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Effect of photooxidative ageing at natural conditions on dynamic mechanical properties of PE-LD/PE-LLD blends

Summary — The blends of low density polyethylene with linear low density polyethylene and pure polyolefins were blown for their use in agriculture. These films were stabilized with a commercial Hindered Amine Light Stabilized (HALS). Blends with this stabilizer were photodegraded under natural outdoor weathering conditions during two years. Photodegradation involves oxidation of the polymer chain and causes modifications of the mechanical properties of the exposed films that were monitored by dynamic mechanical spectroscopy. The mechanical relaxation spectra show the α, β and γ relaxation zones, in decreasing order of temperature. Their characterization was carried out using the deconvolution method proposed by Charlesworth, together with the Fuoss-Kirkwood equation. The results obtained for pure PE-LLD and PE-LD and their blends show that the storage modulus increases as a function of the exposure time. The maximum storage modulus is reached at different exposure times depending on the blend composition. The β relaxation zone is the most affected by weathering. A new relaxation was detected between -85 °C and -75 °C, which was modified as a function of the exposure time, and finally even disappeared. All the samples exhibit the same evolution, but at different time scales. It has been found that after two years of exposure, the degradation of the interfacial region is already initiated. The blends with 50 % of PE-LD are the most resistant to weathering.

Key words: PE-LD/PE-LLD blends, photooxidation, dynamic mechanical properties, relaxation processes.

WPŁYW FOTOOKSYDACYJNEGO STARZENIA W WARUNKACH NATURALNYCH NA DYNAMICZNE WŁAŚCIWOŚCI MECHANICZNE MIESZANIN PE-LD/PE-LLD

Streszczenie — Przedmiotem badań były mieszaniny polietylenów małej gęstości (PE-LD/PE-LLD) w pełnym przedziale ich składu. Metodą dynamicznej analizy termomechanicznej (DMTA) określono wpływ składu i czasu ekspozycji (do 24 miesięcy) na przebieg fotooksydacyjnego starzenia tych układów w warunkach naturalnych (Hiszpania, tabela 1). Scharakteryzowano zachodzące w toku starzenia zmiany modułu zachowawczego (*E*', rys. 1), tangensa kąta stratności (tgδ, rys. 2) oraz modułu stratności (*E*'', rys. 3). Na tej podstawie wyodrębniono trzy obszary relaksacyjne (α, β, γ) określając ich przedziały temperaturowe (tabele 2, 3, 4); w odniesieniu do nakładających się obszarów relaksacji α i β zastosowano przy tym zaproponowaną przez Charleswortha metodę dekonwolucji wraz z równaniem Fuossa-Kirkwooda (rys. 4). Ustalono, że zmiany spowodowane starzeniem uwidaczniają się najbardziej w obszarze relaksacji β. Najodporniejsze na starzenie są mieszaniny zawierające 50 % PE-LD.

Słowa kluczowe: mieszaniny PE-LD/PE-LLD, fotooksydacja, dynamiczne właściwości mechaniczne, procesy relaksacyjne.

Blends of polyethylenes with different branching degrees are commonly used in order to adjust the properties of these polymers, such as their modulus and toughness, or to improve their melt properties during processing. However, the miscibility or immiscibility of the components might affect the mechanical properties as a result of their weak interfacial adhesion, which may even induce severe degradation and reduce the service life [1, 2].

Blends of low density polyethylene (PE-LD) with linear low density polyethylene (PE-LLD) and pure polyolefins were blown as films for agricultural applications. A common drawback of these blends is their tendency to oxidize when they are exposed to ultraviolet (UV) radiation.

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Understanding how the mechanical behavior could be affected by the oxidation of the blends under natural conditions may provide useful information to researchers and producers for the prediction of the service life of these polymers.

In this paper, stabilized films of blends of PE-LD with PE-LLD and of these two pure polyolefins were submitted to photodegradation under natural weathering conditions during two years. Photodegradation involves oxidation of the polymer chain, produces chain scission and modifies the mechanical properties of these blends. These changes were monitored in this work by dynamic mechanical thermal spectroscopy and related to the PE-LLD content in the blends.

