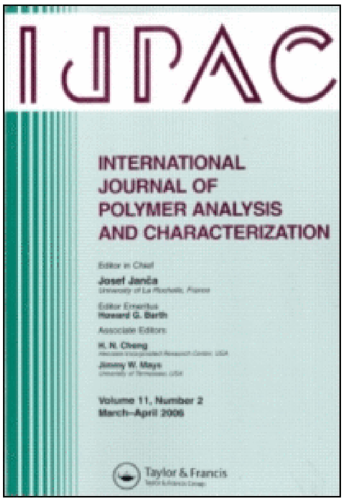

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Crystallinity Measurements of Unstabilized and HALS-stabilized LDPE Films Exposed to Natural Weathering by FT-IR, DSC and WAXS Analyses

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The crystallinity of unstabilized low-density polyethylene (LDPE) films and those stabilized with hindered-amine light stabilizers (HALS) was studied under natural weathering conditions, up to 170 and 650 days, respectively. The HALS tested was Tinuvin 783, added to the polymer in the concentration of 0.6% (wt/wt). The crystallinity changes were evaluated by means of Fourier-Transform Infrared (FT-IR) spectroscopy, wide-angle X-ray scattering (WAXS), and Differential scanning calorimetry (DSC). The comparison of the results obtained by FTIR and WAXS confirmed the accuracy of using the rocking bands 730 and 722 cm^{-1}. The trends of the crystallinity measured by DSC were different from those determined by FT-IR and WAXS.

Keywords: Low-density polyethylene; Hindered-amine light stabilisers; Crystallinity; FT-IR; WAXS; DSC

INTRODUCTION

Crystallinity is one of the most important morphological characteristics in the studies of polymer.[1,2] It is dependent on the composition

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*Corresponding author. Tel.: 213-5-214333 Ext. 269, Fax: 213-5-214332, e-mail: kacimu@yahoo.fr of the polymer and crystallization conditions and affects many of the macroscopic properties, especially mechanical properties.[3] Due to crystallinity, polyolefins are micro-heterogeneous in the solid state.[4] Many authors[5-7] pointed out that degradation reactions occur predominantly in the amorphous region and are controlled by the diffusion of oxygen in this region. This implies that in the crystalline portion, oxygen is not consumed for oxidative degradation reactions.[8,9] Moreover, it was also reported[10] that chain scissionmechanism resulting from photochemical degradation of polyethylene affects amorphous phase giving rise to chemicrystallization.

There are several methods[11-14] used for the determination of crystallinity content in polymers, namely, density, X-ray diffraction, infrared spectroscopy, nuclear magnetic resonance (NMR) and differential scanning calorimetry (DSC). However, the main problem is that each method provides different results, which are not often comparable.[12] DSC is cited[13] as the most widely used technique for measuring crystallinity in polymers, and infrared spectra are reported to be sensitive to the conformation and packing of chain molecules, and so this sensitivity has been widely exploited to characterize semicrystalline polymers in terms of their crystallinity.[15] Characteristic bands can be associated with the ordered fraction and with the disordered fraction. In fact, Zerbi *et al.*[16] suggested the use of spectral bands corresponding to the bending vibrations 1474 and 730 cm^{-1} (crystalline phase) and 1464 and 720 cm^{-1} (amorphous phase). The integrated infrared intensities are preferred to peak heights for quantitative measurements. As reported in the literature,[17] the peak heights depend on band shapes, which are considerably affected by dynamic factors that influence vibrational relaxation as well as by local inhomogeneities in the microstructure of the system.

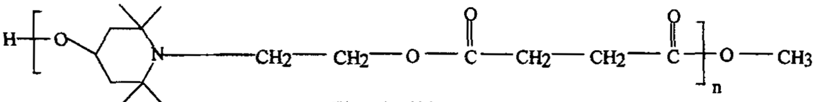
Since FT-IR spectroscopy is a relatively simple, fast, and potentially quantitative approach, we have undertaken a study to investigate the use of this technique for the crystallinity content in unstabilized and HALS-stabilized LDPE films exposed to natural weathering for two years. The crystallinity values obtained are compared to those determined by DSC and WAXS.

