Anisotropic Character and Ultrasonic Stiffness Changes During the Natural Weathering of LDPE Films

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ABSTRACT: Blown extruded polyethylene films without stabilizers have been exposed outdoors under severe weathering conditions in the Sahara. The chemical aspect of aging has been followed by IR spectroscopy. The mechanical aspect of aging has been monitored by means of a nondestructive method. It consists of measuring velocities and attenuations of ultrasonic waves propagating in several directions in the film plane. Stiffness constants and energy dissipation terms have been calculated. From the results obtained it is shown that stiffening of the material leads to an increase of velocities and a decrease of wave attenuation. Moreover, the stiffness constants as well as the energy dissipation terms vary with aging and show a changing anisotropic character of the films. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 559–564, 2003

Key words: aging; films; polyethylene (PE); ultrasonics; viscoelastic properties

INTRODUCTION

Blown extruded polyethylene films used for greenhouse coverings experience a rapid degradation when exposed outdoors. An extended exposure time leads to a drastic decrease in mechanical strength.[1,2]

The aim of this work is to study the dynamic mechanical properties evolution and the change in the anisotropic character of naturally weathered LDPE films in the process relating two different experimental approaches: physico-chemical and mechanical.

Being a semicrystalline material, polyethylene is constituted by two solid phases: one is amorphous and the second is crystalline.[3] On a microscopic scale, the only chemical reactions able to affect the mechanical properties are oxidation, crosslinking, and chain scissions. These reactions occur mainly in the amorphous phase of the material. Crosslinkings cause LDPE to become a three-dimensional polymer. However, crosslinkings do not extend a long time and take place only at the beginning of the exposure. The characteristic effects of crosslinking on mechanical properties disappear after a short time corresponding to vinylidene consumption.[4,5]

In addition, since polyethylene is a polymer comprised of saturated units, it is considered that aging leads mainly to chain scissions, with crosslinkings playing only a secondary role in the degradation.[5] Consequently the chain scissions lower the average molecular weight, and moreover the molecular weight distribution is also modified and the polydispersity ratio decreases with exposure time.[6]

The increase in concentration of low molecular weight chains can affect the mechanical resistance and leads to a drastic modification of the mechanical properties even for a very slight average molecular weight change.[5,7] The increase in crystallinity during photooxidation is caused by the diffusion of short chain segments to crystallites. This morphological change can lead to micro-crack formation, and lowering of the mechanical properties at the breaking point.[5]

Concerning the mechanical characterization, it is conducted by means of a nondestructive dynamic method based on ultrasonic (US) wave propagation in the material. The US technique involves material deformation at a high strain rate of $10^3\ s^{-1}$ but at very low deformation magnitude.

Ultrasound has in the past been used for the characterization of the dynamical properties of oriented polymers,[8,9] and low frequency oscillation methods have been applied to polyethylene,[10–12] but seldom have either of these techniques been applied to polymers weathered under severe conditions.[13]

This article points out that the material response to such excitations makes the calculation of the elastic and the dissipative parts of the dynamic properties in tension and shear deformations modes possible. The latter properties are quite difficult to obtain under traditional uni-axial tensile test.

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EXPERIMENTAL PROCEDURES

Material, samples preparation, and weathering procedure

A low-density polyethylene (B24/2, ENIP Skikda, Algeria) without stabilizer was used for the production of blown extruded films for greenhouses covering. The drawing speed of the production process was fixed at 9 m/mn, the bubble diameter was 4.4 m, and the wall thickness was about 180 μm. It is known that the films produced by the blow extrusion process are subjected to molecular orientation.[14] Consequently the properties in the extrusion direction depend on the draw down ratio (DDR) and those of the transverse direction to the blow up ratio (BUR).

The films were mounted on a wooden panel, facing the south and inclined at 45° (NF T51-165) and exposed to sunlight for periods of up to 8 months, from October 1999 to June 2000, at Laghouat, Algeria (38° 48′ N). A sampling was done approximately bimonthly (0, 2, 3, 4, 6, and 8th month).

IR spectroscopy

The spectroscopic analysis was performed for each sample on a Fourier transform infrared apparatus (FTIR) (Nicolet 210) and the optical density (OD) of the chemical species was determined from the corresponding absorption spectrum.

