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Crystallinity enhances light transmissivity through low-density polyethylene sheets

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The effect of the crystalline structure (crystallinity and crystallite size) on the light transmissivity in low-density polyethylene sheets has been studied. Wide-angle X-ray diffraction, DSC, and UV/visible spectroscopy techniques have been used. The increase in crystallinity enhanced the light transmissivity in the visible region, but no significant effect in the UV region was obtained. The crystallite size showed no clear relation to transmissivity.

1. Introduction

Low-density polyethylene (LDPE) sheets are now widely used as covers in agricultural greenhouses. In addition to protecting the plants against winds, they provide appropriate climatic conditions for plant growth by means of adequate light transmission through the sheets and preservation of the temperature and humidity of the internal atmosphere. Such sheets are successfully used at present in the Jordan Valley.

LDPE sheets are produced by an extrusion process. Their fine structure and physical properties depend on many factors, including molecular weight of the polymer, degree of branching, and extrusion conditions such as temperature, speed and pressure [1–4]. UV light initiates and promotes polymer degradation. UV stabilizers, which can be added to the polymer before extrusion, are known to affect the absorption of light in the UV region and protect the polymer by preferentially absorbing or screening the UV part of the spectrum [5–8]. Crystallinity and orientation are also of considerable importance, due to their effects on the properties of materials. These two structural parameters in polyethylene have been studied by several workers [9–15]. The effects of annealing and drawing on the crystallization or modification of the morphology are also of interest [16–18], but there is little information in the literature on the effect of crystalline structure on the transmission of light. This paper reports an experimental investigation of the effect of crystallinity, crystallite size and orientation on the transmission of light in the UV and visible regions.

2. Experimental procedure

2.1. Materials

Four categories of samples of LDPE sheets were studied.

1. Portions were cut from the same sheet and annealed in a vacuum in the temperature range 50 to 117° C to prepare samples from the same polymer brand but with different values of crystallinity and/or crystallite size.
2. Portions were cut from the same sheet as above, hot-stretched to ratios between 1.25 and 2, and annealed at 105° C to prepare samples with different crystallinities and slightly improved crystallite orientation.
3. Two commercial samples were obtained from the same producer but differed in degree of crystallinity and crystallite size.
4. Four commercial samples were obtained from various sources, and possessed different values of crystallinity and crystallite size.

2.2. Annealing

Annealing was carried out in a vacuum oven either at constant length, by keeping the sample dimensions constrained in a frame holder, or at free length without using a frame. The temperature of the oven was raised at the rate of 2° C min^{-1} until a selected annealing temperature was attained. The sample was kept at this temperature for 20 min and finally quenched at room temperature.

2.3. Stretching

The sample was held in a stretching frame, then heated to 105° C, stretched to draw ratios between 1.25 and 2, and finally annealed for 20 min at 105° C.

2.4. X-ray diffraction

The wide-angle X-ray diffraction data for the determination of crystallinity and crystallite sizes $\bar{D}_{110}$ and $\bar{D}_{200}$ was obtained in a Phillips PW1050 diffractometer operated in the step-scan mode at angular intervals of 0.1° (2θ) in the range 10 to 35° (2θ). Nickel-filtered CuK_α radiation was used. The data was then analysed using the multipeak resolution procedure of Hindeleh and Johnson [19–24]. The crystallinity is then a parameter defined as the total scatter under the resolved peaks to the total scatter under the intensity-corrected and normalized scan:

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$$X_{\mathrm{cr}} = \frac{\sum_{t=1}^{B} \int_{2\theta_1}^{2\theta_2} I_t(2\theta)d(2\theta)}{\int_{2\theta_1}^{2\theta_2} I_{(\mathrm{norm})}(2\theta)d(2\theta)} \qquad (1)$$

The crystallite size was calculated according to Scherrer's equation:

$$\bar{D}_{\mathrm{hkl}} \approx \frac{1}{\delta b} = \frac{K\lambda}{\cos\theta\ \delta\ (2\theta)} \qquad (2)$$

