Ageing effects on the creep-recovery behavior of blown extruded low density polyethylene film

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ABSTRACT: Low density polyethylene films used for greenhouse covering were naturally weathered for 6 months in sub-Saharan region (Algeria). The microstructural and morphological changes have been checked by infrared spectroscopy. The changes of the mechanical properties have been followed by tensile and creep-recovery tests. The measurements were carried out in the two main directions of the film plane. Besides oxidation, chain scission and crosslinking are competing during all the ageing protocol, affecting thereby, the mechanical properties as well as the viscoelastic behavior revealed by creep-recovery curves. The anisotropic character of the film is preserved during ageing. The improvement of the creep resistance via crosslinking in both directions, affects the different deformations. The short chain segments coming from chain scissions increase the crystallinity ratio (via a chemo-crystallization process) lowering by consequence each of the minimum strain rate ($\dot{\varepsilon}_{min}$), the instantaneous (ε_a), and delayed recoveries (ε_b and ε_c) as well. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 44209.

INTRODUCTION

This article aims to investigate the degradation induced by weather ageing of a commercial grade low density polyethylene film (LDPE) used for greenhouse covering in the agricultural industry. LDPE as raw material offers many advantages for the plastic industry, because of its relative low cost, ease of processing, and many practical applications. One of its more popular applications is for greenhouse covering. Polyethylene film is subjected to a variety of environmental stresses such as: day/night temperature gradients, sun irradiation, wind strength variations, and mechanical creep since they are strongly hung and taut for long periods of time. This type of ageing leads to significant microstructural changes in LDPE films. Indeed, macromolecules are altered mainly by the oxidation process which results either in crosslinking or in chain scissions reactions as previously revealed by Fourier transform infrared spectroscopy analysis.[1,2] The development of a tridimensional macromolecular architecture involves an increase of the elastic modulus toward the two main film chains orientations, whereas chains reptation affects the semi-crystalline morphology leading to a sensitive increase of the crystallinity ratio via a chemo-

crystallization process. This provokes an important drop of the mechanical properties at break.[2]

Low density polyethylene is a semi-crystalline thermoplastic polyolefin which exhibits an important viscoelastic behavior well revealed by creep.

The creep behavior of polyethylene has extensively been studied in literature,[3–9] but the ageing effect on the viscoelastic behavior has never been pointed on yet. In thermoplastic polymers, the rate-controlling creep mechanism involves a cooperative motion of molecular chain segments with respect to each other. Indeed, ageing increases the crosslinking density between the molecular chains in the amorphous phase which increases in return the average molecular weight. As a result, a decrease of the extent and the rate of the creep strain are usually observed.[7] The effect of the branching density on the creep behavior is known to decrease the total creep strain for long-test time deformation while they increase the creep strain and the creep rate for the short-term creep.[5–7] It has also been shown that the creep rate is lowered by the methyl branch contents.[6] The creep behavior in polyethylene films is mainly controlled by the deformation of the amorphous phase, which is itself strongly affected by the

variation of the crystallinity and the tautness of the tie molecules.[8]

In the present work, blown extruded polyethylene films have been weathered in severe climatic conditions in sub-Saharan facility characterized by an average temperature of 7.8 °C in winter, 28.9 °C in summer (T_{max} = 45 °C), a precipitation of 176 mm, an average wind speed of 17.2 km/h, and sun radiation which can reach 1100 W/m². The changes undergone by the microstructure and their impact on the mechanical properties (i.e., elastic and properties at break) have been checked for each ageing stage by spectroscopic analysis and tensile test, respectively. These types of tests and the description of the relation between the structure and the properties have already been widely described elsewhere.[2,10]

However, many works dealing with the effect of structure and morphology on the creep behavior of polyethylene films can be found in literature but seldom on ageing effects. In this work the effects of ageing on the mechanical properties and on the creep behavior of a LDPE film tested in the two main directions of the plane are studied. The goal of this work is to apply a long-term mechanical deformation mode, much more sensitive than tensile to the elementary microstructural changes.

In this work the effects of ageing on the mechanical properties and on creep behavior in the two main directions of the LDPE film plane are studied by applying a long-term mechanical deformation mode, much more sensitive than tensile to the elementary microstructural changes.

Indeed, creep-recovery which is another aspect of creep provides additional information on the structural changes undergone by the films via their impact on the viscoelastic properties.

The testing of the films in the two main directions highlights their anisotropic character. This can be useful to select the appropriate direction to place the film on the greenhouse to ensure a greater creep resistance and a longer service lifetime.

EXPERIMENTAL

Material and Ageing Protocol
The LDPE used in this investigation is a commercial grade supplied by the Saudi Basic Industries Corporation (SABIC) as "LDPE 2100 T N00W," (ρ_s = 0.92 g/cm³, Melt Flow Index [MFI] = 0.33 g/10 min). This polymer is a neat grade exempt of any stabilizing agents. Films were produced by blowing extrusion at Sofiplast, an Algerian industry located at Sétif. The drawing speed of the production line was fixed to 15 cm/s. The melt was extruded at about 175 °C and blown in a continuous process characterized by a bubble diameter of 4.4 m and a wall thickness of 160 μm. The properties in the machine direction (MD) depend on the draw down ratio (DDR) and those in the transverse direction (TD) to the blow up ratio (BUR).[11]

The exposition took place in Laghouat, Algeria (33°48′N 2°52′E) from December to June. The films are exposed on a south oriented metal support and inclined by 33° relatively to the ground according to the NF51-165 standard. Sampling was done bi-monthly, from the film zones distant from the contact points with the holding frame. This precaution was taken to avoid uncontrolled overheating of the material. The maximum of 6 months of exposure corresponds to the time at which the film became too brittle to resist to the wind strength.

