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Effect of photochemical ageing on the tensile properties and behaviour law of unstabilized films of low-density polyethylene

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Films of low-density polyethylene (LDPE) were exposed to artificial ageing in a photochemical reactor, and photochemical ageing was observed by tensile measurements. Oxidative degradation was characterized from carbonyl groups formation using infrared spectroscopy. Only ultimate properties seem to be affected, elastic properties being practically unaffected. In fact, the most obvious chemical effect induced in LDPE by exposure is the formation of carbonyl groups easily observable by infrared spectroscopy. Some elementary acts of the oxidation process induce chain scissions responsible for the decrease of elongation at break.

1. Introduction

For a long time glass was the only material used for greenhouses until the availability of synthetic materials, i.e. plastics, which have low cost in comparison to glass. However, though many plastic materials are in use as alternative glazing for greenhouses, they have the disadvantage that they are not sufficiently durable. The use of polymers depends on considerable development in their physical and mechanical properties in terms of time and environment in which they are used. This development was followed by several modifications of structure, chemical composition and morphology (i.e. the crystallinity, deformation of amorphous regions, etc.) of polymers. Thus, when polyethylene is exposed to heat and/or ultraviolet light, it undergoes a process of oxidation reaction, the consequences of which can be seen at the microstructure level. At the molecular level, oxygenated storage areas (alcohols, hydroperoxides acetones, acids, etc.) can be observed which, therefore, like carbonyls, can be easily detected and dosed by infrared spectroscopy. These areas include the advances of process techniques. At the macromolecular level, photochemical degradation results from the competing reactions of chain scission and cross-linking [1], the latter prevailing in the case of ionizing radiation. Under ultraviolet radiation, chain scission will always predominate [2]. At the morphological level, polyethylene is a semicrystalline polymer, and its crystalline phase is considered to be virtually unaffected owing to its relative impermeability to oxygen. The oxidation is confined to the amorphous phase [3], it is essentially the chain scission in the amorphous phase which is responsible for inducing brittleness in polymers [4] and hence the decrease of strain at the rupture point. Therefore, oxidation gives rise to a considerable loss in mechanical properties, and it was deduced that it did not influence the elastic properties [5].

2. Experimental procedure

2.1. Material

Extruded films of LDPE of Riblene type (El-Kurty, Algeria) were studied. These films, used for greenhouse coverings, are unstabilized. The main mechanical characteristics deduced by tensile testing are listed in Table I.

2.2. Exposure

The accelerated ultraviolet photo-irradation exposures tests were carried out with a medium-pressure

TABLE I Mechanical characteristics of LDPE at $T = 22\,^\circ\mathrm{C}$

	Extrusion direction	Perpendicular extrusion direction
Stress at break (MPa) $V = 100\ \mathrm{mm\,min^{-1}}$	21	18
Elongation at break (%) $V = 100\ \mathrm{mm\,min^{-1}}$	616	789
Secant modulus at 1% strain (MPa) $V = 2\ \mathrm{mm\,min^{-1}}$	241	262
Yield stress (MPa) $V = 100\ \mathrm{mm\,min^{-1}}$	12	11.5

mercury lamp (400 W) in a 70 ± 1 °C regulated drying-oven which provides a good representation of the solar spectrum. The test specimens were removed at periodic intervals of 8 h and stored at 23 ± 1 °C, at relative hygrometry of 50% and in darkness.

2.3. Methods

Tensile tests are used as a systematic means of characterizing unaged and aged specimens. Tensile tests were performed on an Instron 1186 machine, monitored by velocity. All tests were conducted at $20 < T\,°\mathrm{C} < 25$ and $40 < \mathrm{RH}\% < 45$. The characteristics at break, such as conventional stress at break, σ_r, elongation at break, ε_r, and yield stress, σ_e, were estimated for a strain rate of 100 mm min^{-1} (NF T54-102) in order to minimize the viscoelastic effects. The secant modulus (at 1% strain), E_s, was estimated at 2 mm min^{-1}. Test specimens had a gauge length of 60 mm, a width of 10 mm and an average thickness of 200 μm.