2.5. UV/visible absorption spectroscopy

The absorbance, A, of a sample at a particular wavelength is defined [25] as:

$$A = \ln\left(I_0/I_t\right) \qquad (3)$$

where I_0 and I_t are the intensities of the incident and transmitted beams of light through the sample, respectively. Transmittance bears a reciprocal logarithmic relation to absorbance:

$$A = \ln\left(1/T\right) \qquad (4)$$

UV/visible spectroscopic measurements were carried out in a Perkin Elmer UV/visible spectrometer model 555 which functions in the wavelength range 190 to 860 nm and absorbance range 0.001 to 3.0. A blank test was first carried out to determine the correction background level of the absorbance A along the full range of wavelengths. The scanning of absorbance in the presence of the sample was repeated four times, the thickness, x, of the sample being increased by one layer each time. A computer programme was written up to analyse the data and calculate the absorption coefficient μ:

$$I_t = I_0\, e^{-\mu x} \qquad (5)$$

For making a comparison among the six commercial samples, which did not contain UV stabilizer (see Table I), the transmission percentage, T, of light at selected wavelengths through an assumed 0.01-cm-thick sample was calculated according to the following equation:

$$T\% = 100e^{-\mu(0.01)} \qquad (6)$$

2.6. Differential scanning calorimetry

The DSC analysis was achieved in a Mettler DSC calorimeter model TA 3000 where the heat flow (endothermic) against the temperature was scanned. The heating rate was $20^\circ\mathrm{C\,min}^{-1}$. The system incorporated computerization facilities which performed the following analytical functions: assignment of the peak melting point, determination of the base line, integration of the total heat of fusion, and calculation of crystallinity.

The determination of the crystallinity by the DSC technique [26, 27] is based on the principle of comparing the heat of fusion ΔH_f (represented by the area under the curve of the semicrystalline sample under investigation) with the heat of fusion ΔH_f^* of a 100% crystalline sample of the same polymer:

$$\text{Percentage crystallinity} = \left(\Delta H_f/\Delta H_f^*\right) \times 100 \qquad (7)$$

For polyethylene, $\Delta H_f^* = 290\,\mathrm{J\,g}^{-1}$ [28]

3. Results and discussion

Figure 1 illustrates an equatorial X-ray diffraction scan of LDPE sheet (sample 2b, Table 1), resolved into two peaks and background scatter. The X-ray crystallinity was then calculated according to Equation 1, and the crystallite sizes were calculated according to Equation 2. Figure 2 shows a typical DSC curve relating the heat flow (endothermic) to the temperature. After subtracting the background, the heat of fusion was calculated and the DSC crystallinity was determined according to Equation 7. Figure 3 illustrates typical transmissivity curves in the wavelength range 200 to 850 nm, showing the dependence of transmissivity on crystallinity and wavelength. Table I gives the X-ray crystallinity, DSC crystallinity, crystallite sizes $\bar{D}_{110}$ and $\bar{D}_{200}$, and the peak melting point of the samples in the four categories, described above.

3.1. Relationships between light transmissivity and crystalline structure

3.1.1. Category 1

Figure 4 compares the effects of constant-length and free-length annealing on the crystallinity of the

TABLE I Crystallinity, crystallite size and peak melting point of LDPE samples

Sample		Crystallinity (%)		Crystallite size (nm)		Peak melting point (°C)
Category	Symbol	X-ray	DSC	$\bar{D}_{110}$	$\bar{D}_{200}$	
1	a	37	31	11.3	7.5	113.1
	b	40	35	11.3	8.0	114.9
	c	43	30	9.2	6.9	116.9
	d	46	33	–	–	117.4
	e	55	38	7.6	6.4	117.8
2	a	37	–	11.3	7.5	–
	b	40	–	9.6	5.1	–
	c	43	–	9.3	4.8	–
	d	45	–	7.2	4.3	–
3	a	31	25	8.4	7.7	111.5
	b	41	26	10.2	8.5	116.3
4	a	28	26	12.0	9.2	114.7
	b	34	26	10.6	8.8	113.8
	c	37	24	11.3	7.5	113.1
	d	39	26	9.8	7.7	112.3

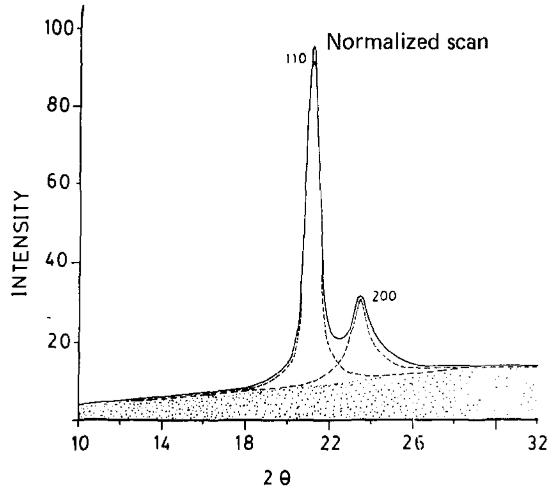

Figure 1 Equatorial X-ray diffraction scan of LDPE sheet resolved into two peaks and background scatter.

samples in category 1. By constant-length annealing, the crystallinity increased from 37% at 20° C to a maximum of 43% in the temperature region 92 to 109° C. On the other hand, by free-length annealing, the crystallinity reached 55% at 109° C, that is, at a few degrees below melting point. These findings indicate that free-length annealing allowed more freedom of motion for the chain molecules to rearrange themselves and form ordered (crystalline) regions. Analysis of the results in Table I indicates that XRD disclosed the variations in the crystallinity among the samples more clearly than DSC. This observation is also valid for the samples in the other categories. Moreover, the peak melting point correlates directly with the X-ray crystallinity, but no correlation exists with the DSC crystallinity.