Fourier Transform Infrared Spectroscopy
FTIR spectroscopy was conducted on "Spectrum Two" maintained by Perkin Elmer to provide information of the functional groups present at the surface of the samples in the wavelength range 4000 to 400 cm⁻¹. Scans were run at a resolution of 4 cm⁻¹. The specific absorption peaks were analyzed from the FTIR-spectra delivered by the equipment. For each peak the "optical density" (OD) was determined following the usual definition as: OD = $\ln(I_0/I)$, were "I_0" is the reference infrared intensity corresponding to the baseline of the spectrum at the peak wave number and "I" is the minimum intensity at the base of the peak. The ATR-spectra obtained by analyzing the samples surfaces in contact with a Diamant crystal. Crystallinity of LDPE was determined using the method described by Zerbi et al.[12]

$$X(\%) = \left[1 - \left(\frac{1 - \frac{I_a}{I_b}}{1 + \frac{I_a}{I_b}} \right) \right] \times 100 \qquad (1)$$

where I_a and I_b are the peaks area of the characteristic bands intensity at 1474–1464 cm⁻¹ corresponding to the crystalline (1474 cm⁻¹) and the amorphous (1464 cm⁻¹) phases, respectively. The constant 1.233 is the relation between these two (1474 and 1464 cm⁻¹) for a completely crystalline polyethylene.[13,14]

Tensile Tests
The stress–strain curves for all the samples were obtained by using Roell Zwik machine at room temperature (T = 21 ± 1 °C) at a nearly constant relative humidity (RH = 50 ± 5%). The rectangular tensile test specimens were cut out of the original and the aged film with an overall length of L_0 = 70 mm, gauge length L_G = 40 mm, width W_0 = 10 mm, and thickness T_0 = 0.16 mm (Figure 1). The results of the tensile test are presented in term of true stress, $\sigma = F(1+\varepsilon)/A_0$, and true strain $\varepsilon(t) = \ln(L(t)/L_0)$. To optimize the duration of the test, the strain rate was fixed at a low value to the yield point ($d\varepsilon/dt$ = 8 × 10⁻⁴ s⁻¹) (determination of the Young modulus) and then stepped to a higher value ($d\varepsilon/dt$ = 8 × 10⁻² s⁻¹) for the rest of the test until fracture occurred. To check the anisotropic character of the film, the test pieces were cut and tested in the two main directions corresponding to the MD and TD.

Creep Experiments
The creep test has been performed on a creep tester developed in the laboratory with rectangular specimens cut out of the original and aged film. The geometry and the dimensions of the test pieces are described in Figure 2. All the tests were conducted at room temperature (T = 21 ± 1 °C, temperature very far above T_g = −110 °C). The creep tests were conducted by applying a constant load delivering an initial stress of 7.6 MPa (i.e., 1500 g) for duration of 8 h by specimen. The recovery starts immediately after the stress removal and for a period of 8 h as well. The load was chosen in an optimal way in order to develop a sufficient stress below the elastic limit initially
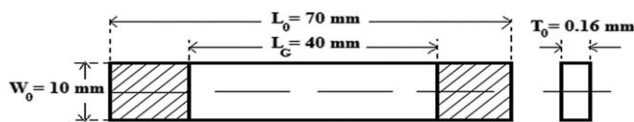
Figure 1. Tensile test specimen geometry.

measured by tensile test on the original film, knowing that aging affects mainly the amorphous phase. To perform the test, equidistant markers have been drawn on the sample surface, symmetrically distributed with respect to the middle of the specimen (d_0) and separated by 10 mm, respectively. This precaution has been taken to ensure a homogeneous deformation in the total effective length.

In order to optimize the recording of the markers displacement by a camera, the monitored section is delimited by an effective length of 6 cm (L_e). The camera lens is then centered with respect to the marker in the middle of the sample.

Photography is taken before starting the creep experiment (initial state). After loading, pictures were taken at regular time intervals. Then, they were processed by means of the Matlab software to determine the total and relative deformations.

The creep-recovery behavior of different grades of polyethylene has been extensively studied.[6,8,9,13] Figure 3 shows a typical creep-recovery curve of polyethylene. It provides a crude qualitative representation of the phenomena generally observed with viscoelastic materials where the following deformations can be defined: instantaneous elastic strain "ε_1," delayed elastic strain "ε_2," viscous flow "ε_3," instantaneous elastic recovery "ε_a," delayed elastic recovery "ε_b," and plastic deformation (permanent set) "ε_c." Under creep, the total strain is the sum of three components ($\varepsilon_1, \varepsilon_2, \varepsilon_3$), as shown in the following equation[15,16]:

$$\varepsilon(t) = \varepsilon_1 + \varepsilon_2 + \varepsilon_3 \qquad (2)$$

The elastic portion $E_e(t)$ is defined as:[8]

$$E_e(t) = [(\varepsilon_a + \varepsilon_b)/\varepsilon] \times 100\% \qquad (3)$$

