Characterization to the Weathering Extent of LLDPE/LDPE Thin Film

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ABSTRACT: A kind of LLDPE (linear low density polyethylene)/LDPE (low density polyethylene) thin film for farm applications was subjected to accelerated and natural weathering. Carbonyl group, melting point, tensile elastic modulus, and high-temperature shearing modulus of weathered films were investigated as function of weathering time. Two kinds of carbonyl index, I_1 and I_2, which result from infrared spectroscopy (IR) spectra of the weathered films, were defined to characterize the weathering extent of the LLDPE/LDPE thin film. Based on I_1 and I_2, a correlation is made between the artificial and natural weathering of the film: 1 h of the artificial weathering is equivalent to about 10.73 h of the natural weathering. The difference between the accelerated weathering and the natural weathering was also discussed. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 12–16, 2003

Key words: thin-films; polyethylene (PE)

INTRODUCTION

Due to its lower cost of production, LLDPE was accepted rapidly, and received good development in the industry of PE.[1] For example, by blending LDPE with LLDPE, thinner film can be produced without the need for extruder modifications.[2] The LLDPE/LDPE thin film is characterized by reduced haze and better bubble stability. It has been a very important role in film market.[3] Although many applications of LLDPE/LDPE film require it to be employed outdoors, much fewer attempts have been made to study the weathering of LLDPE/LDPE than that of low- or high-density polyethylene.[1] In fact, with the expansion of its application as farm film, the requirement of its regeneration is more and more urgent. In this respect, the characterization to the weathering extent of the films is important, because films of different weathering extent have different physical and chemical properties, which means different regeneration process and different application fields.

During the weathering of films, crosslinking and scission of molecular chain take place at the same time; therefore, it is very difficult to find a index to characterize the weathering extent of the weathered films, because many properties of the weathered films do not show monotone trend with the weathering time. In this article, a kind of LLDPE/LDPE thin film for farm applications was subjected to natural weathering and accelerated weathering. IR, differential scanning calorimeter (DSC), dynamic-mechanical thermal analysis (DMTA), and advanced rheology expansion system (ARES) were applied to characterize the change of carbonyl group, melting point, tensile elastic modulus, and high-temperature shearing modulus with weathering time. A method based on carbonyl groups was established to characterize the weathering extent of the LLDPE/LDPE thin film. Difference between the accelerated weathering and the natural weathering was also discussed in this article.

EXPERIMENTAL

Material

Unstablized LLDPE/LDPE thin film (LLDPE 80% + LDPE 20%) with a thickness of 0.015 mm was used.

Accelerated weathering

Accelerated weathering was carried out in a Xenon weatherometer, using the following conditions (Operation according to ASTM G26): radiation 0.35 w/m^2 (340 nm); power of San lamp: 6.5 kW; light filter pipe (inner/outside): Boro/Boro; temperature of black board: $65 \pm 2°C$; working temperature: $45 \pm 1°C$; humid ball temperature: $40 \pm 1°C$; relative humidity: 60–80%; cycle of raining: 18 min/120 min (nonionic water, impurity: under 1 ppm).

Samples with the size of 48×24 cm were held in frames that rotated around the Xenon lamp. They were taken out after designed time as follows: 24, 45, 135, and 270 h.
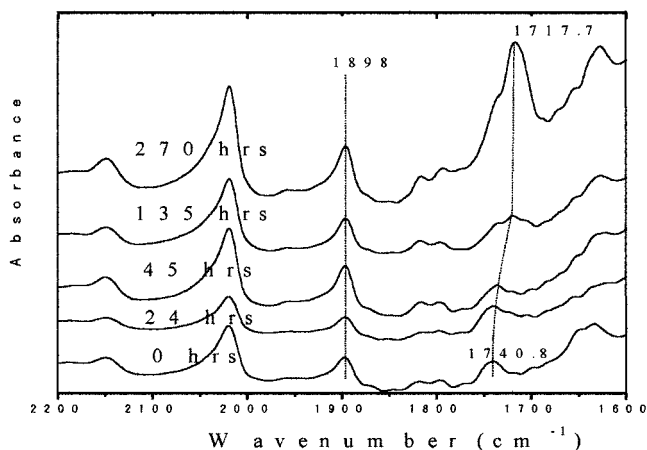
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Figure 1 IR spectra of the accelerated weathered LLDPE/LDPE thin films.