An accurate analysis of the specimens was realised by using the chemical characteristics of the material. The infrared spectra were recorded using a Perkin–Elmer 683 attached to a CDS data station model 3500. The percentage crystallinity was calculated from differential scanning calorimetry (DSC) results by the following relation [6]

$$X(\%) = (\Delta H_f / \Delta H_f^0)\,100 \qquad \Delta H_f^0 = 285\ \mathrm{J\,g^{-1}} \quad (1)$$

where ΔH_f (J g^{-1}) is the heat of fusion of the sample, and ΔH_f^0 (J g^{-1}) the heat of fusion of the 100% crystalline polymer.

3. Results

3.1. Orientation effect on the tensile behaviour

The conventional tensile stress–strain curves of polyethylene achieved for both principal directions of the unaged specimen are plotted in Fig. 1 (average of ten tests). These tests provide an anisotropy on account of the method used. The fact that transverse elongation, ε_r, is greater than longitudinal elongation, ε_r, shows that, in the aggregate, macromolecular chains are oriented in the extrusion direction.

3.2. Effect of photochemical ageing on modulus and yield stress

The secant modulus, E_s, and the yield stress, σ_e, are plotted, for both principal directions, in terms of exposure time in Figs 2 and 3. There is no significant variation of E_s or σ_e throughout the duration of the tests.

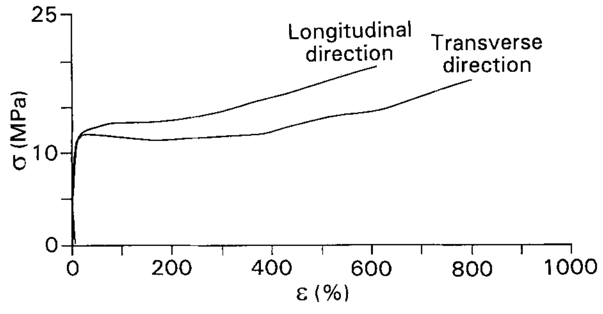

Figure 1 Tensile stress (σ)–elongation (ε) curve of LDPE ($T = 22\,°\mathrm{C}$, RH = 32%).

3.3. Effect of photochemical ageing on properties at break

The conventional stress and strain at break are plotted in Figs 4 and 5. The main phenomenon is a sudden loss in the value of elongation at break which is from more than 600% to less than 150%, thus characterizing the changeover from a plastic to brittle behaviour. This limit is relatively brutal, because after 35 h exposure, ε_r is always in the region of its initial value, while after 50 h, it reaches 50% of its initial value. After this rapid decrease, ε_r becomes steady around ε_e, the initial elongation at threshold plasticity.

The initial period, in which ε_r is stable is subsequently termed the incubation phase. The transition phase, corresponds to the period of rapid decrease of ε_r, and the terminal phase to the period beginning at the end of the transition phase, at moment where the material assumes a brittle behaviour. It can be observed that the anisotropy of ε_r disappears rapidly

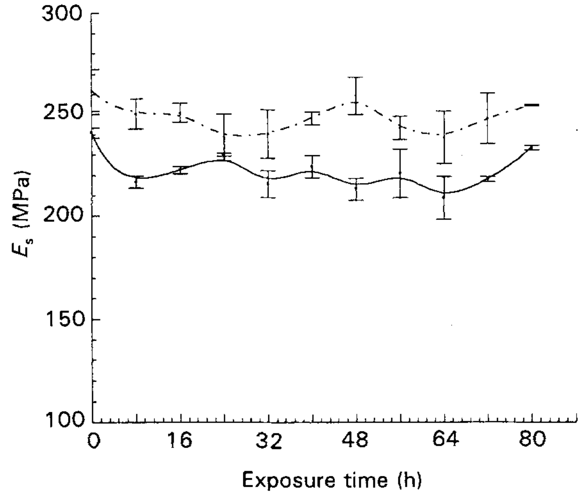

Figure 2 Secant modulus, E_s in terms of exposure time: (———) longitudinal direction, (— · —) transverse direction.