To optimize the accuracy of the measurements for each creep-recovery curve, an average of five test pieces has been tested and this for all the different ageing stages. Also the curves represented in this work have been plotted with the average values. The standard deviation for each point around the average value never exceeds 5%.
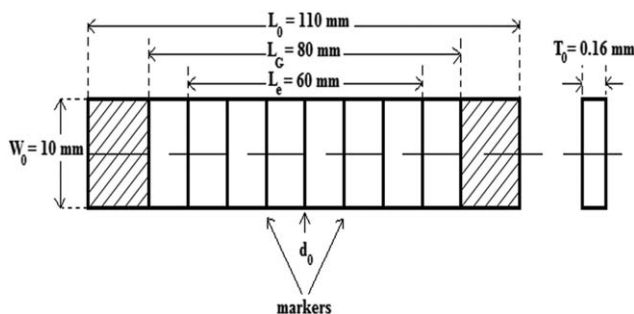

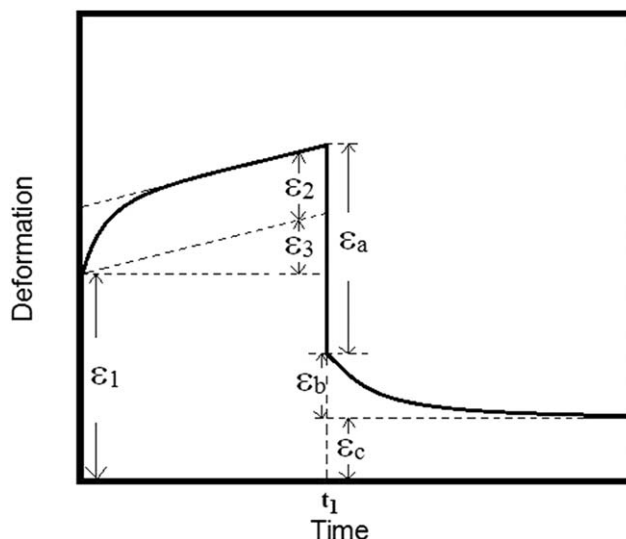**Figure 2.** Creep specimen geometry examined in this study.

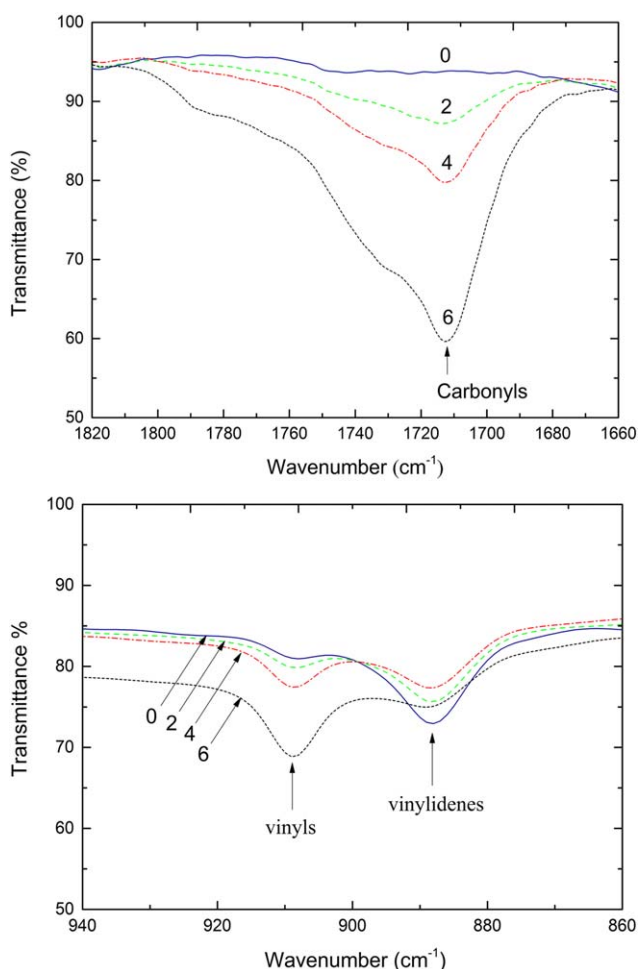**Figure 3.** Typical creep-recovery curve of PE.

Figure 4. (a) Infra-red transmission spectra recorded from the LDPE 2100 T N00W films for various ageing stages (0, 2, 4, and 6 months): carbonyl stretching region. (b) Infra-red transmission spectra recorded from the LDPE 2100 T N00W films for various ageing stages (0, 2, 4, and 6 months): unsaturations stretching region. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

RESULTS AND DISCUSSION

Infrared Analysis

Exposure of polyethylene film to solar irradiation leads to an irremediable modification of the microstructure. The comparison of the IR spectra of the film samples picked up at regular intervals of time shows that some regions of the spectrum change with ageing. The most affected ones are those of the hydroperoxides (3300–3600 cm^{-1}), the carbonyls (1680–1780 cm^{-1}), and the double bonds (880–1100 cm^{-1}). The carbonyls absorption band [Figure 4(a)] is certainly the most indicative of the extent of damages caused by oxidation to the macromolecular structure.