Natural weathering

The films were exposed in a frame (1.0×1.0 m) facing the south with a inclination angle of 45°. The lowest side of the frame is 1.0 m far away from the ground.

Location: Shanghai, P.R. China; weathering time of samples: 7, 14, 21, 28, 42, 74, 121, and 161 days.

Characterization

A BRUKER EQUINOX55 infrared spectrometer was used to record IR spectra of the weathered films that were cut into small round pieces (d = 1.0 cm), and then filed in mold (d = 1.0 cm) followed by hot pressed under 150°C for 1 min to get samples for IR measurement. The thickness of the samples range from 0.18–0.30 mm.

Melting points of the weathered films were obtained from a DSC SP differential scanning calorimeter (Rheometric Scientific Company). Heating speed is 10°C/min.

Tensile elastic modulus was measured by DMTA IV of Rheometric Scientific Company. (Bi-centilevered beam mode, Sample size: $50 \times 5 \times 0.015$ mm, scanning temperature range from 20–150°C.)

High-temperature shearing modulus under of the weathered films were measured by ARES of Rheometric Scientific Company. The films were molded into round pieces whose thickness is 2 ± 0.1 mm, diameter is 15 ± 0.2 mm, being measured at 140 and 200°C with the frequency ranging from 0.1 to 100 Hz.

RESULTS AND DISCUSSION

Definition of I_1 and I_2

In many articles, it were reported that "carbonyl index" defined based on the absorbance or transmittance of peak at about 1710 cm^{-1} increase monotonously with weathering time.[4–9] Figures 1 and 2

shows that the peak located at about 1717 cm^{-1} also increase monotonously with the weathering time; however, at the early stage of the weathering process, the peak is too weak to be distinguished clearly, which means this carbonyl group cannot reflect the early stage of the weathering. Fortunately, there is another carbonyl group that was located at about 1740 and 1717 cm^{-1}, and obviously also changed with the weathering time. Therefore, it is considered to define two "carbonyl index" as:

$$I_1 = \Delta A_{1740} / \Delta A_{1898}; \quad I_2 = \Delta A_{1717} / \Delta A_{1898}$$

where ΔA is the difference between absorbance of the peak with baseline of the peak.

The peak at 1898 cm^{-1}, which ascribed to C—H deformation modes in polyethylene is used as internal standard to minimize errors due to radiation in sample thickness as well as due to the instrument, because this band whose intensity is proportional to film thickness was found to remain unchanged during weathering process.[7]

Figures 3 and 4 show the relation curves between I_1 and I_2, respectively, with the weathering time in the case of the accelerated weathering and the natural weathering.

The same as the results in previous articles,[4–8] I_2 shows a monotone correlation with weathering time. With the help of I_1, the early stage of the weathering such as 10 days of natural weathering can also be reflected. Although the weathering of material is very complicated, physical and chemical behavior relate to not only the material but also other factors such as spectral distribution as well as the quantity of ultraviolet energy.[10] In the case of the weathering conditions and the material having been determined, actually the weathering time almost amounts to the weather ex-