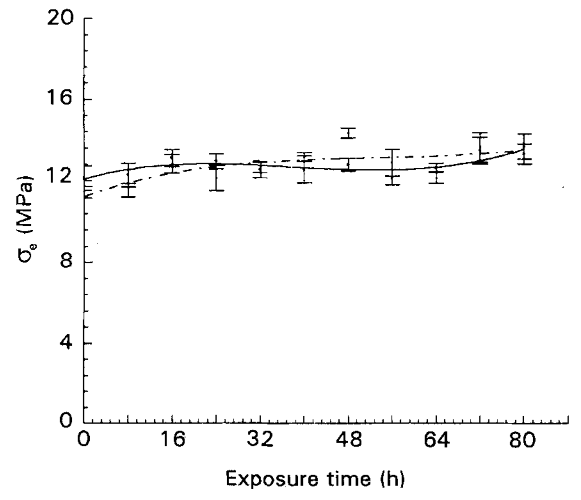

Figure 3 Yield stress, σ_e, in terms of exposure time: (———) longitudinal direction, (— · —) transverse direction.

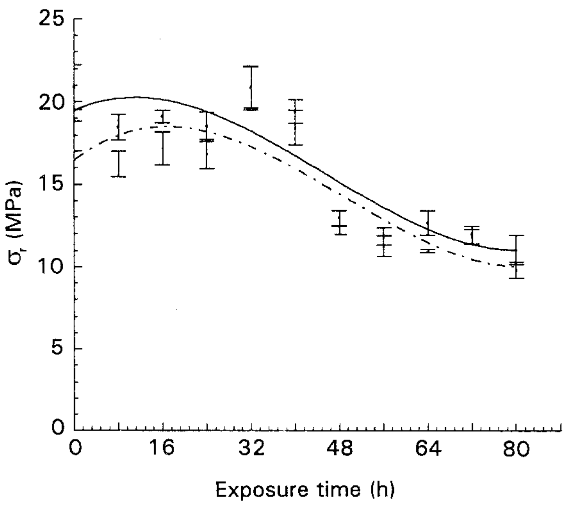

Figure 4 Stress at break, σ_r, in terms of exposure time: (———) longitudinal direction, (— · —) transverse direction.

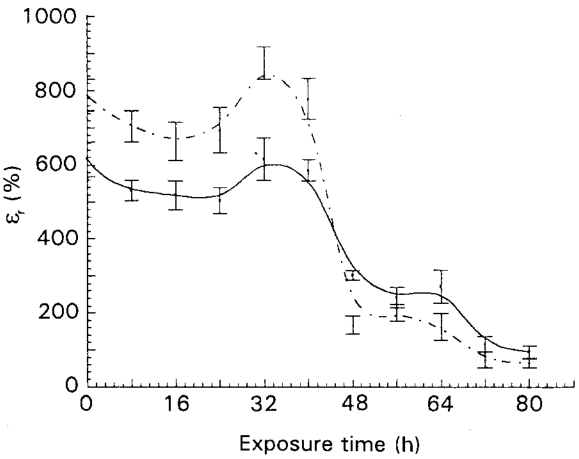

Figure 5 Elongation at break, ε_r, in terms of exposure time: (———) longitudinal direction, (— · —) transverse direction.

during the transition phase, and in the terminal phase the reverse is true.

The stress at break slowly increases during the incubation period, decreases to about 30% during the transition phase, and becomes stable at the level of σ_e, the initial stress as threshold plasticity.

3.4. Aspects of physical–chemical ageing

Fig. 6 shows that the concentration of carbonyl groups (DO) increases by auto-acceleration. In fact, the oxidation products, such as acetones and especially hydroperoxides, principally contribute to the creation of new oxidation chains. The chain scissions occurring at the chains extremities act as imperfections in the network and can lead to the formation of initiators crack faults affecting the mechanical properties [7]. The DSC analysis indicates an increase in the percentage crystallinity during the incubation period and an obvious stabilization later on (Fig. 7).

