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Elastic properties of degraded polypropylene

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Abstract Even though the ultimate mechanical properties of degraded polymers are widely reported in the literature, few papers dealt with the elastic properties of polymers after submitted to a degradation source. This topic is important to the understanding of the effects of degradation in polymer chemical and physical structure and also in the design of products where load bearing capability is a relevant requirement. The aim of this paper was to investigate and effects of photodegradation on the Young modulus of polypropylene. Several exposure conditions were applied in order to get a wide picture of this effect and hence to propose a reasonable mechanism for this influence. The elastic characteristics were discussed based on the variations in carbonyl index and in crystallinity during exposure and a new elastic property, named global compliance, was proposed. This article also analyses the influence of ultraviolet source on the photodegradation behaviour.

Introduction

It is well known that the various sources of degradation like thermal, photo or biological cause deterioration in the mechanical properties and surface appearance of polymers. The main reasons for the reduction in the product lifetime are the scission of molecules, especially the taut molecules, and the formation of surface cracks [1, 2]. Even though the mechanisms of chemical degradation and the consequences to the mechanical properties of polymers were extensively investigated throughout the years, the elastic properties of degraded polyolefins are rarely dealt with in the technical literature [3–6]. In principle, the Young modulus of semi-crystalline polymers can be affected by degradation in two different ways: (i) the reduction in molecular size facilitates the molecular motion and hence the modulus is reduced; (ii) the increase in crystallinity increases the modulus. The trend, however, may not be straightforward, making the understanding of the effects of degradation processes on this property more difficult. The ultimate consequence is a lack of information and consistent interpretation of this property in the literature, despite the widespread results of the other tensile properties (strength and elongation).

The few works published about the effects of degradation on the elastic modulus of polypropylene show conflicting results and/or few data to make a consistent proposal of interpretation. In a study of thermodegradation of polypropylene, Uzomah and Ugbolue [3] observed a decrease in elastic modulus with exposure, and attributed this behaviour to density decrease. On the other hand, other authors [4] observed that the Young modulus of polypropylene may either increase or decrease during ultraviolet exposure, but this was not correlated to the crystallinity. Accordingly to them, small molecules formed during the oxidative process migrate from the amorphous to the crystalline

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phase. Since these molecules are bulky, they reduce the compacity of the crystalline phase and, consequently, the density and crystallinity of the polymer are reduced. More recently, Yakamits et al. [7] tried to interpret the effect of photodegradation on the Young modulus based on a fracture mechanics approach. They argued that the modulus is governed by both the chemical degradation and the presence of surface cracks. One of the present authors conducted some work on the mechanical properties of photodegraded PP [1, 8–13] but the results for Young modulus were not reported since a consistent trend was not identified at that time nor a suitable interpretation for the results.

Since the knowledge of the stiffness properties is highly important, for instance, in the design of polymer products exposed to hostile environments, we consider this lack of information and discussion an unacceptable gap in the literature of polymer degradation. Variations in Young modulus during degradation may cause significant change in the performance of products in situations where load bearing and stiffness are important. Furthermore, the few studies available were done mostly with thin films, with no consistent information about the elastic properties of thick samples after photo or thermal exposure. This paper deals with the effects of artificial weathering on the elastic characteristics of thick polypropylene samples. Injection-moulded bars were exposed for several periods of time in a weathering chamber and then characterized for chemical degradation, fractional crystallinity and mechanical properties.

Experimental

The polymer used was an injection-moulded grade of isotatic polypropylene (Prolen KM 6100, manufactured by Polibrasil) with MFI 3.5 g/10 min. This is a general purpose grade used for injection moulding and does not contain additives to protect against ultraviolet radiation but we suppose it has thermal stabilizers to avoid extensive degradation during processing. Tensile test bars were produced with dimensions in accordance to ASTM D-638 standard using a MG 80/150 injection moulding machine operating at 180 °C (barrel temperature) and with an injection pressure of 32 MPa. The sample thickness was approximately 3 mm.