EXPERIMENTAL

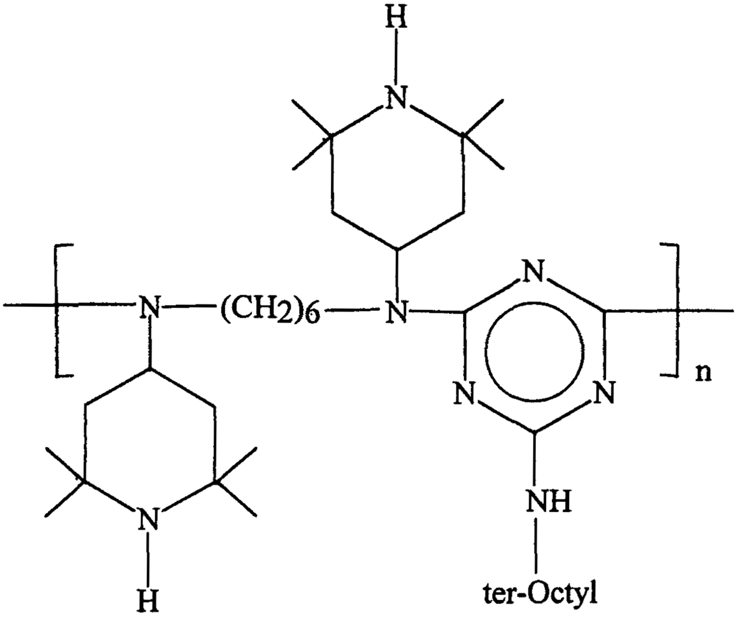
Materials

LDPE used is manufactured by the Algerian Company ≪ENIP≫ and commercialized under the trade name of B 24/2. The main physical properties of the material are density, 0.923 g/cc, and melt flow index (MFI), 0.3 g/10 min.

HALS, a mixture of 50 wt% of Tinuvin 622 and Chimassorb 944, was added to the material for stabilization against photooxidation at a concentration level of 0.6 % (wt/wt). The mixture is known as Tinuvin 783 and was provided by Ciba-Geigy. The chemical structure of the stabilizers, and the molecular weight are given below:



Tinuvin 622 (M_n>2500)



Chimassorb 944 (M_n>2500)

Preparation of Samples

80-µm thick films were prepared by blown extrusion process. A Battenfeld SFB 400 extruder with a ratio $L/D = 24$ was utilized. The temperature in the extruder varied from 160° to 180°C along the barrel, while in the die, it decreased from 180° to 160°C. The total residence time was about 20. The films were stretched in air after leaving the die at a pulling speed of 6 m/min. They were cooled by air passing through the die into the bubble. Finally, the films were cooled with a large volume of air upward over the surface of the bubble. WAXS experiments showed that the films did not undergo any significant orientation during preparation.

Natural Weathering Exposure

Natural weathering of unstabilised and HALS-stabilised LDPE films was carried out according to ASTM D 1435. The samples in the form of rectangular bands (30 x 20 cm) were mounted on 45° racks, facing south. The exposure was carried out at Bejaia (Mediterranean town on the eastern coast of Algeria, latitude 36° 43′ N and longitude 5° 4′E). The samples were exposed from December, 1996 and removed periodically for analysis. The average radiation in the experimental period was 160 Kcal/cm^2 per year. The average temperature varied between 15°C (winter) and 25°C (summer). The humidity level varied between 48% (winter) and 94% (summer). The amount of rain was 760 mm/year.

Analytical Techniques

Fourier-transform Infrared

Mainly two infrared spectral zones were analyzed: 600–800 cm^{-1} (containing the bands 720 and 730 cm^{-1}) and 1400–1550 cm^{-1} (containing the bands 1464 and 1474 cm^{-1}) using a Shimadzu FT-IR spectrophotometer model 8001 M. The crystallinity was determined by the method using 735–715 cm^{-1} and the following relationship:[17]

$$X_c = I(722 + 730)/I(722 + 730) + \alpha I(723) \quad (1)$$

where X_c is the percentage of the crystallinity content, and I represents the observed infrared intensities for the bands indicated. The integrated intensities were obtained by band-fitting methods. The bands at 730 and 722 cm^{-1} are the crystalline bands and that at 723 cm^{-1} is associated with the amorphous component. The coefficient α is defined as

$$\alpha = I^{\text{intr}}(722 + 730)/I^{\text{intr}}(723) \tag{2}$$

From intensity measurements α has been found to have a value of about 1.2 that must be included to account for the fact that the intrinsic intensities of the crystalline and amorphous bands are not exactly equal.

