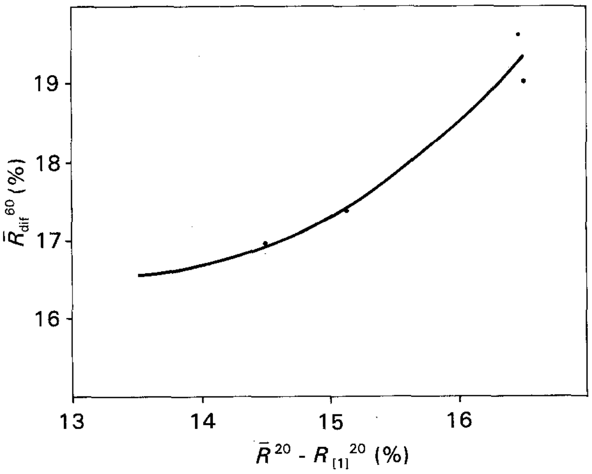


Figure 4 Average diffuse reflectance values with incidence angle $\phi = 60°$ versus the values obtained with incidence angle $\phi = 20°$. Parabolic function fittings.

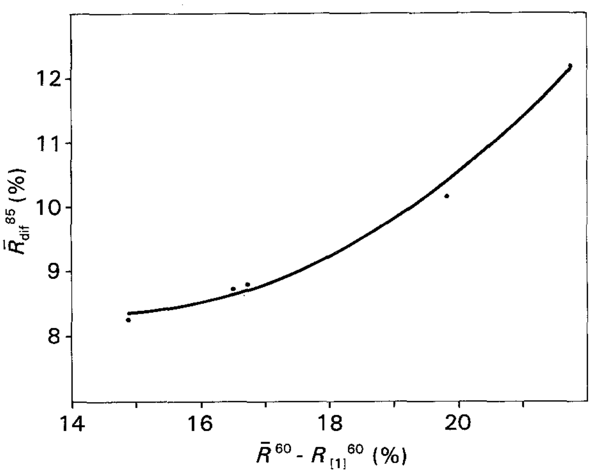


Figure 5 Average diffuse reflectance values, with incidence angle $\phi = 85°$ versus the values obtained with incidence angle $\phi = 60°$ Parabolic function fittings.

following expression

$$\bar{R}^{85}_{dif} = -1.46\,\bar{R}^{60} + \frac{30.58}{R^{60}_{[1]}} - \frac{7.64}{[R^{60}_{[1]}]^2} + 44.38, \qquad (16)$$

and the fitted parabolic function

$$\bar{R}^{85}_{dif} = 0.073\,[\bar{R}^{60}_{dif}]^2 - 2.114\,\bar{R}^{60}_{dif} + 23.743, \qquad (17)$$

with the correlation coefficient $r(\bar{R}^{85}_{dif}) = 0.9957$. In Fig. 5, we have plotted this relation, with discrete values.

From the data of the average diffuse reflectances and the data of average roughness of the polyethylene films shown in Table I, we concluded that the diffuse reflectance values increase with increasing average roughness, as expected, due to the fact that the irregularities spread out the incident light on a surface, whereas a hypothetic perfect and plane surface would cause only specular reflection.

Fig. 6a, 6b and 6c illustrates the effect of varying the average surface roughness on the calculated diffuse reflectance values with incidence angles of 20°, 60° and 85°, respectively. The hyperbolic (see Fig. 6a and 6b) function fits better for incidence angles of 20° and 60°,