The exposures were carried out in a Comexim (C-UV type) weathering chamber using two fluorescent ultraviolet lamps. The chamber was programmed to operate at two cycles defined as follows: 4 h at 50 or 60 °C with the UV lights on and absence of moisture, and 4 h at the same temperature with the lights off and in the presence of moisture. This cycle intends to be a simulation of the natural environment in which temperature, sunlight and humidity vary during the exposure. To evaluate the effect of ultraviolet source, two types of lamps were used: F351 (hereinafter named UVA, produced by Q-Panel Co. with intensity of 0.83 W/m^2 in the range 300–320 nm) and FS-40 (named UVB, produced by Phillips with intensity of 12.4 W/m^2 in the same range of wavelength). The emission spectra for these two lamps are given in Fig. 1. Note that the sources are rather different in respect to the intensity and to the wavelength cut-off.

The fractional crystallinity, X_C, was calculated from X-ray diffractograms obtained from a D-5000 SIEMENS diffractometer, in the range of $2\theta = 5$–$35°$, operating at 40 kW and using the CuK$_\alpha$ radiation. The calculation of crystallinity was done following the method described by Weidinger and Hermans [14].

The extent of chemical degradation was evaluated by the carbonyl index (CI), the most used parameter to estimate chemical degradation of polypropylene [15]. Samples collected at a depth of 0.2 mm from the exposed surface and cold pressed were analysed in transmission using a NICOLET 360 FTIR Spectrophotometer, in the range of 400–4,000 cm^{-1} with resolution of 2 cm^{-1}. The spectra obtained are averages of 20 scans. The CI of the samples was determined from relative areas under the carbonyl peak (at ~1,600–1,800 cm^{-1}) and a reference peak (centred at 2,721 cm^{-1}). A typical FTIR-spectrum of an exposed polypropylene sample is given in Fig. 2 showing the two peaks cited above.

The mechanical tests were performed accordingly to ASTM D 638 using a LLOYD LR10K universal testing machine. The samples were conditioned at 25 °C for about 12 h before testing and the crosshead speed was set at 20 mm/min. The elastic modulus was determined, by the greatest slope in a stress–strain curve as shown in Fig. 3, with the aid of NEXYGEN 2.0®

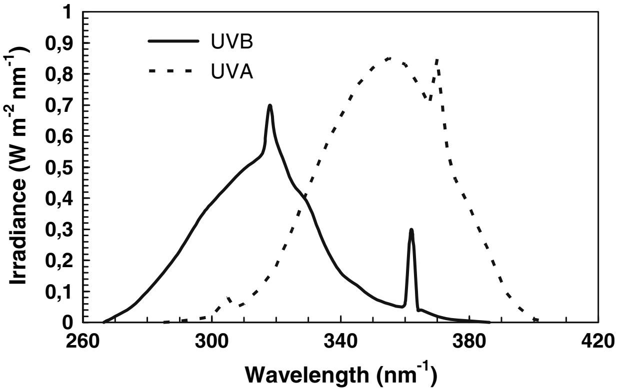

Fig. 1 Emission UV-spectra of UVA and UVB lamps

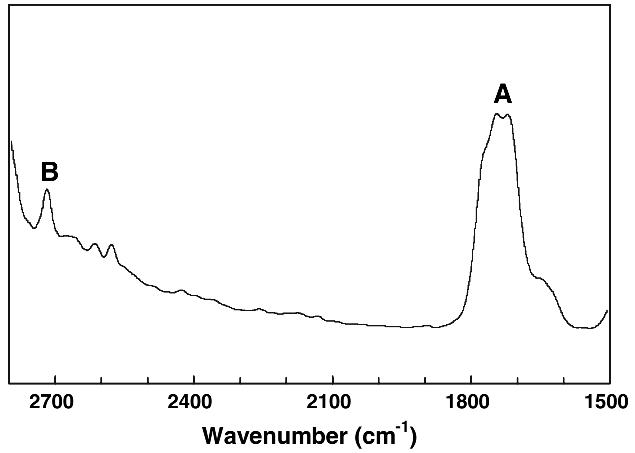

Fig. 2 Part of a FTIR spectrum of a PP sample exposed to UVB for 1,584 h at 50 °C. A and B are, respectively, the carbonyl and the reference peaks

software from the load and elongation data provided by LR10K machine. After tensile testing, selected samples had their fracture and moulded surfaces inspected by scanning electron microscopy (Zeiss DSM 960) using secondary electron imaging at 15–20 kV after being sputtered with a carbon layer.