The measurement of crystallinity through the bands 1474 and 1464 cm^{-1} attributed to scissoring modes leads to unreliable results. As reported by Hagemann *et al.*[17] the 1475 – 1420 cm^{-1} bands present an amorphous band, which is highly asymmetric. This asymmetry results in band fitting more difficult and less accurate. For this reason, it is preferred here to use the rocking mode bands in the 735 – 715 cm^{-1}.

Differential Scanning Calorimetry

The thermograms were obtained from a DSC 30 Mettler analyzer. The sample of about 10 mg were heated from – 120° to 150°C at 20°C/min. Five experiments were performed for every sample.

The overall crystallinity of a polymer was calculated from the heat of fusion.[18] Determination of the heat of fusion per gram of the sample ΔH_s allows determination of the weight fraction crystallinity X_c *via*

$$X_c = \Delta H_s/\Delta H_c \tag{3}$$

In many cases ΔH_c may not be well determined, but for comparative purposes, this is relatively unimportant. ΔH_c value used here is 294 J/g.[19]

Wide-angle X-ray Scattering

WAXS measurements were carried out on a Philips (PW 1050 model) powder diffractometer (CuNi-filtered radiation) equipped with a rotative sample holder device. The percent crystallinity was computed by using the following procedure: the background line is drawn between two points which are chosen so that all diffraction patterns have minima at these points; the amorphous peak is sketched somewhat arbitrarily drawing a line connecting the two extreme minimum points of the baseline and the minima of the crystalline peaks; the ratio of the area under the crystalline peaks and above the amorphous peak to the total area above the background line, multiplied by 100, is taken as the percent crystallinity.

RESULTS AND DISCUSSION

The crystalline fraction of both unstabilized and HALS-stabilized LDPE films exposed to natural weathering is calculated from the peak areas of the methylene rocking bands at 722 and 730 cm^{-1}. The amorphous fraction is calculated from the peak area at 723 cm^{-1}. The quantitative evaluation was carried out according to Eqs. (1) and (2). The values of the percent crystallinity at different exposure times measured by FTIR are reported in Tables I and II and compared to those determined by WAXS and DSC. The trends of the values are shown in Figures 1 and 2.

Unstabilized LDPE Films

In Table I and Figure 1, the X_c values of the unstabilized films as a function of the exposure time are reported. All three methods show an increase of the X_c values with exposure time. Moreover, a close concordance of the crystallinity values obtained by FT-IR and WAXS

TABLE I Crystallinity content by FT-IR, WAXS and DSC as a function of exposure time for unstabilized LDPE film

Exposure time (days)	*Crystalline content (%) by FT-IR*	*Crystalline content (%) by WAXS*	*Crystalline content (%) by DSC*
0	39 ± 1	41 ± 1	38 ± 2
44	41 ± 1	43 ± 1	38 ± 2
70	42 ± 1	44 ± 1	39 ± 2
100	43 ± 1	47 ± 1	37 ± 2
170	46 ± 1	49 ± 1	42 ± 2

TABLE II Variation of crystallinity content by FT-IR, WAXS and DSC as a function of exposure time for HALS-stabilized LDPE film

Exposure time (days)	*Crystalline content (%) by FT-IR*	*Crystalline content (%) by WAXS*	*Crystalline content (%) by DSC*
0	41 ± 1	41 ± 1	35 ± 2
100	43 ± 1	41 ± 1	34 ± 2
170	44 ± 1	42 ± 1	36 ± 2
280	45 ± 1	45 ± 1	36 ± 2
391	44 ± 1	45 ± 1	38 ± 2
450	44 ± 1	43 ± 1	38 ± 2
650	45 ± 1	44 ± 1	40 ± 2

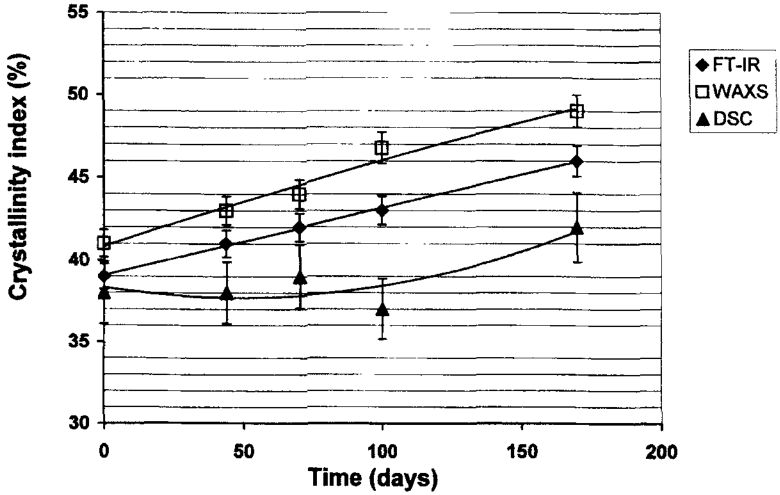


FIGURE 1 Crystallinity index of unstabilized LDPE films.

is observed confirming the accuracy of using the methylene rocking bands at 730 and 722 cm^{-1}.

