Comparative Morphological Investigation between Natural Photo-Aged of Two Different Low Density Polyethylene Green House Covers

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Abstract

This work studies and compares the degradation performance of two different types of blown extruded films of low density polyethylene films used as greenhouse covers. The first one is LDPE (B24/2) supplied by ENIP Skikda and the other one is LDPE (2100 T N00W) supplied by SABIC, Saudi Arabia. Both films are commonly used in Algeria as greenhouse covers. The films were exposed outdoors over a period of 8 months for natural ageing. XRD and DSC analysis were conducted to characterize the thermal properties of the materials and compare between their degradation behaviors. The results revealed that the degradation resistance of LDPE (B24/2) is better than LDPE (2100T N00W) in term of their degree of crystallinity.

Keywords: Natural Ageing, LDPE (B24/2); LDPE (2100 T N00W); Degree of Crystallinity, XRD; DSC.

Introduction

Polyethylene (PE) is one of the mostly studied and exploited polymers due to its characteristics and wide range of applicability [1-5]. Depending on the density, polyethylene are classified as Linear low density (LLDPE), low density (LDPE), High density (HDPE) and ultra-high molecular weight (UHMWPE) [6-10]. Low density polyethylene films has a big demand on its use in agriculture field as greenhouse cover [11-15]. They have several appropriate characteristics (lightness transparency), however its exposure to UV radiations leads to a dramatical loss in its properties (mechanical, chemical and morphological) due to the oxidation of its initial molecular structure [16- 22]. The life time of the films is an essential factor. In this study the morphological aspect (crystallinity degree) during a natural ageing of a pair of films produced using two different raw materials (LDPE B24/4 a local product and LDPE 2100 T N00W an imported product) was the focal point. The techniques conducted to follow the evolution of the crystallinity degree for both materials were the Differential Scanning Calorimetric DSC (thermal method) and the X-ray Diffraction analysis XRD (an optical method) [23-25].

Experimental

Material and procedures

The first raw material of LDPE used in this investigation is a commercial film produced by the ENIP Company, Skikda, Algeria under the reference "B24/2". The second raw material was a commercial grade produced in Saudi Arabia basic industries cooperation (SABIC) as pellets under the reference "LDPE 2100 T N00W". The polyethylene has been transformed to films from both materials under the same processing conditions in an Algerian industry SOFIPLAST. Both materials are a neat grade exempt of stabilizing agents.

Film cuts were mounted within wooden frames facing south, inclined at 45°, according to the standard NF T51-165. The solar exposure took place at Laghouat, Algeria (38°, 48 N) from March to November for both LDPE B24/2 and LDPE 2100T. The maximum time at which the films became too brittle to resist to the wind strength was found to be 8 months. Sampling process was done monthly.

Characterization methods

Differential Scanning Calorimetry(DSC)

DSC measurements were performed for the LDPE B24/2 on a DSC Mettler TA 3000 interfaced to a microcomputer controller

and for LDPE 2100T on a NETZSCH DSC 204F1Phoenix. Indium was used for calibration and nitrogen as atmosphere for both. Samples of about 7-9 mg were heated from -150 to 200° C with a heating rate of 10°C/min [26-30].

X ray Diffractometry (XRD)

X-ray diffractograms were obtained for both materials by means of an (XRD, PW3040 Philips Diffractometer, Cu K α radiation, $\lambda = 0.154056 \text{ \AA}$, voltage of 40 kV and current of 50 mA) over a range of $2\theta = 50 - 60^\circ$ with step of 0.04 and acquisition time of 3s.