Results and discussion

Evolution of crystallinity and chemical degradation

X-ray diffractograms of unexposed and UV-exposed polypropylene samples are given in Fig. 4. The as-moulded sample is composed mainly of monoclinic (α-phase) but the presence of the hexagonal (*β*-phase) crystals was also noted (at $2\theta = 16.1°$). The exposure did not cause any significant change in the position or shape of the peaks, in agreement with what was obtained before [16]. From the X-ray diffractograms the crystallinity index was calculated and the results are plotted in Fig. 5. A progressive increase in crystallinity with UV exposure was observed, following other results obtained in the literature [6, 8, 11, 16–19]. This behaviour can be attributed to the scission of tie chain molecules in the amorphous phase that are released and hence may crystallize onto pre-existing crystals, a process called chemi-crystallization. A detailed description of this mechanism was presented previously by one the authors [16]. The crystallinity starts to increase when a sharp decrease in molecular weight occurs but the continuous increase is limited by chemical irregularities (like carbonyl and hydroperoxide groups) that are formed after prolonged exposures and hence the molecules become too defective to continue chemi-crystallization. In the present study,

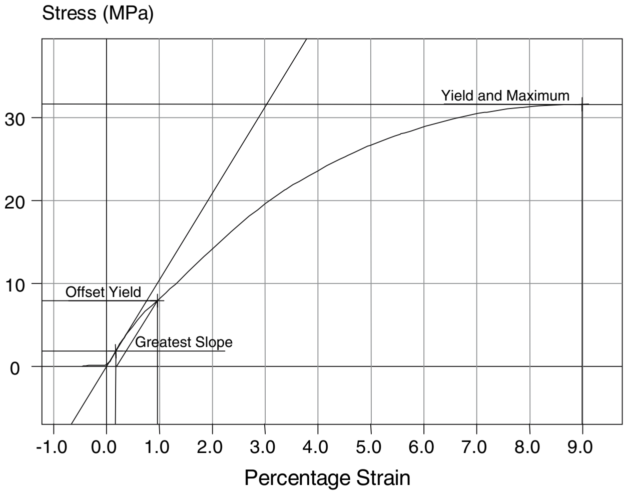

Fig. 3 Stress–Strain default curve for unexposed sample of polypropylene with the procedure used by the NEXYGEN software for measuring the Young modulus

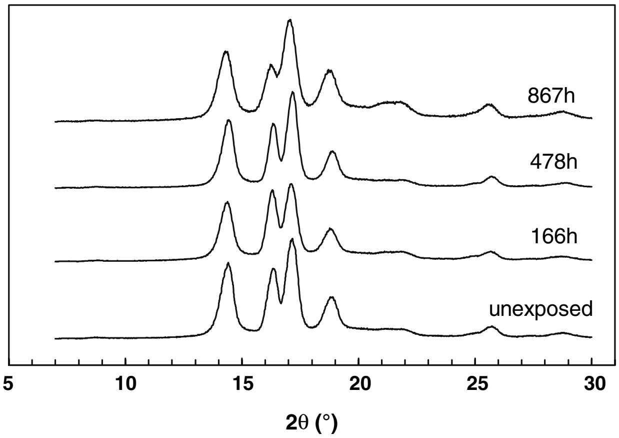

Fig. 4 X-ray diffractograms of unexposed and UV-exposed PP samples. The samples were exposed to UVB at 50 °C