Nondestructive evaluation

This section concerns the nondestructive evaluation of dynamical properties of the polyethylene films. The theory concerned with the US wave propagation and the experimental device adapted to this purpose are dealt with below.

Assumptions and theory

Because the films studied are 180 μm thick and LDPE is well known to be a viscoelastic medium, the thin plate assumptions are valid.[15] However, in order to render this technique applicable to a large variety of materials, we assume the material mechanical behavior to be orthotropic and viscoelastic. In this case, the intrinsic stiffness matrix has nine independent complex components $c_{ij} = c'_{ij} + i\, c''_{ij}$ ($i^2 = -1$) under harmonic excitation. Their real parts c'_{ij} are related to the material elastic character, their imaginary parts c''_{ij} represent dissipative effects.[16]

It has been shown that the technique described here[15] allows principally the calculation of four equivalent stiffness constants.[17] Two of them, a_{11} and a_{22}, correspond mainly to the propagation of US plane waves along the anisotropic principal axes. The third one, a_{12}, represents a coupling effect applicable to propagation between the x_1 and the x_2 axes and a_{66} is associated with the shear deformation mode.

The "rigidities" called a_{ij} are the following nonlinear combinations of the complex elastic stiffness c_{ij} (eq.1):

$$a_{11} = c_{11} - \frac{c_{13}^2}{c_{33}} \qquad a_{22} = c_{22} - \frac{c_{23}^2}{c_{33}} \qquad a_{12} = c_{12} - \frac{c_{13}c_{23}}{c_{33}} \qquad a_{66} = c_{66} \quad (1)$$

Experimental set-up

The experimental set-up developed for the thin polymeric film characterization is based on the generation of low frequency quasi-plane waves. These waves are transmitted and received by means of two sets of contact piezoelectric transducers, which are arranged differently for each mode. Each transducer has an 80 kHz central frequency and a 42 mm^2 effective area. The working surface of each individual transducer generates a quasi-unidirectional displacement on the upper side of the plate. Therefore there are no displacement conditions other than those imposed by the emitting transducers.

One test performed on the acoustical experimental set-up allowed recording a series of waveforms corresponding to varied propagation distances (d_{S0} and d_{SH0}) and 25 directions varying with a 15° angular step (Fig. 1) for each mode.

The signal analysis consists of performing the correlation of waveforms acquired for 6 different propagation distances, 25 different directions, and 2 propagation modes. Then, the corresponding velocities C and the spectral amplitude ratios R are calculated.[15,17] This allows for reducing the terms A related to the wave attenuations (k''). Finally, the a_{ij} were obtained by numeric optimization using the k'' values.

The average velocity of all the samples measured in the direction ($\theta = 0$) for the QS_0 mode is about 1.2 km/s and 0.6 km/s for the QSH_0 mode. The attenuation values obtained for the same direction and the same modes are about 6.7 m^{-1} and 9.3 m^{-1}, respectively. These are in good agreement with the literature.[15]

PHOTOCHEMICAL ASPECT OF WEATHERING

The exposure of the PE films to UV light leads to rapid oxidation. The carbonyls (1720 cm^{-1}), which are absent from the IR spectrum of the unexposed material, appear and increase rapidly after a few weeks (Fig. 2). This effect is followed by the growth of the absorption band at 910 cm^{-1} of the vinyl groups ($CH_2{=}CH{-}R$), the concentration of which increases progressively with the exposure time. These terminal