EXPERIMENTAL

Materials and samples preparation

The blends were prepared from two commercial polyethylenes:

— Low density polyethylene (PE-LD) Escoren 182BA (Exxon Chemical) with MFR = 0.8 g/10 min and density = 0.919 g/cm^3.

— Copolymers of ethylene-*co*-octene (PE-LLD) Dowlex NG 5056E (Dow Chemical, Tarragona) with MFR = 1.1 g/10 min and density = 0.920 g/cm^3.

Since polyolefins cannot be used outdoors without the addition of suitable stabilizers, a high Hindered Amine Light Stabilizer (HALS), which commercial label is Chimasorb-119 (Ciba-Geigy), has been added in a weight ratio of 1/1000.

Films of 200 μm thickness were processed using a flat die extrusion unit with L/D = 25 (Dr Collin GmbH extruder). Films of pure PE-LLD and PE-LD as well as of PE-LLD/PE-LD blends with 15 %, 32 %, 50 %, 68 % or 85 % PE-LD weight content were prepared.

Weathering test

A natural weathering test was carried out during two years at Aimplas (Paterna, Spain, 39°33′ North). Samples were mounted on a special aluminum panel, facing southwards with an angle of 45° to the normal, at 50 cm from the ground and free from shadows. The films were subjected to natural weathering conditions during one and two years. Global horizontal sunlight, inclined UV-radiation, wind horizontal speed and direction, temperature, moisture and rain were measured near the exposure panel during the test [3]. Table 1 shows a short summary of the weathering condition during the exposure time.

Table 1. Climatic data of Aimplas station (Metereológica Aimplas)*)

Month	TM, °C	TM_{max}, °C	TM_{min}, °C	Energy MJ/m^2
First year				
July	26	31	18	803
August	**)	**)	**)	**)
September	20	27	13	438
October	19	26	14	365
November	16	23	10	280
December	14	19	9	150
January	13	18	8	232
February	14	17	5	339
March	12	19	7	454
April	16	21	10	580
May	18	24	13	697
June	21	27	14	601
Second year				
July	25	31	18	614
August	26	30	18	633
September	22	27	12	459
October	19	26	13	398
November	**)	**)	**)	**)
December	**)	**)	**)	**)
January	12	16	8	178
February	11	18	7	352
March	**)	**)	**)	523
April	16	21	10	596
May	20	25	14	681
June	24	29	17	710

*) TM — monthly average temperature; TM_{max} — monthly average temperature of daily maximums; TM_{min} — monthly average temperature of the minimums; Energy — received total incident energy.

**) No data from this period (calibration and/or repair of the equipment).

DMTA measurements

The degradation process of polyethylene blends can also be studied by means of the characterization of their mechanical behavior. For this purpose, the complete relaxation spectra of all the samples have been obtained. The viscoelastic properties were determined by means of Mark II Dynamic-Mechanical-Thermal Analyzer (DMTA) from Polymer Laboratories. Deformation was applied in the cantilever double-clamping bending mode. The storage modulus (E') and the loss tangent (tanδ) were measured from -80 °C to 120 °C, at five different frequencies: 0.3, 1, 3, 10 and 30 Hz, with a heating rate of 1 °C/min.

RESULTS AND DISCUSSION

Figures 1 and 2 show as examples, the relaxation spectra of 85 % PE-LD blend, in terms of the storage modulus (E') and the loss tangent (tanδ), respectively, as a function of temperature, for different weathering periods. Similar spectra have been obtained for pure PE-LLD, pure PE-LD and the other blends. All these spectra display three clearly distinguishable relaxation zones, denoted α, β and γ in order of decreasing tem-