Its growing width and amplitude give a good insight on the relative concentration and the kind of the carbonyl species which develop through the ageing protocol.[16,17] Of course, a cursory observation of this complex absorption band at the latest ageing stage allows seeing that it points drastically at 1712 cm^{-1} and there are many shoulders on its left side. It contains a variety of carbonyl species; among them one can quote the carboxylic acids (1712 cm^{-1}), the ketones (1718 cm^{-1}), the esters (1730–1740 cm^{-1}),[18–20] the peresters (1763 cm^{-1}), the peracids (1785 cm^{-1}),[19,20] and the γ lactones (1788 cm^{-1}).[21,22]

Besides oxidation reactions, unsaturations also play a key role in the modification of the molecular structure affecting the mechanical response of the material under stress. During the first 2 months, it has been noticed a lowering of the vinylidenes (888 cm^{-1}) followed by an increase of the vinyl groups concentration (910 cm^{-1}) [Figure 4(b)]. Four months later, chain scission reactions which can be estimated, thanks to the vinyl groups (910 cm^{-1}) concentration since they appear subsequently to chain cleavage in the close vicinity of carbonyls via the well-known Norrish type II process, become predominant compared with crosslinking reactions. As a result, the average molecular weight of the material decreases that should affect strongly the mechanical properties of the materials.[2]

Ageing Effects on the Tensile Properties

The variations of the Young's modulus measured in the two main directions of the film (MD and TD) are reported in Figure 5. During the whole duration of the ageing protocol, the modulus in the TD remains always greater than the one in the MD. With ageing time, the modulus in both directions slightly increases, meaning a gradual stiffening of the material. This variation of the modulus can be ascribed to two main structural changes: (i) the crosslinking reactions which is prevalent during the first ageing stages (reaction of the vinylidenes with alkyl radicals) and (ii) the chain scission reactions which are responsible of the increase of the crystallinity ratio via a chemo-crystallization process predominant at the later stages of ageing.[17,23]

The variations of the stress (σ_b) and the elongation (ε_b) at break represented as a function of the ageing time in Figure 6(a,b), respectively, are characterized by: (i) an alike plateau during the first 4 months, (ii) followed by their drop until the end of the ageing protocol. The elongation at break in the TD remains always greater than in the MD. The opposite evolutions are observed concerning the stress at break. The behavior of the
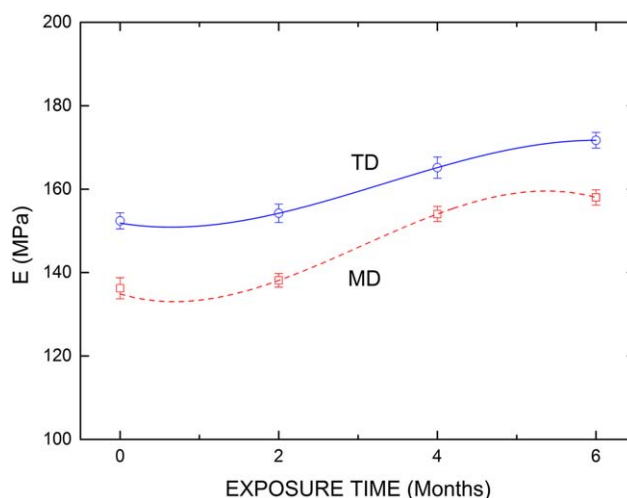

Figure 5. Variation of the Young's modulus. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
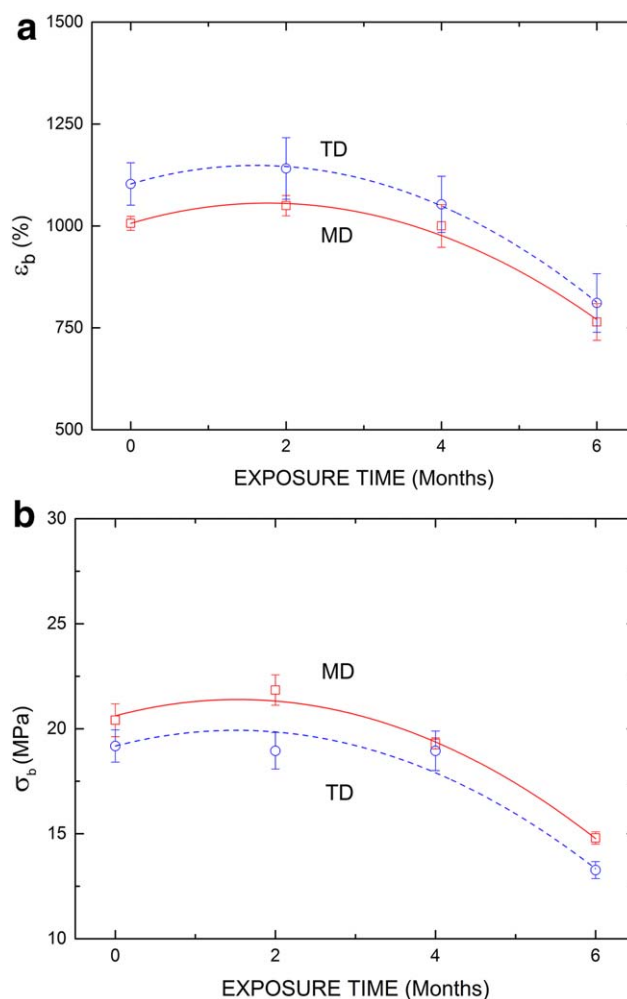