Figure 5 shows the dependence of transmissivity on the X-ray crystallinity at constant wavelengths in the range 300 to 800 nm. The curves in Fig. 5 reveal clearly the following:

1. At a constant value of wavelength, the increase in crystallinity enhances transmissivity.
2. At a constant value of crystallinity, transmissivity increases with increased wavelength.
3. The effect of crystallinity is insignificant in the UV region.

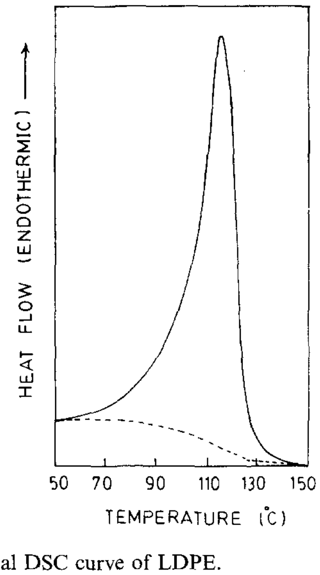

Figure 2 Typical DSC curve of LDPE.

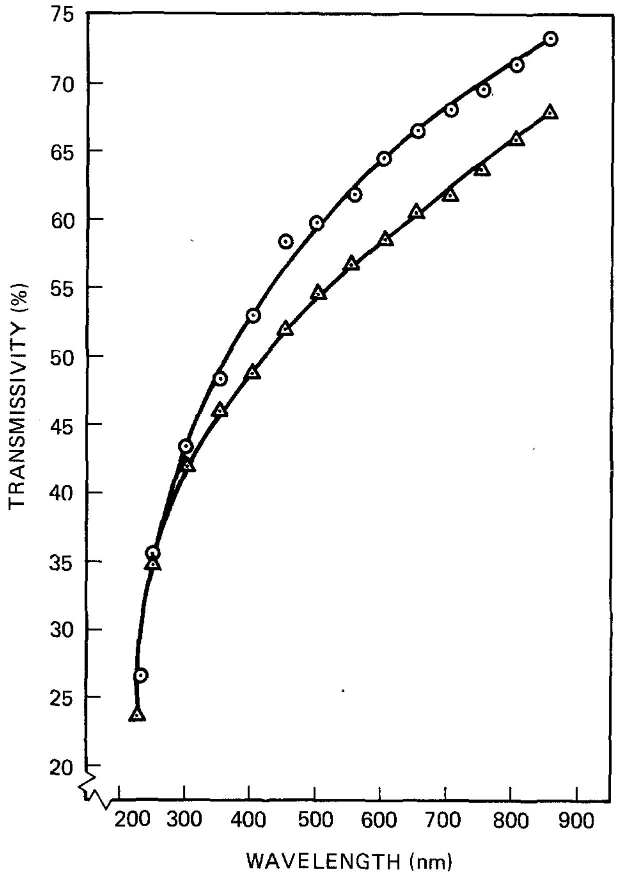

Figure 3 Dependence of the transmissivity of light on crystallinity in two commercial samples of LDPE sheets. Crystallinity: ⊙, 41%; △, 31%.

A comparison between crystallite size and transmissivity did not indicate any definite relationship.