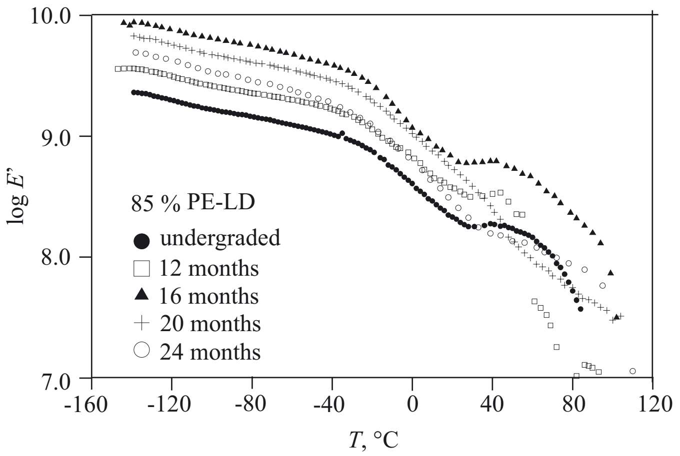

Fig. 1. Storage modulus (E') of 85 % PE-LD blend at 1 Hz of frequency after different exposure time

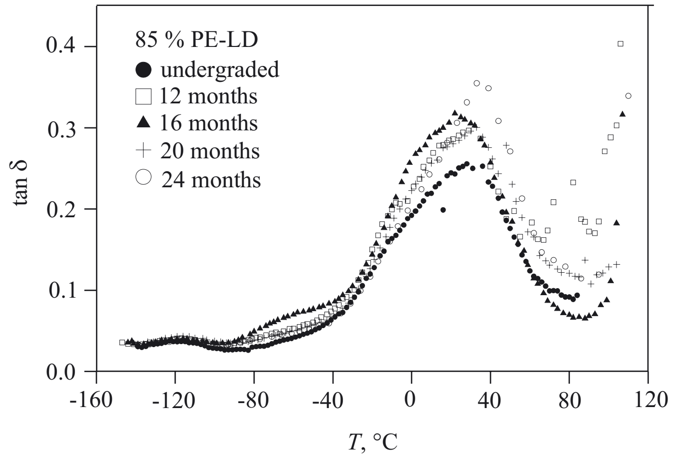

Fig. 2. Loss (tanδ) of 85 % PE-LD blend at 1 Hz of frequency after different exposure time

perature, in accordance with those referred by other authors [4—8].

The storage modulus of all the samples initially increases with the exposure time. However, the maximum value of the storage modulus is reached at different weathering times, depending on the blend composition. For 85 % PE-LD and 32 % PE-LD blends, the maximum storage modulus is observed after a weathering period of 16 months. For 65 % PE-LD and 15 % PE-LD blends, the maximum storage modulus is reached after 20 months. Only for the 50 % PE-LD blend, *E'* value is still increasing after 24 months of exposure time.

In a second stage, the storage modulus tends to decrease, although its values remain higher than that of the original blend. This suggests that the material becomes more brittle, as a result of the degradation process.

The mechanical spectra of all the samples in terms of the loss tangent (tanδ) show a prominent and asymmetric peak related to the α relaxation process. The shape of this peak reveals that it results from more than one single relaxation.

Other authors as well as ourselves have associated the α relaxation to motions of the chain folds at the crystal surface. These motions require some mobility of the crystals, and are hence related to the crystallite thickness distribution [6—8]. It has been shown in a previous work that degradation modified the crystallite thickness distribution of these blends [2, 3]. Mechanical results reveal the changes in the maximum temperature of the α relaxation that can be related to this morphological behavior, since this maximum increases as the thickness distribution increases.

On the other hand, the β and γ relaxation processes appear as small peaks in tanδ versus *T* spectra. Consequently, their evolution with the exposure time can only be slightly detected by means of these curves.

However, in the mechanical spectrum in terms of the loss modulus (*E''*, Fig. 3), the β relaxation is a well-defined absorption process, being the most significant relaxation. The α relaxation appears now as a small shoulder overlapped with β relaxation. A marked decrease in its intensity at temperatures near to the melting can be observed.