Figure 6. (a) Variations of the elongation at break. (b) Variations of the stress at break. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
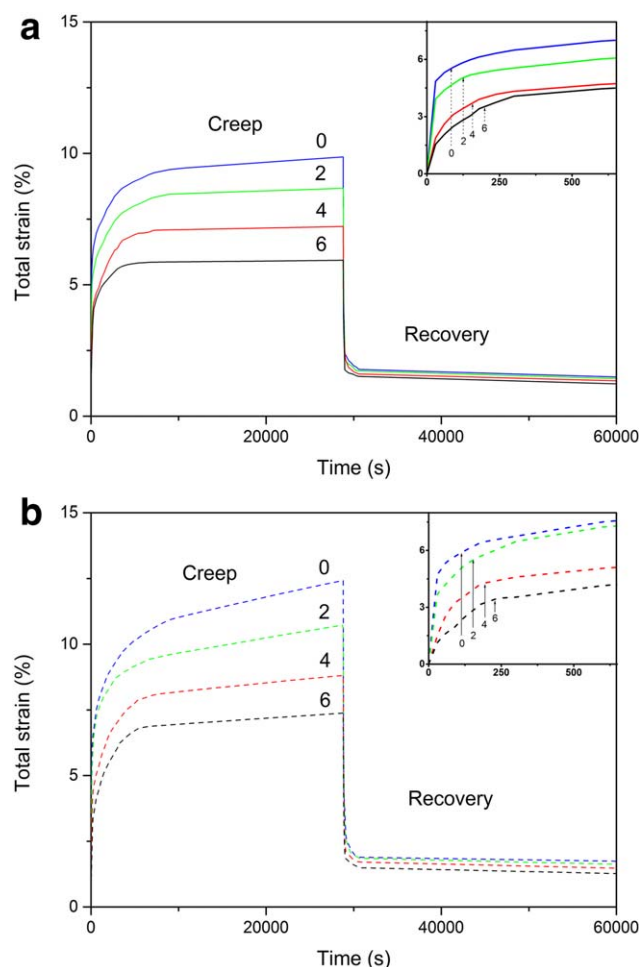
Figure 7. (a) Ageing effects on the creep-recovery behavior of the LDPE 2100 T N00W films for different exposure time (0, 2, 4, and 6 months) stretched along the machine direction (MD). (b) Ageing effects on the creep-recovery behavior of the LDPE 2100 T N00W films for different exposure time (0, 2, 4, and 6 months) stretched along the transverse direction (TD). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ultimate properties confirms the fact that crosslinking are predominant during the first four months of ageing, consolidating somehow the material mechanical properties. Afterward, the chain scissions become progressively predominant, thus significantly affecting the film toughness.

Ageing Effects on the Creep-Recovery Behavior

The creep-recovery curves for both directions of the LDPE films are represented as a function of ageing stages (0, 2, 4, and 6 months) in Figure 7(a,b). It can be noticed that whatever the stretching direction or the ageing time, samples do not show a tertiary creep regime which is consistent with typical LDPE creep-recovery behavior.[24]

An observation of the curves shape lets appear for both directions and all ageing stages, during the loading phase, that after the instantaneous strain "ε_1," the creep rate decreases progressively until it reaches a minimum value. This phase corresponds to the primary creep domain "ε_2." After that the creep rate

Table I. Ageing Effects on the Different Characteristic Strains Identified in the Creep Behavior Curves of LDPE Loaded in the Two Main Directions MD and TD of the Films

Ageing (Months)	Orientation	$\varepsilon_1(\%)$	$\varepsilon_2(\%)$	$\varepsilon_3(\%)$
0	MD	4.86	4.32	0.69
	TD	4.79	5.49	2.14
2	MD	3.92	4.31	0.45
	TD	4.37	4.81	1.55
4	MD	3.40	3.62	0.20
	TD	3.23	4.64	0.93
6	MD	2.81	3.05	0.07
	TD	2.43	4.29	0.66

becomes stable ($\dot{\varepsilon}_{min}$) for the remaining loading duration. This phase corresponds to the secondary creep domain "ε_3." During this phase the total strain and the creep rate are comparatively higher in the transverse direction than in the machine direction.

After stress removal, much of the deformation is almost instantaneously recovered "ε_a," then the delayed recoveries "ε_b and ε_c" tend quickly to minimum values.

Creep Behavior (Loading Phase). The analysis of the mechanical properties of the original samples shows that the value of the instantaneous elastic strain (ε_1) is slightly higher in the MD than in the TD. In the opposite, the delayed elastic strain (ε_2) and the viscous flow (ε_3) are lower in the MD (Table I).

With the increase of the ageing time, all the different strain values (ε_1, ε_2, ε_3) decrease whatever the solicitation direction. The ε_3 values in the MD are much lower than in the TD; however, the rate of lowering is almost the same for the two directions.