3.5. Failure envelope, σ_r–ε_r

The rupture coordinates σ_r and ε_r corresponding to different ageing states are plotted in Figs 8 and 9. The

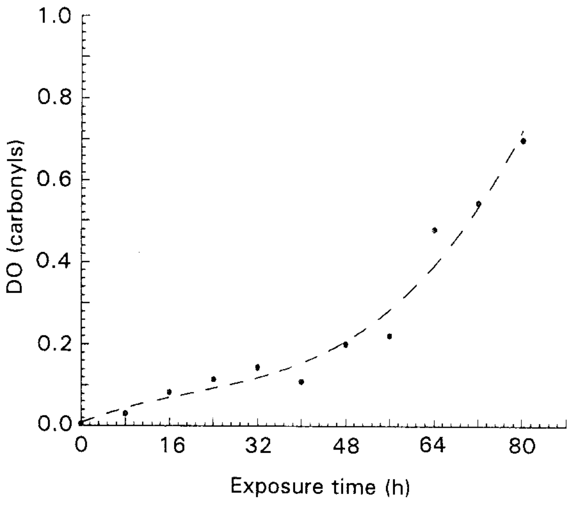

Figure 6 Optical density of carbonyl groups (1715 cm^{-1}) in terms of exposure time.

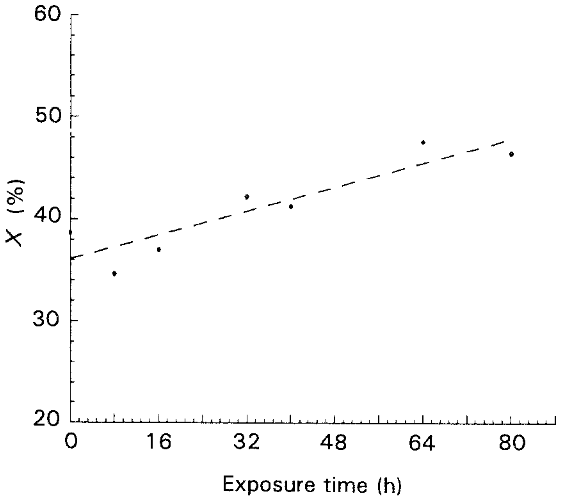

Figure 7 Percentage crystallinity in terms of exposure time.

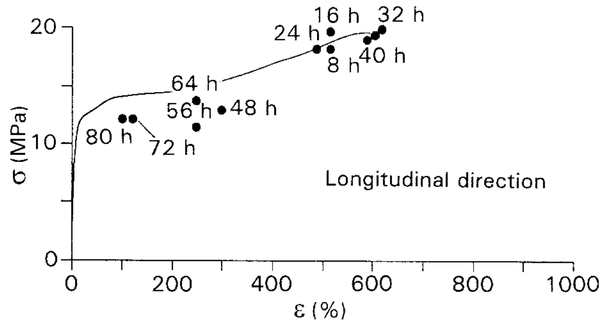

Figure 8 (●) Failure envelope (σ_r–ε_r) in the longitudinal direction. (———) Tensile curve of the unaged specimen.

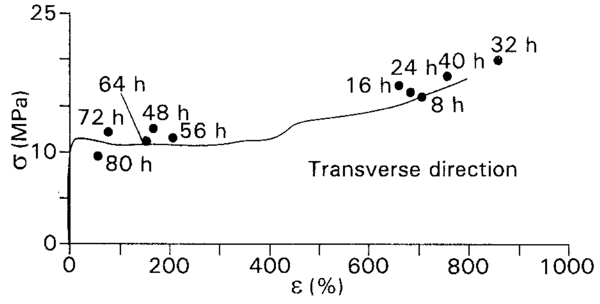

Figure 9 (●) Failure envelope (σ_r–ε_r) in the transverse direction. (———) Tensile curve of the unaged specimen.

failure envelope ($\sigma_r = f(\varepsilon_r)$) shows two distinct zones: one located on the upper part of the tensile curve which identifies the incubation phase where properties did not undergo sensitive variation during ageing, the other is localized on the yield part of the tensile curve, identifying the terminal phase. The tensile curve in the transverse direction, representing an upper and lower yielding stress, σ_r, is capable of passing through a maximum.