Table 1: Degree of crystallinity for both films calculated from the DSC and XRD curves

Samples	T_m (°C)		ΔH_f (J/g)		X% (DSC)		X% (XRD)	
	LDPE (B24/2)	LDPE (2100 T)	LDPE (B24/2)	LDPE (2100 T)	LDPE (B24/2)	LDPE (2100 T)	LDPE (B24/2)	LDPE (2100 T)
A0 (0 month)	107.5	111.1	100.9	139.29	35.40	47.54	36.01	47.1
A4 (4 months)	108.7	111.4	104.9	150.08	36.81	51.19	37.43	51.33
A8 (8 months)	108.87	112.4	110.2	191.52	38.67	65.36	41.67	59.08

Results and Discussion

The DSC analysis has been conducted for the virgin material and for 4 and 8 months aged material. Figure 1 shows the peaks of fusion of both materials for the different exposure periods. It can be observed that peaks of fusion of LDPE 2100 T N00W films are larger and sharper than those of LDPE B24/2 which can be related to the rate of material crystallinity.

The area under the melting peak represents the heat of fusion which is proportional to the amount of crystals present in the sample. Its value is given directly by the DATA Analysis program of the apparatus. The mass-based degree of crystallinity noted Xc, corresponds to the ratio of the heat of fusion of the current sample and that of a 100% crystalline polyethylene ($\Delta H_f = 285 \text{ J/g}$) [31-32] by the relationship:

$$x\% = \frac{[\Delta H]_f}{([\Delta H]_f)_{100\%}} \quad (1)$$

Based on the melting of the total volume of the sample the measurement is linked to the whole material under test which provides information with fidelity over the real crystallinity degree. In Table 1 the crystallinity degree is presented for three stages of ageing for both materials.

The melting temperature, heat of fusion and the degree of crystallinity of both films are given in Table 1. It is noted that the degree of crystallinity increases with ageing exposure time and the melting temperature and heat of fusion follow the same trend. This trend of variation can be also seen in Figure 2. The T_m

for unaged film was found to have value of 107.5 °C for LDPE B24/2 and 111.1 °C for LDPE 2100T, respectively. The maximum increase in the T_m for both materials is about 1.37 °C and 1.30 °C. It can be concluded that the natural ageing time has no significant effect on the T_m of both films. The results show that LDPE 2100 T is more affected by ageing. Such observation can be linked to the structural changes undergone by the material during exposure to solar radiation. UV radiation causes the breaking of molecular chains having the effect of increasing the crystallinity through a process of chemocrystallisation [32, 33]. Indeed, these reactions confined to the amorphous phase leads to a decrease in the average molecular weight of the chains [33]. Short chain

segments resulting tend to diffuse to the crystal lamella thus increasing both the crystal concentration and the value of the melting temperature.

To obtain another estimation of the crystallinity degree for both materials, the X-ray diffraction analysis was conducted on virgin and aged (for 4 and 8 months) films. The XRD at large angles enables the calculation of the crystalline concentration. The diffraction profile was analyzed as a superposition of an amorphous halo and crystalline spectrum. After deconvolution of the crystalline peaks and amorphous halo, the crystallinity is determined according to the method of Hermans and Weidinger [34,35] by calculating the total area of crystalline peaks divided by the total area of all crystalline and amorphous diffracting elements $S_{sc} + S_a$ [34,36]. The calculated degree of crystallinity X% of both materials is presented in Table 1. These results show an overall increase in the crystallinity (Figure 2) with ageing which confirms the results obtained by the DSC technique. The magnitude of the crystallinity degree is almost the same for each material using the two techniques. It is noteworthy that the crystallinity degree is higher for the SABIC film which explains the degrading rate is faster.

Conclusion

Based on the results of the DSC and XRD techniques, the ageing exposure time has an adverse effect on both films. The results of DSC and XRD regarding the degree of crystallinity are very close. The severe effect that the sunlight has on the 2100 T N00W film compared to that of B24/2 film is due to the rapidity of the rate of chain scissions and in turn the high degree of crystallinity in this last one. This can be argued that the chemocrystallisation phenomenon has taken place earlier in the LDPE (2100 T N00W) than in the LDPE (B24/2). The results of this work released that the LDPE B24/2 film has a relatively better thermal stability if compared to LDPE 2100 T N00W film.

Figure 1: DSC curves of unstabilized LDPE (B 24/2) and unstabilized LDPE (SABIC) (0 month, 4 and 8 months of ageing)

Figure 2: X% (XRD and DSC) and enthalpy of melting vs. ageing time (solid lines for X%).

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