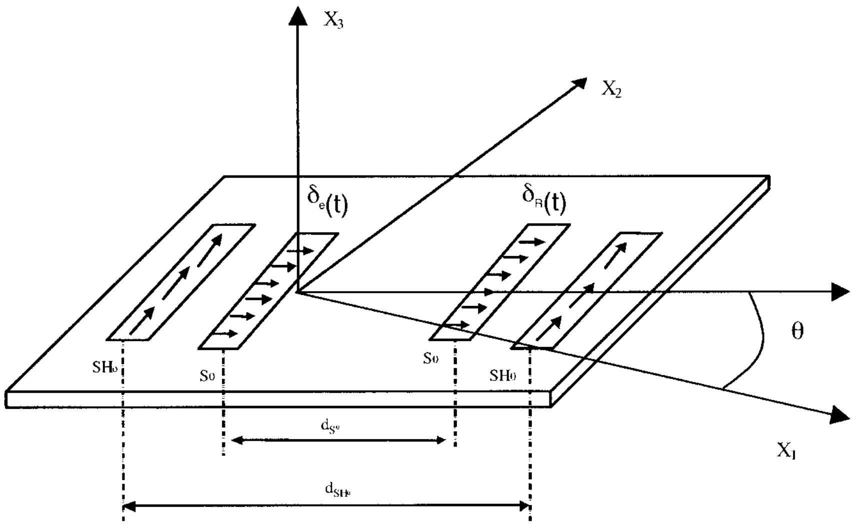

Figure 1 Transmission modes of S_0 and SH_0 waves between emitting and receiving transducers.

groups come mainly from the photolysis of carbonyls via the well-known Norrish type II reaction.[5,18]

Vinylidene, (R—R′—CH═CH$_2$) at 888 cm^{-1}, present in the starting sample decreases progressively with the exposure time. The consumption of this chemical species is due to its reaction with alkyl radicals (RH°) leading to crosslinking. This restricts the chain segments mobility between entanglements.[4]

Because crosslinking is predominant in the beginning of the exposure, it follows that for a longer exposure time the chain scissions become more important. However, the scissions are expected to play a significant role in weakening the sample because they modify the molecular weight distribution (MWD) and the polydispersity ratio ($P = Mw/Mn$) decreases with the exposure time.[6]

Consequently, as said before, the increase of the low molecular weight chain concentration is known to lead to a drastic loss of the quasi-static material mechanical strength.[5,7,18] In the two following sections we describe the mechanical phenomena accompanying the chemical changes using an US characterization.

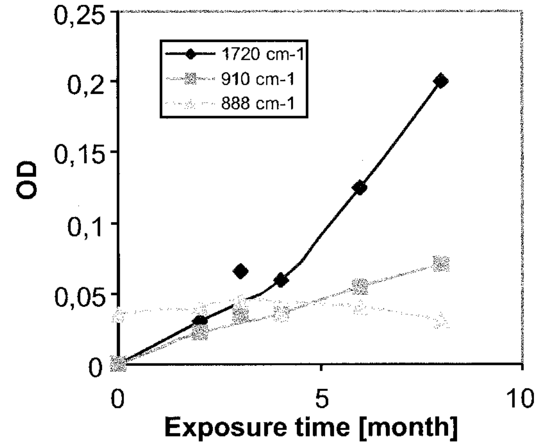

Figure 2 Optical density (OD) of carbonyls (1720 cm^{-1}), vinyls (910 cm^{-1}), and vinylidenes (888 cm^{-1}) versus exposure time.

EFFECT OF WEATHERING ON THE PROPAGATION OF US WAVES IN LDPE SAMPLES

This section presents the waveforms related to each propagation mode S_0 and SH_0 measured in ($\theta = 0$) direction. The signals are represented in a temporal window with an arbitrary origin (Fig. 3). The two waveforms have a different shape according to the generated mode. Their correlation allows the calculation of the wave phase velocities and their associated attenuations for each mode.

Aging effect on acoustic wave velocities

Velocity measurements on the propagation modes QS_0 and QSH_0 for three aging stages and for each chosen direction of the film plane have been performed (Figs. 4 and 5). The polar representations for each propagation mode show a weak anisotropic distribution and an increasing phase velocity with exposure time.

The average velocity of the QS_0 mode in the starting sample is equal to 1.21 km/s and becomes 1.26 km/s at the last stage of aging. For the QSH_0 mode, the starting velocity is equal to 0.59 km/s and reaches 0.65 km/s at the end of the exposition.