The failure envelope is the initial tensile curve. This involves a slight variation of σ_r at the beginning of the exposure and a rapid decrease in the yielding zone.

4. Discussion

Even if the slight initial increase of stress at break suggested the existence of a cross-linking process (already observed elsewhere [8]), the results show clearly that ageing results essentially in chain scissions. They are localized exclusively in the amorphous phase, involving an increase in percentage of crystallinity. It is well known that the crystallization of a polymer is restricted by structural irregularities carried by chains (in particular, branching) and also by cross-links.

Chain scissions in the amorphous phase promote disentangling and allow a "post-crystallization" named "chemecrystallization". This process, as a rule, cannot exist if macromolecular mobility is high, i.e. if the amorphous phase is on or above its melting temperature, which is the case here. The chemecrystallization will stop when the amorphous phase consists of the branched species and is high in structural irregularities of all sorts, and therefore incapable of integrating to crystallites. It seems that this situation was reached at the time of the incubation period.

In the case of unaged polyethylene, we know that modulus and yield stress are almost proportional to percentage crystallinity [9, 10]. The fact that, in our case, they appear to be independent of X, may be interpreted in different ways.

(i) The crystallization does not occur during ageing but rather during thermal analysis (the effect of annealing on account of crossing between ambient temperature and melting temperature).

(ii) The increase due to the chemecrystallization is compensated by a decrease due to another mechanism. Perhaps it is a relaxation of orientation, for example, but without any effects (during the incubation period) on the mechanical properties.

In the absence of complementary experimental data, we assume provisionally the first assumption to apply.

The following comments on the evolution of ultimate properties may be made.

1. Examination of the failure envelope $\sigma_r = f(\varepsilon_r)$ (Figs 8 and 9) allow us to understand one important characteristic of ageing of this polymer [2]. When the failure envelop is superimposed on the initial tensile curve, it suggests that ageing simply accumulates "defects", inducing failure earlier and earlier, while mechanical characteristics other than the ultimate properties are not modified by degradation. One extremely important characteristic of this brittleness process is that it occurs suddenly when the degradation of the material at the molecular, macromolecular and morphological level is, on its part, progressive. This suggests that a structural state "threshold" exists, and indicates a transition from plastic to brittle behaviour.

2. Beyond the incubation period, the evolution rate of different rupture coordinates (stress and elongation in the longitudinal direction or in the transverse direction) notably depend upon each other. We can see, therefore, that the characteristics are dependent on the amount of ageing after the incubation period.

3. The properties at break do not allow, from the kinetic point of view, as the structural variables descended from the physical–chemical analysis.

5. Conclusions

1. The polyethylene studied, in its unaged state, exhibited an anisotropy with regard to mechanical properties. The different fluctuations observed in the tensile curve in the transverse direction are due to the different localized necking during testing. Photochemical ageing produces the same evolution of properties at break in longitudinal and transverse directions: the phenomenon involved is consequently inherent in ageing.

2. A study of the evolution of these properties at the time of photochemical irradiation in air showed that the modulus and characteristics at the threshold plasticity are unaffected when properties at break develop in a catastrophic manner, during the incubation period.

3. The evolution of properties at break can be described as ductile–brittle transition induced by chain scission in the amorphous phase. These chain scissions also lead to chemecrystallization.

4. The mechanism of brittleness can be described as follows.

(a) Chain scissions decrease the density of entanglements in the amorphous phase. The disappearance of cross-links leads to the impossibility of stretching the tie molecules which ensure the liaisons between crystallites.

(b) The absence of tensile strength in tie molecules prohibits the extraction of chains of crystallites (shearing of crystallites), the mechanism responsible for yield strain of semicrystalline polymers. Only van der Waals forces subsist for this, but they are insufficient to ensure a yielding process.

(c) The mechanism of brittle fracture by intercrystallite cracking competes with mechanism of yield strain.

(d) By analogy with amorphous polymers, we can assume that the ductile–brittle transition occurs when a molecular mass of polymers reaches the order of the molecular mass of the cross-links. This explains the sudden onset of brittleness compared to the progressiveness of the chemical degradation reaction.

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