Figure 8(a,b) represent the variations of the strain rates ($\dot{\varepsilon}$) during loading for the two directions and the different ageing stages. The main advantage of this type of representation is that it makes easier to determine the stationary stage corresponding to the minimum creep strain rate ($\dot{\varepsilon}_{min}$). It appears that the value of the strain rate is higher in the TD than in the MD for all

Table II. Ageing Effects on the Different Characteristic Strains Identified in the Recovery Behavior Curves of LDPE in the Two Main Directions MD and TD of the Films

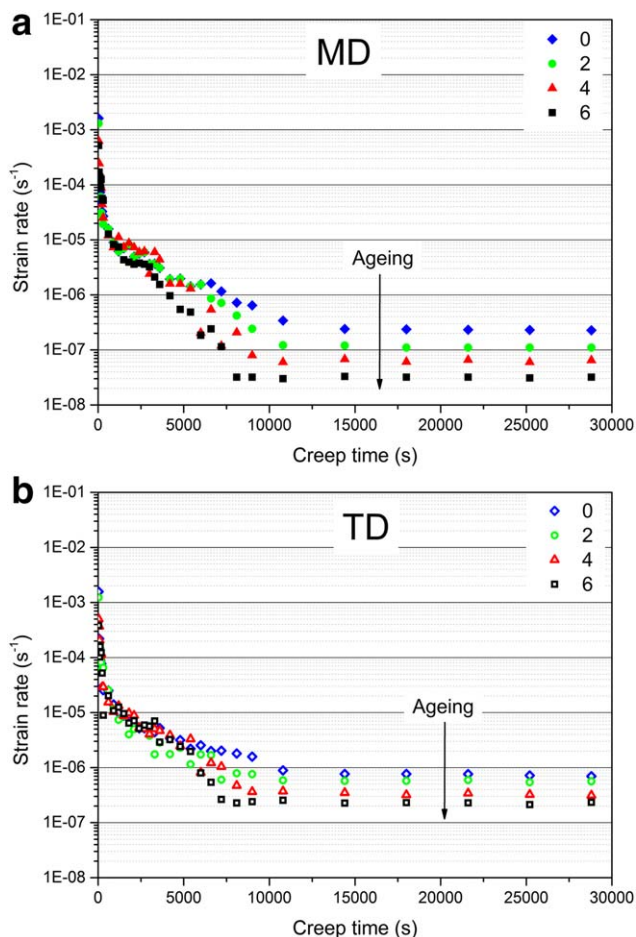| Ageing (months)	Orientation	$\varepsilon_a(\%)$	$\varepsilon_b(\%)$	$\varepsilon_c(\%)$
0	MD	4.80	3.57	1.49
	TD	4.78	5.90	1.74
2	MD	3.90	3.38	1.39
	TD	4.36	4.74	1.62
4	MD	2.93	2.94	1.35
	TD	2.96	4.38	1.47
6	MD	2.58	2.13	1.22
	TD	2.34	3.76	1.28

Figure 8. (a) Strain rates during loading as a function of the creep time of unaged (0 month) and weathered (2, 4, and 6 months) LDPE films in the MD. (b) Strain rates during loading as a function of the creep time of unaged (0 month) and weathered (2, 4, and 6 months) LDPE films in the TD. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 9. (a) Viscous flow (ε_3) as function of the optical density (OD) of vinyl (910 cm^{-1}). (b) Viscous flow (ε_3) as function of the inverted scale of the optical density (OD) of vinylidene (888 cm^{-1}). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the ageing times. In such curves it is possible to distinguish the different creep domains such as the primary creep where the creep rate decreases progressively until reaching a minimum value ($\dot{\varepsilon}_{min}$) and the secondary creep where the creep rate remains constant. It can be observed that with increasing the ageing time, the minimum strain rate ($\dot{\varepsilon}_{min}$) value decreases for both directions. LDPE films reach earlier this domain; however, it remains always higher in the TD.