Aging effect on damping

The attenuation term, corresponding to the imaginary part of the wave vector (see EXPERIMENTAL sec-

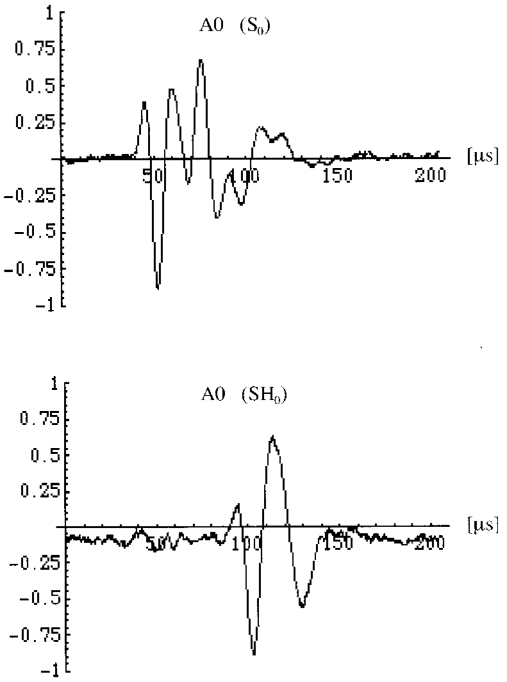

Figure 3 Waveforms with reference to the quasi-longitudinal QS_0 and the quasi-shear QSH_0 modes for unexposed polyethylene (θ= 0°, d = 121 mm, arbitrary time origins).

tion), gives a good insight into the energy dissipation associated with the material viscosity character.

In Figures 6 and 7 the modulus of the attenuation vectors of the two propagation modes are reported for three aging stages. As with the phase velocities, they show an anisotropic distribution. The change in this modulus is neither monotone nor isotropic when successively considering each aging stage. However, for the two propagation modes, the attenuation vector modulus decreases on the whole, with exposure total time in each direction of the film plane. In addition, the US wave attenuation is known to decrease with the material stiffening.[11]

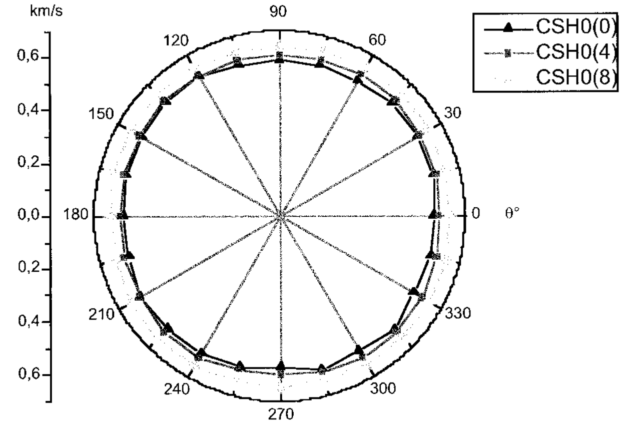

Figure 4 Phase velocities measured in the QS_0 mode, for three aging stages (0, 4, and 8 months), of LDPE films.

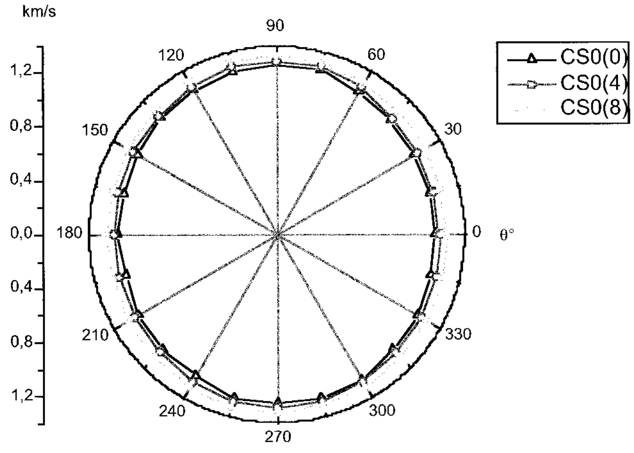

Figure 5 Phase velocities measured in the QSH_0 mode, for three aging stages (0, 4, and 8 months), of LDPE films.

The optimization performed with the 150 sets of measurements (C_n and A_n) leads to the equivalent stiffness a_{ij}, where a'_{ij} is the elastic component and a''_{ij} refers to the viscous character of material.