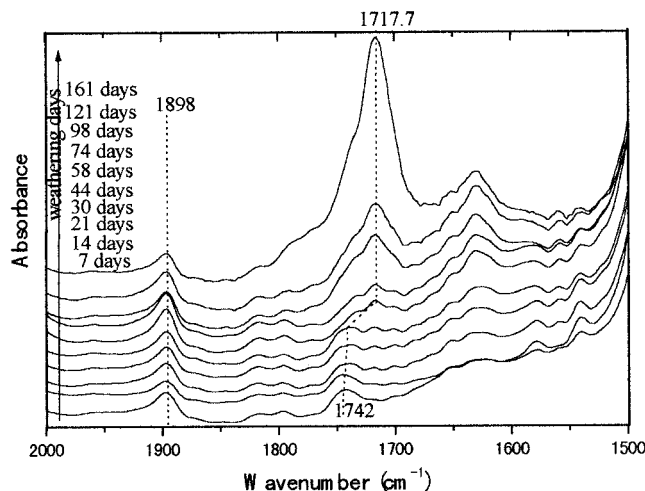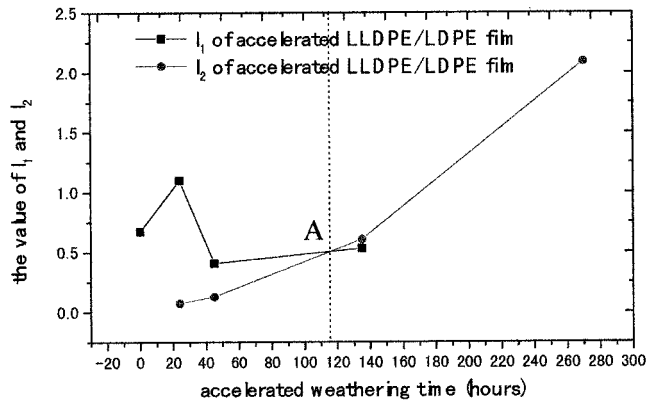**Figure 2** IR spectra of the natural weathered LLDPE/LDPE thin films.

Figure 3 Relation between the values of I_1 and I_2, respectively, with the accelerated weathering time.

tent. By establishing the relations between carbonyl indexes I_1, I_2 with weathering time under certain weathering condition, the weathering extent of the LLDPE/LDPE thin films can be characterized by the value of I_1 and I_2.

Correlation between accelerated weathering and natural weathering

It can be noticed that there are intersection points A and B of I_1 curves with I_2 curves in Figures 3 and 4. The intersection points may represent special stage of the weathering. The values of I_1 or I_2 of point A is 0.5039, and is very close to that of point B, 0.5130. Point A correspond to 115.7 h of accelerated weathering, and point B corresponds to 51.7 days of natural weathering. This means 1 h of accelerated weathering may be equivalent to 10.73 h of natural weathering. According to the correlation, Figure 3 was combined with Figure 4 into Figure 5. As shown in Figure 5, the data of accelerated weathering can almost coincide with the data of natural weathering by the adjustment according to the correlation.
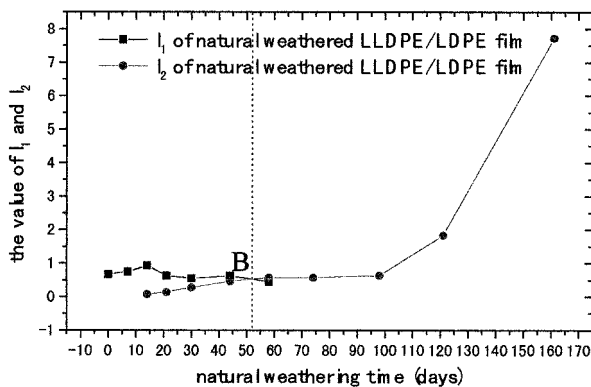

Figure 4 Relation between the values of I_1 and I_2, respectively, with the natural weathering time.
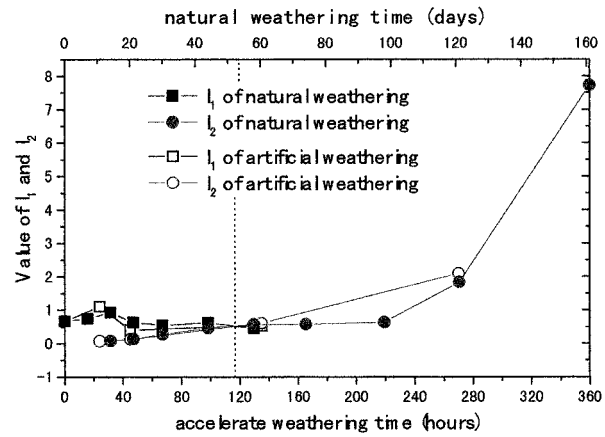

Figure 5 Illustration of the resemblance between the natural weathering and the accelerated weathering.