Both methods provide similar results and the magnitude of the crystallinity values are reasonable. However, the crystallinity values calculated from the DSC thermograms are lower and the trend of the data is different. In fact, up to 100 days of exposure, the crystallinity is almost unchanged, indicating that up to this time the exposition of the unstabilized LDPE does not produce any influence on the crystallinity of the films. Increase of the crystallinity for the unstabilized film is instead expected, as it will be clarified later. This suggests that the

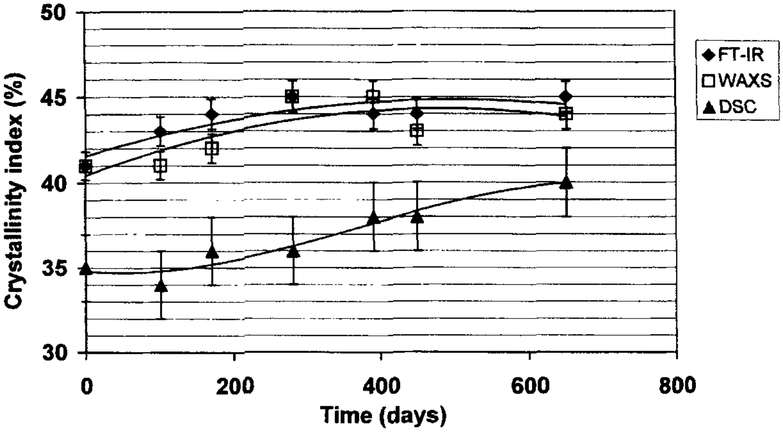


FIGURE 2 Crystallinity index of HALS-stabilized LDPE films.

crystallinity measurement by the enthalpy of fusion may not be adequate. The main practical problems[12, 18] are related to phenomena of melting, recrystallization, and annealing occurring during the scanning. Another important parameter that influences the computation of the enthalpy is the assessment of the baseline for the integration area and the choice of the beginning and final points of integration. These are, in our opinion, probably the main contributing factors to the possible failure of DSC in the measurement of the crystallinity of these samples.

The gradual increase of the crystallinity percentage observed in the unstabilized LDPE films exposed to natural weathering is a well-established phenomenon. In fact, according to the literature,[8, 20] this result is mainly attributed to secondary crystallization localized exclusively in the amorphous phase. The chain scissions resulting from Norrish I and II reactions[21] decrease the density of entanglements in the amorphous phase allowing the shorter molecules to crystallize due to higher mobility.

HALS-stabilized LDPE Films

Figure 2 and Table II exhibit FT-IR, WAXS and DSC crystallinity values for the HALS-stabilised LDPE samples exposed to natural weathering.

A slight increase in the percent crystallinity measured by both FT-IR and WAXS is observed during the first 100 days of exposure, followed by a plateau of X_c up to 650 days. The percent crystallinity by FT-IR increases from 41 to 45% up to 650 days of exposure and a similar trend is found for the WAXS measurements. The X_c values calculated by DSC show instead almost constant values during the first 280 days (35–36%, see Tab. II), followed by an increment of the X_c value up to 650 days (40%). In general, at the same time of exposure, lower crystallinity values are observed for stabilized samples. This clearly indicates that the presence of HALS in the LDPE film reduces the rate of chain scission mechanism.[22]

CONCLUSION

This paper shows the applicability of FT-IR spectroscopy to measure the crystallinity of both unstabilized and HALS-stabilized LDPE films exposed to natural weathering. Reliable quantitative data are obtained from the peak area of the methylene rocking bands at 730/722 cm^{-1}. The results of these measurements are compared with those determined by WAXS and DSC techniques.

It is found that the FT-IR results are in fair agreement with the data determined by WAXS confirming the accuracy of using the bands at 730/722 cm^{-1}. The trends of the results by FT-IR and WAXS are similar for both the unstabilized films and HALS-stabilized LDPE films, as reported in Figures 1 and 2. However, the X_c values obtained by DSC are always lower and the trends are different from those of the other two techniques.

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