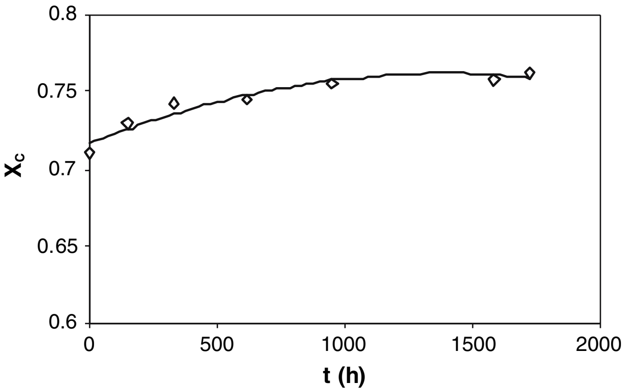

Fig. 5 Crystallinity evolution of polypropylene samples exposed to UVB

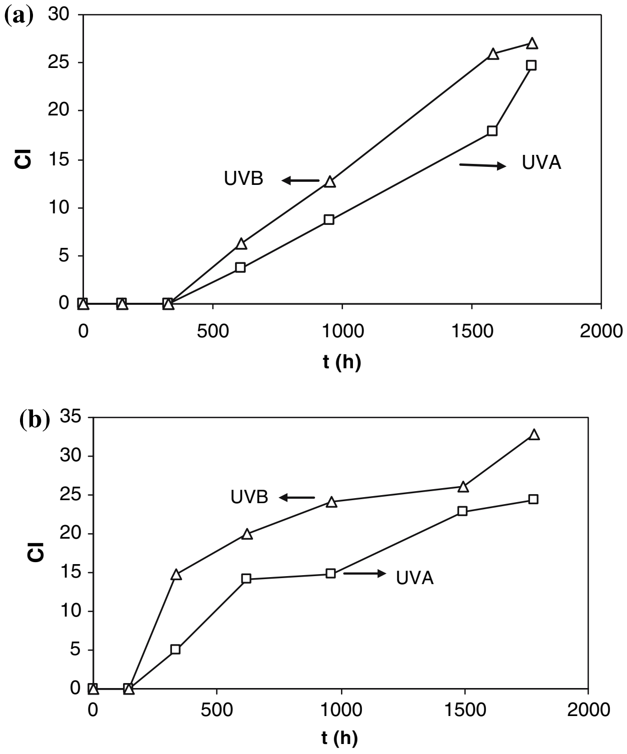

Fig. 6 Carbonyl index for PP samples exposed UVA and UVB at 50 °C (**a**) and 60 °C (**b**)

the increment in fractional crystallinity was about 5%, a value somewhat similar to the ones obtained by Rabello and White [16].

The results of carbonyl index (CI) for samples exposed to the two different UV sources are given in Fig. 6. For exposures done at 50 °C (Fig. 6a) an induction time of approximately 350 h was observed before an intensive increase in CI. This is rather common during the photodegradation of polypropylene, where an autocatalytic process takes place [20]. Exposures at 60 °C (Fig. 6b) had a lower induction time. A comparison between the two light sources, for both exposure temperatures, shows that the samples exposed under UVB had a higher CI for all exposure times. The difference, however, is not as much as would be expected from the difference in irradiance between the two lamps (0.83 W/m^2 for UVA and 12.4 W/m^2 for UVB in the range 300–320 nm). Since the total irradiance of UVB is much higher than that of UVA, one can deduce that total irradiance is not a meaningful exposure variable that could account for large differences in the chemical degradation of PP samples under investigation. Since the intensity of a photon of light is higher for shorter wavelengths, then a higher rate of degradation is expected for the UVB lamps because their emission is higher at shorter wavelengths (Fig. 1). However, one of the main sources of initiation of PP photodegradation are the hydroperoxide groups (–COOH). They easily absorb UV light, and decompose forming free radicals that start the whole process of autooxidation. The hydroperoxides are sensitive to wavelengths of about 340 nm, in which the emission of UVA is much higher than that of UVB (Fig. 1). These two opposite factors seem to have an influence in the degradation of polypropylene and, therefore, the difference between the two light sources is not very large.