3.1.2. Category 2

This category comprises four samples: an untreated

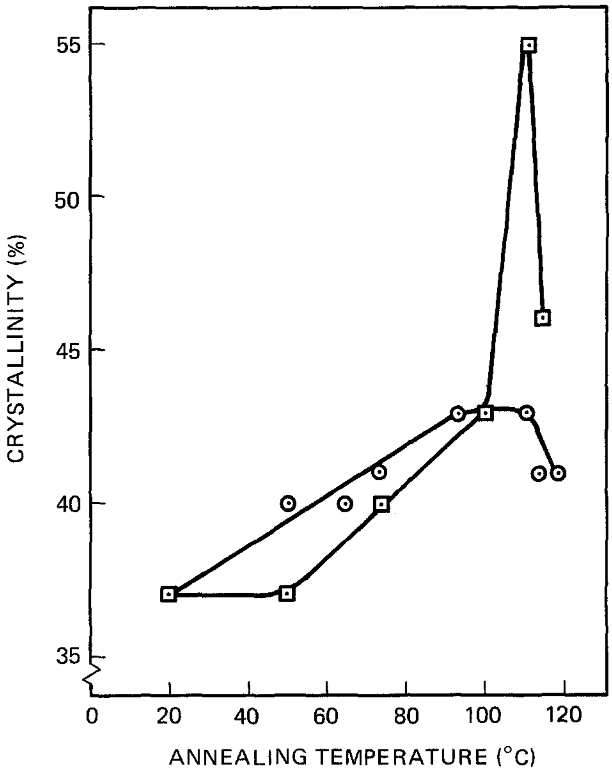

Figure 4 Comparison between the effects of ⊙, constant-length and ⊡, free-length annealing on the crystallinity of LDPE in the temperature range 20 to 117° C.

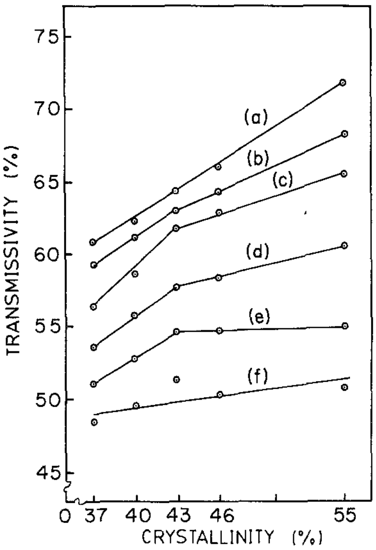

Figure 5 Light transmissivity as a function of crystallinity at constant wavelengths for the annealed samples in category 1. Wavelength: (a) 800; (b) 700; (c) 600; (d) 500; (e) 400; (f) 300 nm.

sample and three that were hot-stretched at draw ratios of 1.25, 1.5 and 2.0, respectively, and annealed at 105° C. Their structural properties are given in Table I, which indicates that this treatment caused an increase in crystallinity from 37 to 45%, and an adverse effect on crystallite size. Figure 6 shows four curves relating transmissivity to wavelength in the region 400 to 800 nm at constant crystallinity values. We conclude that at all wavelengths, in this region, the increase in the crystallinity enhances the transmissivity.

3.1.3. Category 3

Figure 3 shows two curves relating transmissivity and wavelength for two commercial samples obtained from the same source. Their crystallinities are 31 and 41%, respectively. We conclude that:

1. At constant wavelength in the visible region, transmissivity is enhanced by increasing the crystallinity.
2. The transmissivity in the UV region is nearly identical in the two samples.

Although the crystallite sizes in sample (b), which has a higher crystallinity, are larger than those in sample (a), this observation cannot be conclusive if one considers that the crystallite sizes had no bearing on transmissivity in categories 1 and 2.

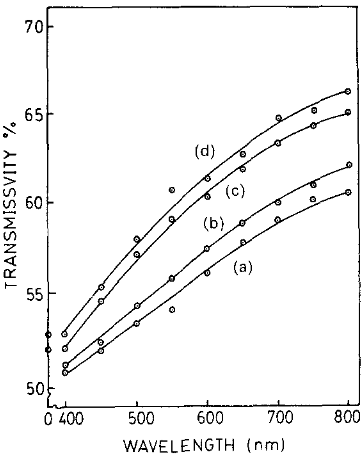

Figure 6 Transmissivity against wavelength at four crystallinity values for the hot-stretched samples in category 2. Draw ratio: (a) 0: (b) 1.25; (c) 1.5; (d) 2.0. Crystallinity: (a) 37; (b) 40; (c) 43; (d) 45.

3.1.4. Category 4

Four commercial samples from various sources were compared in this category. Their structural properties are given in Table I. In this category the transmissivity did not reveal a clear relation to either crystallinity or crystallite size. This could be explained by the fact that the samples were obtained from different manufacturers who use different brands of LDPE and different processing conditions.

4. Conclusions

From the results for the samples in categories 1 to 3, we draw the following conclusions:

1. The commercial samples which came from the same source show a direct relationship between X-ray crystallinity and visible light transmissivity, while in the UV region no influence of crystallinity on transmissivity is found.
2. Post-extrusion annealing increases crystallinity and consequently enhances transmissivity in the visible region.
3. Post-extrusion hot-stretching and annealing at 105° C, a few degrees below the peak melting point, increases crystallinity and also enhances transmissivity in the visible region. A comparison of transmissivity at constant wavelength in the UV region indicates an insignificant relation with crystallinity.

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