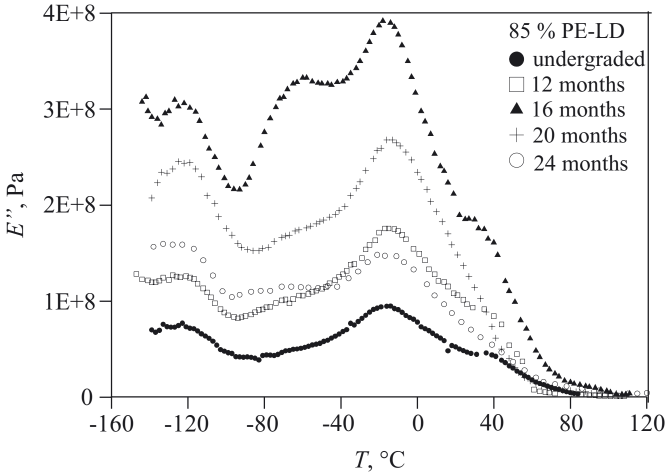

Fig. 3. Loss modulus (E'') of 85 % PE-LD blend at 1 Hz of frequency after different exposure time

Since the β and α relaxations appear as several overlapped relaxations, their characterizations were carried out using the deconvolution method proposed by Charlesworth together with Fuoss-Kirkwood equation [9, 10]. This method considers that the experimental measured values of *E''* are equal to the sum of each of the overlapped relaxations ($E'' = E''_{\beta} + E''_{\alpha}$):

$$E'' = \frac{\left(E''_{\max}\right)_1}{\cosh m_1 \frac{E_a}{R}\cdot\left(\frac{1}{T_1}-\frac{1}{T_0}\right)} + \ldots + \frac{\left(E''_{\max}\right)_n}{\cosh m_n \frac{E_a}{R}\cdot\left(\frac{1}{T_n}-\frac{1}{T_0}\right)} \tag{1}$$

Thus, by fitting the experimental data to the Fuoss-Kirkwood equation, the maximum of the loss modulus

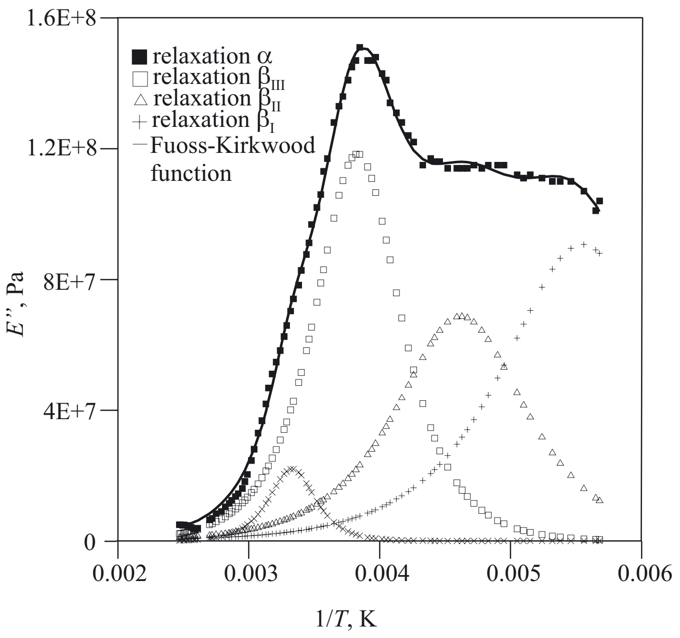

Fig. 4. Deconvolution applied to α and β relaxations

E''_{max}, the temperature of the maximum of the loss modulus T_{max} and the term (m_{FK} E_a/R) have been obtained for each relaxation.

Figure 4 shows an example of deconvolution of the α and β relaxations. This method was also applied to characterize the γ relaxation. Tables 2, 3 and 4 display the temperature of the maximum of the loss modulus (T_{max}) for each relaxation, as a function of the exposure time (0, 16 and 24 months, respectively) in relation to all the blends, differing in compositions.