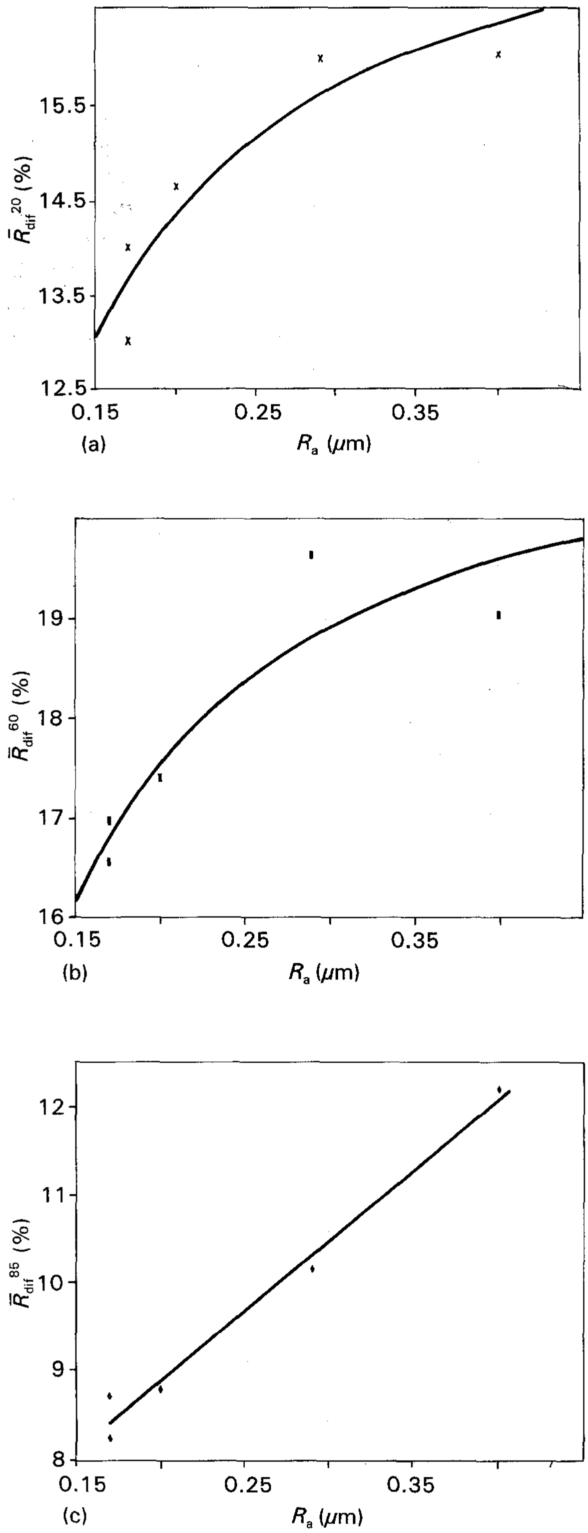


Figure 6 Values of evaluated average diffuse reflectances versus the average roughness, R_a, of polymer surfaces. Hyperbolical functions (a, b) and linear function (c) fittings.

whereas for an incidence angle of 85° there is a high degree of linearity (see Fig. 6c). From standard statistical methods we have determined the following relations

$$\bar{R}^{20}_{dif} = 18.34 - \frac{0.796}{R_a}, \qquad (18)$$

$$\bar{R}^{60}_{dif} = 21.64 - \frac{0.82}{R_a}, \qquad (19)$$

$$\bar{R}^{85}_{dif} = 5.7 + 16.0\,R_a, \qquad (20)$$

with correlation coefficients $r(\bar{R}^{20}_{\text{dif}}, R_a) = 0.9329$, $r(\bar{R}^{60}_{\text{dif}}, R_a) = 0.9212$ and $r(\bar{R}^{85}_{\text{dif}}, R_a) = 0.9917$, respectively.

From the correlation coefficients obtained here, it can be observed that an increase in the angle of incidence of light leads to a relative increase in the relation between surface texture (measured by the average roughness parameter, in μm) and the diffuse reflectance. This is expected if we take into account that the increasing incidence angle means a greater grazing incidence of light over the surface, and so a greater portion of radiation on surface irregularities.

6. Conclusions

We conclude that refractometry, combined with the reflectometrical measurements, is a good way of determining the average percentage of diffuse reflectance for a given material. The present results suggest that in polymer surfaces, such as polyethylene films, a parabolic relation exists between average diffuse reflectance evaluated by using two different incidence angles of light.

Finally, the diffuse reflectance values, especially those obtained with an incidence angle of light of 85°, are closely related to the average surface roughness, and those magnitudes can be used for the quantitative characterization of surface textures, a question of increasing industrial interest.

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