Other characterizations

On the basis of the correlation between the accelerated weathering with the natural weathering, effects of weathering time on melting point, tensile elastic modulus, and high-temperature shearing modulus of the weathered LLDPE/LDPE thin films were indicated in Figures 6–9, respectively. In all of the melting points, the tensile elastic modulus, the shearing modulus at 140 or 200°C have no monotonous relation with the weathering time, which suggest that they are unable to be used as an index to characterize the weathering extent of the LLDPE/LDPE film.

During the weathering process, because of the so-called secondary crystallization and scission, the melting point of PE films drop during the weathering process.[8] The LLDPE/LDPE film also shows the trends, but the drop of the melting point occurred mainly at the early stage of the weathering. This phenomenon has no relation with secondary crystallization because at that stage, the content of carbonyl group is still very low. It may relate to the lose of the
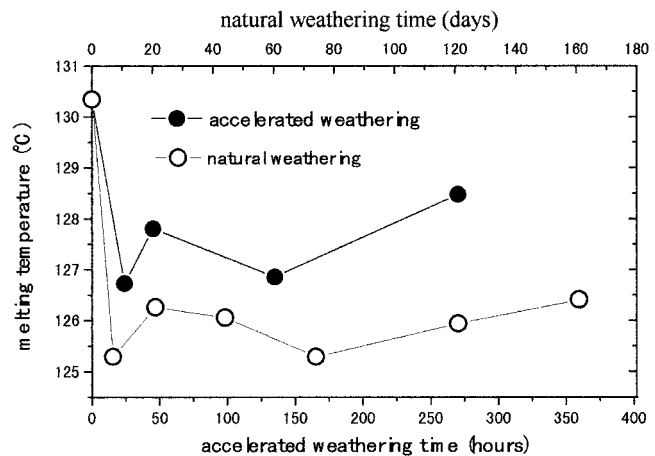

Figure 6 Effect of the weathering time on the melting point of the weathered LLDPE/LDPE thin films.
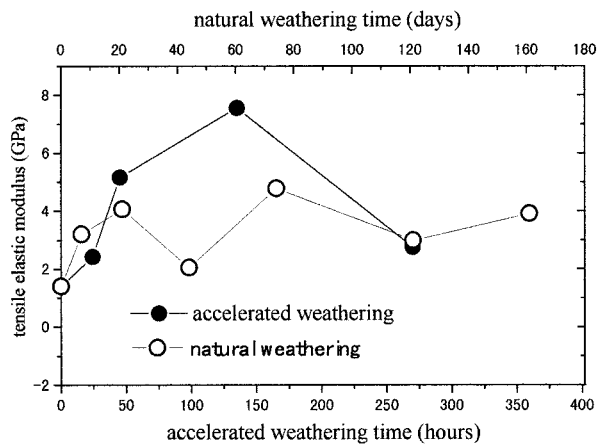
Figure 7 Effect of the weathering time on the tensile elastic modulus of the weathered LLDPE/LDPE thin film.

connection between the crystalline region and the amorphous region in the films. The relief of the limitation from the amorphous region to the crystalline region may lead to such a decrease of the melting point of the films. It is well known that during the weathering process, crosslinkage and scission of the molecular chain of PE take place at the same time in the amorphous region. It can be imagined that the scission of the connection between the crystal region with the amorphous region will happen easier than rebuilding the connection.