On Figure 9(a,b) are reported the viscous flow as function of the vinylidene and the vinyl groups, respectively. The variations of the viscous flow "ε_3" for the two directions is reported as a function of the optical density (OD) of the vinyl groups in Figure 9(a). The results show the same trend for the two directions, since the viscous flow "ε_3" decreases with the increase of the OD of vinyl groups. However, the TD values are higher than that of the MD. As mentioned earlier (section "Infrared analysis"), the appearance and the intensity increase of the vinyl groups absorption band is a good indicator of the short chain segments formation coming from chain scission reactions. This
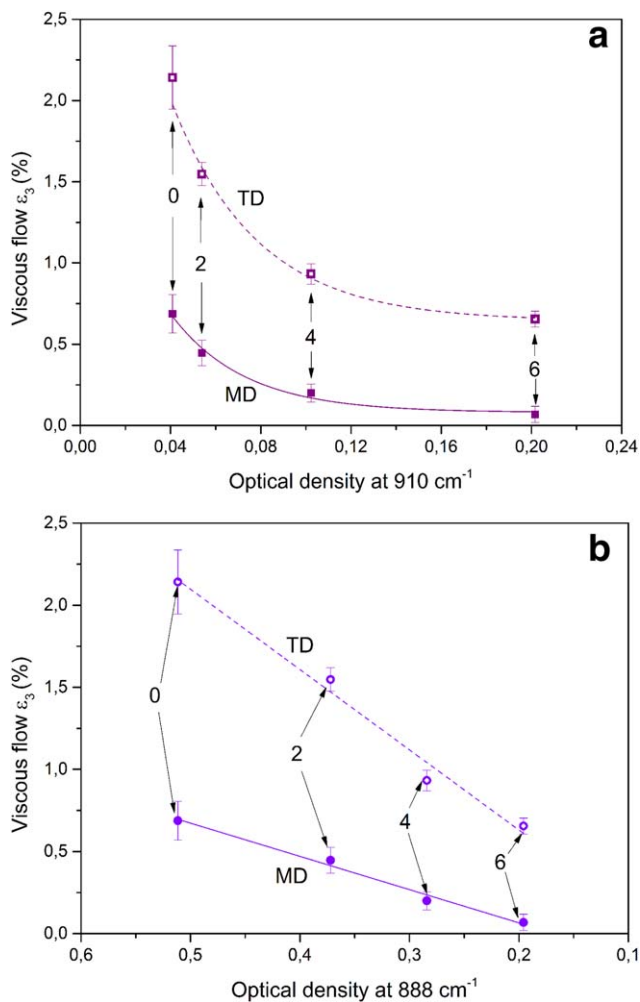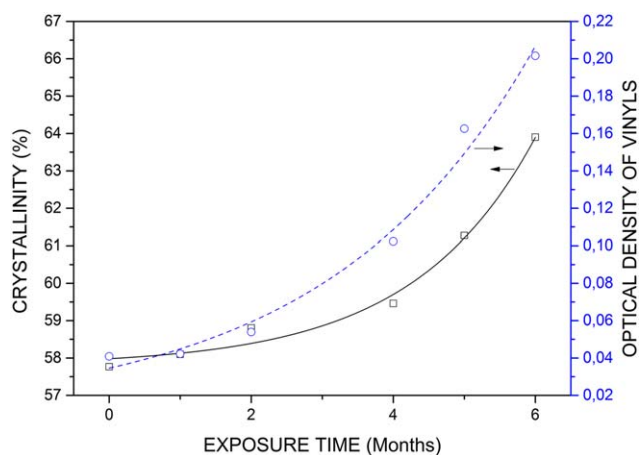

Figure 10. Correlation between the optical density of vinyl groups and the crystallinity with ageing. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
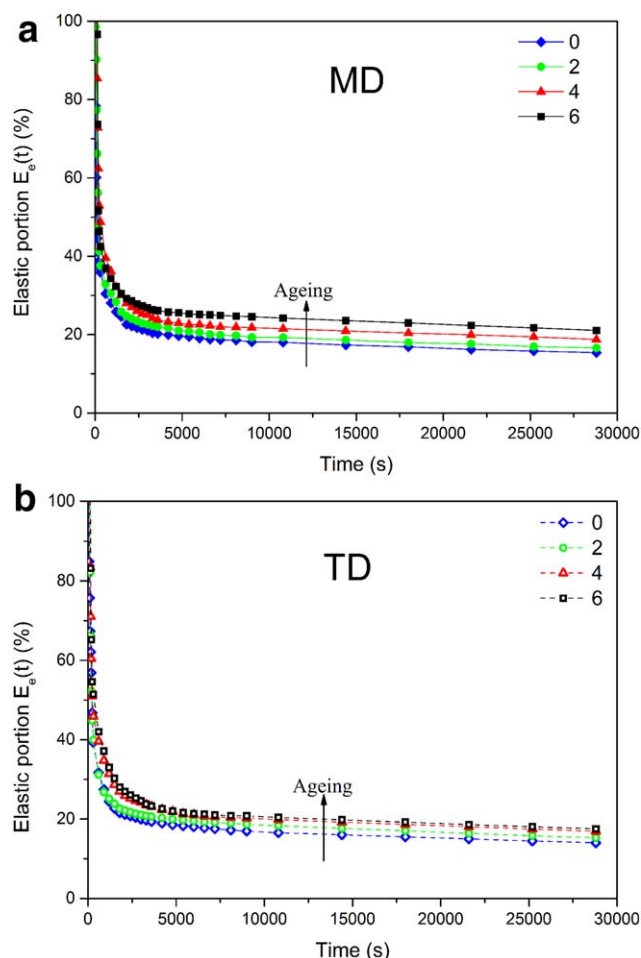
Figure 11. (a) Elastic portion $E_e(t)$ of the total strain $\varepsilon(t)$ as function of the creep time for different ageing exposure times in MD. (b) Elastic portion $E_e(t)$ of the total strain $\varepsilon(t)$ as function of the creep time for different ageing exposure times in TD. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

phenomenon is responsible of the crystallinity ratio increase of LDPE via a chemo-crystallization process. As matter of fact the variation curve of the vinyl groups and that of crystallinity ratio have the same aspect (Figure 10). This indicates that chain scissions via the Norrish type II process are the main factor responsible of the crystallinity ratio increase.[1,2] Chabira et al.[2] have also demonstrated by NMR that shorter branches of butyl and methyl lengths appear with natural weathering. Indeed, Rasburn et al.[7] have verified that the strain rate of the different creep domains lowers with the increase of the short chain branching concentration. As a consequence, the creep resistance increases. As a matter of fact, both effects occur in the studied material (i.e., the increase of the short chain branches and the crystallinity ratio), furthermore the creep-recovery curves display an overall lowering of the strain rate, an increasing creep resistance and an earlier reaching of the secondary creep "$\dot{\varepsilon}_{min}$." The chemo-crystallization process leads either to the thickening of the existing crystalline lamellae or to nucleation of new crystallites, thereby reducing the amorphous region which support the mechanical deformation. This makes the material stiffer.[11] Moreover, the deformation requires more energy. The reduction

of the length of branching tends to increase the cohesion of the chain backbones (by secondary bonds) reducing thereby their slippage;[6] these both effects act in increasing the overall creep resistance of the material.[7]