Table 2. Characterization of the relaxation spectra at 1 Hz of the undegraded samples

Sample	Temperature of the maximum of the loss modulus, T_{max}, K		
	γ relaxation	β relaxation	α relaxation
PE-LLD	150.8	210.0/253.9	293.3/322.1
15 % PE-LD	157.0	254.8	318.7
32 % PE-LD	148.2	197.2/255.8	291.3/321.5
50 % PE-LD	152.7	201.6/258.6	294.4
68 % PE-LD	150.6	216.3/254.7	309.2
85 % PE-LD	146.9	201.4/256.2	312.8
PE-LD	144.6	252.2	319.4

The results show that the position of γ relaxation slightly changes as a result of the weathering. Since this relaxation has been attributed to molecular motions involving three to four methylene groups in the amorphous phase [4], it could be concluded that the degradation process affected the amorphous phase only in a small extent. However, α and β relaxations are more affected by weathering. Particularly, β relaxation that is related to motions in the amorphous-crystalline interface [5—7], is the most sensitive to this degradation process. In β relaxation zone, a new relaxation was detected around 190—180 K, which was modified as a function of the weathering time, and finally even disappeared. It is observed that all the samples exhibit the same evolution, but at different time scales.

Table 3. Characterization of the relaxation spectra at 1 Hz of the samples after a weathering period of 16 months

Sample	Temperature of the maximum of the loss modulus (T_{max}), K		
	γ relaxation	β relaxation	α relaxation
PE-LLD	156.0	193.0/229.3/264.8	314.8
15 % PE-LD	154.6	203.0/262.8	313.8
32 % PE-LD	145.3	194.8/240.6/272.9	320.6
50 % PE-LD	148.4	206.1/261.3	306.9
68 % PE-LD	152.7	208.1/256.1	314.0
85 % PE-LD	148.0	180.4/216.7/261.0	300.4
PE-LD	145.0	200.0/262.6	312.7

Table 4. Characterization of the relaxation spectra at 1 Hz of the samples after a weathering period of 24 months

Sample	Temperature of the maximum of the loss modulus, T_{max}, K		
	γ relaxation	β relaxation	α relaxation
PE-LLD	147.7	203.2/261.0	344.9
15 % PE-LD	161.8	206.2/263.0	306.4
32 % PE-LD	154.5	262.0	303.3
50 % PE-LD	149.0	205.4/265.5	305.3
68 % PE-LD	145.8	200.1/258.1	285.2/314.6
85 % PE-LD	148.2	180.3/216.4/260.9	300.3
PE-LD	144.6	195.3/261.6	322.0

After a weathering period of 16 months, the degradation of the interfacial region is already initiated in 32 % PE-LD blends as the table 3 displays. In contrast to 50 % PE-LD blend, the results in the Tables 3 and 4 show that the new β relaxation around 195—180 K was not detected after 24 months of exposure. These results, together with the other ones in [3], allow to suppose that 50 % PE-LD blends are the most resistant to weathering.

These results also suggest chain scissions takes place initially in the amorphous zone [2], the morphological changes are mainly produced in the crystalline-amorphous interface.

CONCLUSIONS

Weathering modifies the chemical structures of PE-LLD/PE-LD blends, and as results the degradation process takes place in a different time scale, dependently on the blend composition.

The degradation process leads to more brittle films, as it can be deduced from the increase in storage modulus as a function of exposure time. However, the maximum values of E' are reached at different weathering times, dependently on the blend composition.

The analysis of the relaxation spectra show that although in the initial stages chains scission occurs in the amorphous zone, this only causes slight changes in the γ relaxation [while the most affected by weathering is β-relaxation zones].

A new β relaxation was detected in the 180—195 K range, which was modified as a function of the exposure time, and finally even disappeared. All the samples exhibit the same evolution, but at different time scales. After a weathering period of two years, the degradation of the interfacial region has already been initiated. Probably, chain scission leads to changes in the amorphous-crystalline interface and recrystallization of the polymer that modifies this relaxation.

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