Compared with the accelerated weathering, the natural weathering leads to a larger drop of the melting point at the early stage of the weathering. It reflects the difference between the accelerated weathering with the natural weathering. The accelerated weathering succeeds in simulating the ultraviolet radiation of outdoors (proved by I_1 and I_2, as mentioned above); however, it cannot simulate the outdoors environment perfectly. The larger drop of the melting point of the naturally weathered films may mean that more scis-
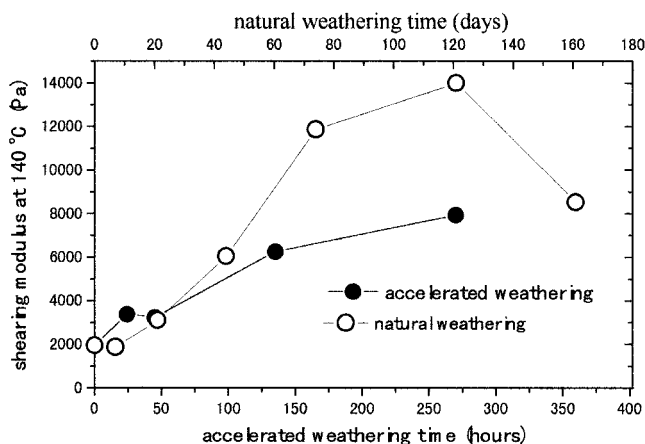
sion of the molecular chains will take place during the natural weathering.

As shown in Figures 7–9, the tensile elastic modulus of the accelerated weathered films is higher than that of the natural weathered films, and the shearing modulus at 140 and 200°C are lower than that of the natural weathered films. The phenomena prove that more scission of the molecular chain takes place during the natural weathering process, which produces more branched molecules showing higher shearing modulus at high temperature. In addition, at the end part of the natural weathering, complying with the intensive increase of the carbonyl group, the shearing modulus at 140 and 200°C drop intensively, which means the molecule of the LLDPE/LDPE thin film breaking in large scale. At this stage, the melting point of the films did not drop; on the contrary, it rise gradually; therefore, the broken molecules still take place only in the amorphous region of the films. That is also the explanation to the phenomenon that the tensile elastic modulus of the natural weathered LLDPE/LDPE thin films do not drop steeply.

CONCLUSION

During the weathering process of the LLDPE/LDPE thin film, two kinds of carbonyl group change obviously with the weathering time. Two carbonyl index, I_1 and I_2, based on the two kinds of carbonyl group was defined and proved to be able to characterize the weathering extent of the LLDPE/LDPE thin film when the weathering conditions is determined.

Correlation between the natural weathering and the accelerated weathering is made according to the values of I_1 and I_2. In this article, 1 h of the accelerated weathering was almost equivalent to 10.73 h of the natural weathering. This correlation was proved to be valid only to the carbonyl groups, which may correspond to UV radiation weathering. The result of DSC,

Figure 9 Effect of the weathering time on the shearing modulus at 200°C of the weathered LLDPE/LDPE thin film.

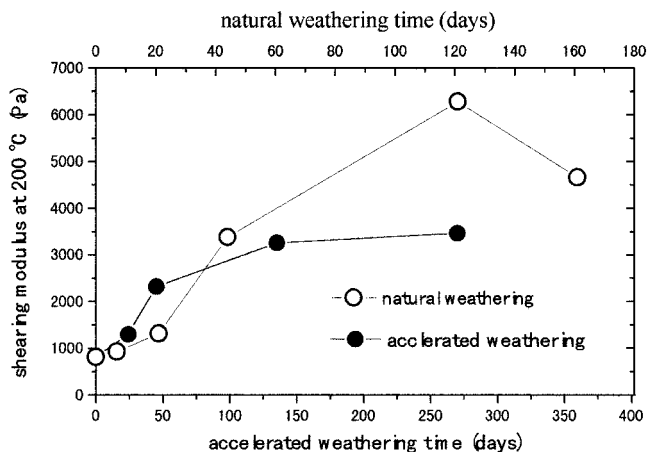**Figure 8** Effect of the weathering time on the shearing modulus at 140°C of the weathered LLDPE/LDPE thin film.

DMTA, and ARES show that the natural weathering may induce more scission reaction of molecular chain than the accelerated weathering.

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