ACOUSTIC STIFFNESS CONSTANT CHANGE WITH AGING

The variations of the four stiffness constants a'_{11}, a'_{22}, $a'_{12,}$ and a'_{66} versus exposure time are reported in Figure 8. The stiffness constants a'_{11} and a'_{22} are relative to the wave propagation along the principal axes of the film plane, which corresponds to the longitudinal and the transverse direction, respectively. In the figure, it can be observed that the stiffness constant a'_{11} is lower than a'_{22}. One also notes that the rate of increase of the stiffness constants varies into three different stages. During the first stage, the increase is small, about 1.3% for a'_{11} and −0.17% in the case of a'_{22}. In the second stage between the second and the fourth months the increase is larger, 7.0% for a'_{11} and 6.7% for a'_{22}. Then,

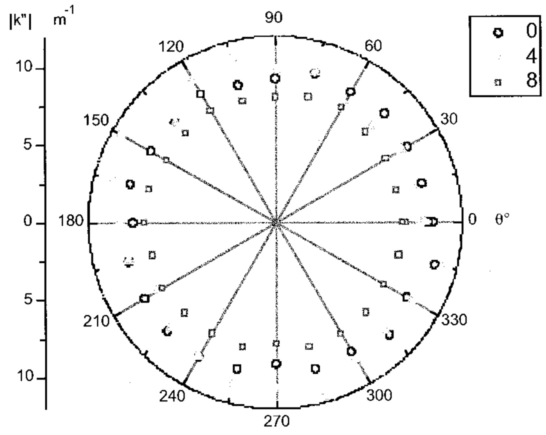

Figure 6 Modulus of the attenuation vector for three aging stages (0, 4, and 8 months), QS_0 mode.

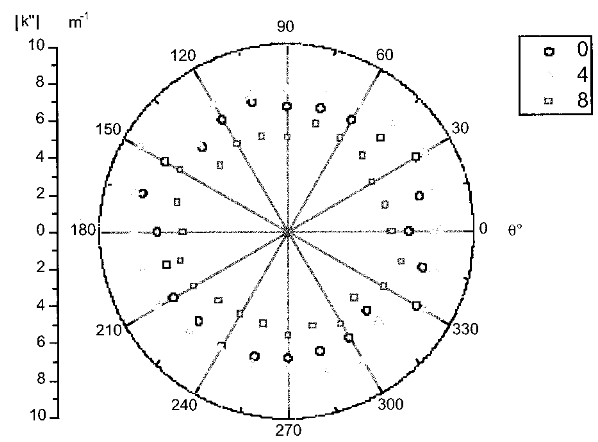

Figure 7 Modulus of the attenuation vector for three aging stages (0, 4, and 8 months), QSH_0 mode.

in the last stage, the rate of increase slows down but remains perceptible, 4.1% and 2.1%, respectively.

The US wave propagation is sensitive to the material anisotropy. The stiffness constant values show that the principal axis of anisotropy is the one corresponding to the transverse direction ($a'_{11} < a'_{22}$). The term a'_{12}, which is the coupling factor between the principal axes, does not undergo marked change during aging. The in plane shear stiffness constant a'_{66} (difficult to determine in a tensile test), increases progressively by about 18% during the exposure time.

The plotting (Fig. 9) of the dissipation energy terms a''_{11}, a''_{22}, a''_{12}, and a''_{66} versus the exposure time reveals the variation of the damping character of the material. We note that the analysis of the a''_{ij} and its relation to the energy dissipation in a viscoelastic medium versus exposure time is not a simple task since a''_{ij} are not linearly dependant of a'_{ij}.[15,17,19]

The a''_{22} term is higher than the a''_{11} term throughout the treatment. The coupling factor a''_{12} is lower than the two first terms but follows the same variation. As for the stiffness constants a'_{ii}, it is also possible to find an inelastic shear term a''_{66}. that does not undergo a noticeable change during the aging.