The representation of the viscous flow as a function of the optical density of vinylidene groups for the different ageing stages is reported in Figure 9(b). It decreases with the consumption of the vinylidenes; however, the values in TD are higher than in the MD. For both directions, it appears that there exists a quasi-linear relationship between the viscous flow and the vinylidenes consumption; this reveals the importance of the cross-linking effects on this rheological greatness. Indeed, the formation of crosslinking via the reaction of these double bonds reduces dramatically the polymer chains slippage. Unigovski et al.[9] have demonstrated that highly cross-linked polymers do not show the viscous flow (ε_3), and this is true to a very good approximation for highly crystalline polymers as well.

Recovery Behavior (Unloading Phase). The recovery of the films is never achieved completely. In all the cases, the tested samples do not return to their original length due to a permanent strain, noted "ε_c," involved during loading.

Table. 2 and Fig. 7 show that the longer the creep time, and more the chains are oriented, the lower are the instantaneous elastic recovery "" and delayed recoveries "". Chains orientation seems to play a key role in the recovery, since the material elongation is greater and easier in the TD than in the MD. Indeed, as suggested above the initial deformation e1 is mainly due to the unrolling of the molecular chains in the amorphous phase, then, this is followed by their progressive disentanglement for a longer loading time. The chain alignment becomes slightly more perfect and the chains become closer to each other, allowing the creation of secondary bonds, these last ones oppose to the complete recovery of the polymer chains to their initial state after unloading.[8] In Figure 11(a,b) are represented, the variation of the recovered elastic portion $E_e(t)$ as a function of the creep time and for the MD and TD, respectively.

The variation of $E_e(t)$ for all the different ageing stages shows a rapid drop during the first 300 seconds of the creep test to reach then an asymptotic trend. Practically 60% of the elastic portion $E_e(300 \text{ s})$ for the unaged films is transformed into an irreversible plastic creep deformation for both directions. The value of the $E_e(300 \text{ s})$ decreases significantly and progressively with ageing (~55, 50, and 40% for the aged samples of 2, 4, and 6 months, respectively).

The reduction of $E_e(t)$ is a consequence of the effects described above which encompass cross-linking, chain scissions and the reduction of the chains branching length. The combination of these effects is also responsible for the decrease of both directions of each of the instantaneous elastic (ε_a), the delayed elastic (ε_b), and the final recovery (ε_c) (Table I).

CONCLUSIONS

The effect of ageing by natural weathering on the mechanical properties of LDPE films used for greenhouse covering exposed in Sub-Saharan facility has been investigated. The energy carried by the UV portion of sunlight is responsible of the radical

reactions and to oxidation due to oxygen absorption by the amorphous phase. This leads to microstructural and morphological changes which results from competition between crosslinking and chain scission reactions affecting adversely the mechanical properties. Both contribute in increasing the Young's modulus (E) in the two main directions of the film plane leading to a global material stiffening. In the same vein, it has been found that the strain at the break (ε_b), remains always higher in the TD than in MD. This is explained by the fact that the unrolling and the disentanglement of the long chains, is easier in the TD than in the MD. Per contra, the stress at break (σ_b) remains always lower in the TD than in the MD, probably because the chains are slightly more oriented during the film's processing in the MD than in the TD. It has been shown that the properties at break show a slight increase during the two first months of exposure in both directions consequently to crosslinking reactions. During ageing, crosslinking, and the increase of crystallinity seems to not affect the anisotropic character of the film which remains preserved during all the ageing protocol.

The creep-recovery tests are sensitive to the microstructural and morphological changes undergone by the material. In fact, during the loading phase, the curve shape is higher in the TD than MD. This difference is explained by the fact that when the film is stretched in the TD, the chains in the amorphous phase being less oriented make more time to reach their total tautness.

In the first time of ageing, the lowering of the creep curves in both directions, and therefore the decrease of ε_1, ε_3, is due to crosslinking reactions. Also, it has been found a close relationship between the viscous flow and the vinylidene groups, these last ones have thus revealed the effect of crosslinking on the viscoelastic properties. This is due to crosslinking in the beginning and to chain scissions for longer ageing time. The viscous character of the material is strongly lowered by the two last chemical reactions, but also by crystallinity.

The minimum strain rate ($\dot{\varepsilon}_{min}$) higher in the TD than MD, is a good indicator of the effects of the structural changes on the ability of the material to deform, this difference is related to the molecular orientation which is mainly connected to the capability of chain unrolling and slippage. With ageing the lowering of the branch lengths increases the cohesiveness of the main chains (by formation of macromolecular secondary bonds) which acts also negatively on the creep rate. Recovery has revealed a very fast drop of the elastic portion occurring in reason of the degradation process. The instantaneous (ε_b) and the final recoveries (ε_b , ε_c), diminish with increasing exposure time supporting the findings of creep.

It can be concluded that creep-recovery test on LDPE films is very efficient in the recognition of the extent of structural damages caused by ageing on their viscous-elastic behavior.

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