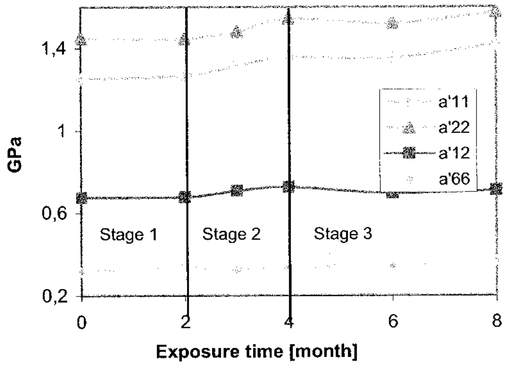

Figure 8 Stiffness constants a'_{ij} versus exposure time.

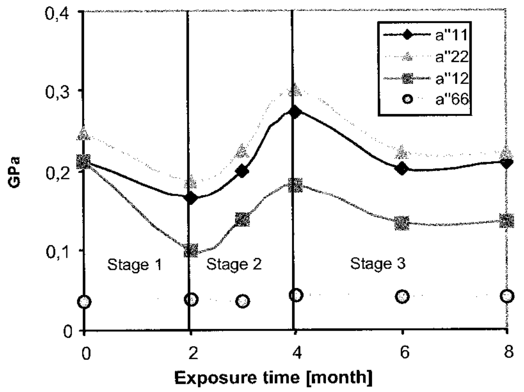

Figure 9 Dissipation energy terms a''_{ij} versus exposure time.

The results presented above strongly suggest that a LDPE global stiffening occurs and the anisotropic character of the films is maintained during all the aging process, whereas the principal axis of anisotropy changes from the machine to the transverse direction.

DISCUSSION

Natural weathering of LDPE films under severe weathering conditions induces structural modifications, which affect their dynamic mechanical behavior.

As a matter of fact, the chemical process of aging is dominated by an oxidative-type reaction, and as it proceeds, competing reactions of chain scission and crosslinking take place. The crosslinking reactions, shown by vinylidenes consumption, are predominant at the beginning of exposure. Afterwards chain scission reactions (viewed by the build-up of vinyl groups) become predominant and occur close to carbonyl groups via the well-known Norrish type II reaction. The chain scissions affect the molecular weight distribution and lower the polydispersity ratio. This is accompanied by an increase of crystalline concentration. As a consequence, the mechanical properties measured by the acoustic method are sensitive to the anisotropic character of the films and to the photochemical governed morphological transformations.

It follows that the anisotropic behavior of the films is probably due to chain orientation during the processing, which is more important in the transverse direction. This anisotropic character estimated by the ratio (a'_{22}/a'_{11}) remains always greater to one and varies with aging (Fig. 8).

The mechanical properties were found to vary in three different stages, which could be linked to specific chemical reactions. Concerning the first one, the a'_{ij} stiffness constants increase coincides with the predominant crosslinking reactions in the beginning. At the same time a significant drop of the energy dissipation terms occurs.

The observed drastic increase of the stiffness constants might be connected to chain scissions. In this second stage they become more important and cause a global crystallinity concentration increase via a chemocrystallization process. This is accompanied by the increase of the energy dissipation terms.

In the third advanced aging stage, a variety of oxidation products such as acids, esters, peresters, peracids, and so on, appears. In spite of the stiffness constants continue to increase slightly while the energy dissipation terms decrease in a first step, then stabilize. The explanation could relate to the well-known complexity of the accompanying oxidation process, which involves an indistinguishable competition between crosslinking and chain scission reactions.[4,5]

CONCLUSION

The change undergone by the molecular structure (oxidation, crosslinking, and chain scissions) of naturally weathered LDPE in the Sahara modifies the morphological structure of polymer. The US technique, which is a nondestructive method, allows following the effect of this modifications by measuring the velocities and the attenuations of waves propagating through the material.

Unlike tensile testing, this technique allows for the measurement of four local stiffness constants and four energy dissipation terms. These are sensitive with aging to the global stiffening and give good insight into the anisotropy ratio changes. At an advanced stage of aging, it can be difficult to clearly relate the stiffness evolution and the structural modifications, although this technique still shows an increase in stiffening.

The sensitivity of this dynamic method to the anisotropic character of films is due to the fact that US waves travel by molecular interaction, making it sensitive to minute changes in the material structure, even for very degraded films, because it is intrinsically a measurement method generating very small mechanical perturbations.

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