Stress–strain curves and elastic modulus

Typical stress–strain curves for unexposed and UV-exposed polypropylene samples are given in Fig. 7. From a ductile nature with large deformation, the polymer changed to a brittle behaviour, with very low deformation at fracture. The tensile strength is also reduced, a common aspect in degraded PP where chain scission is the most frequent degradation pathway. Another reason for the decay in mechanical properties is the formation of surface cracks caused by surface densification. This is the ultimate result of chemicrystallization and was observed by several authors with PP [1, 2, 7, 21]. The pattern of surface cracks was suggested to be closely related to molecular orientation during processing [13] and this also affects the failure mechanisms [21, 22]. In the present work, surface cracks were also observed and some SEM pictures are depicted in Fig. 8. The cracks show a preferred orientation perpendicular to the main sample bar, which is consistent with the observations made before [13]. Note in Fig. 8 the increasing deterioration with exposure time. The fracture surfaces of these samples are given in Fig. 9. The unexposed PP showed typical

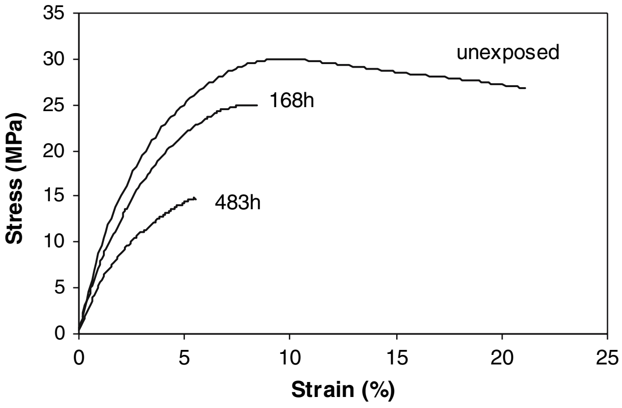

Fig. 7 Stress–strain curves for unexposed PP and exposed samples under UVB at 60 °C

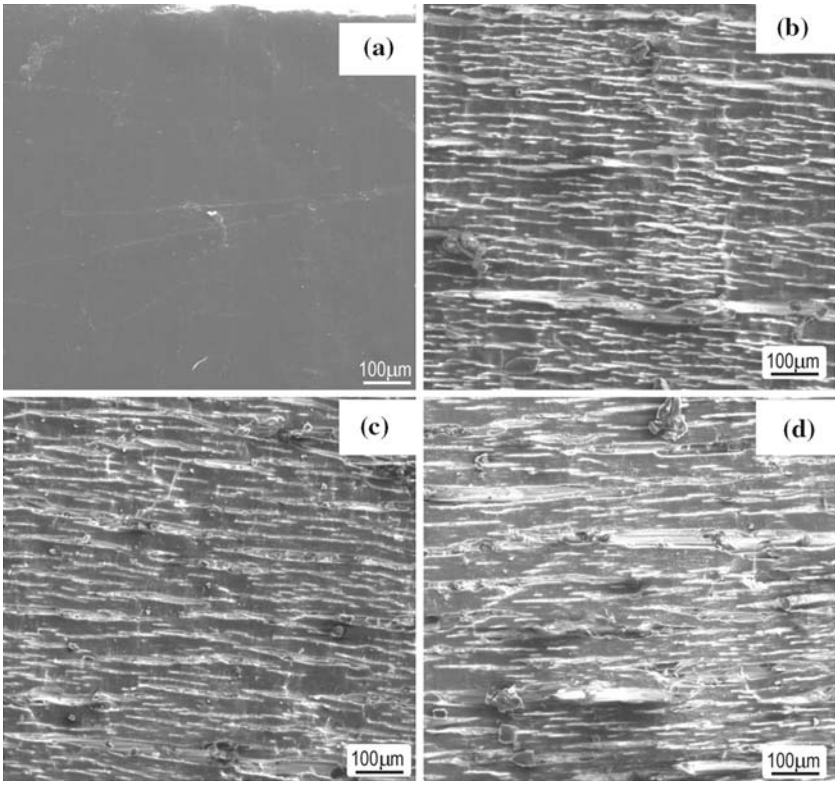

Fig. 8 Scanning electron micrographs of moulded surfaces after tensile testing. (**a**) Unexposed; (**b**) 310 h; (**c**) 483 h; (**d**) 749 h. The samples were exposed under UVB at 60 °C

ductile fracture whereas the degraded samples (Fig. 9b, c) had a transition between the fragile region near the moulded surface and the bulk region where intense fibrillation was observed. Similar results were also registered by Schoolenberg [2] and Rabello and White [9–11, 13]. This ductile region indicates that the

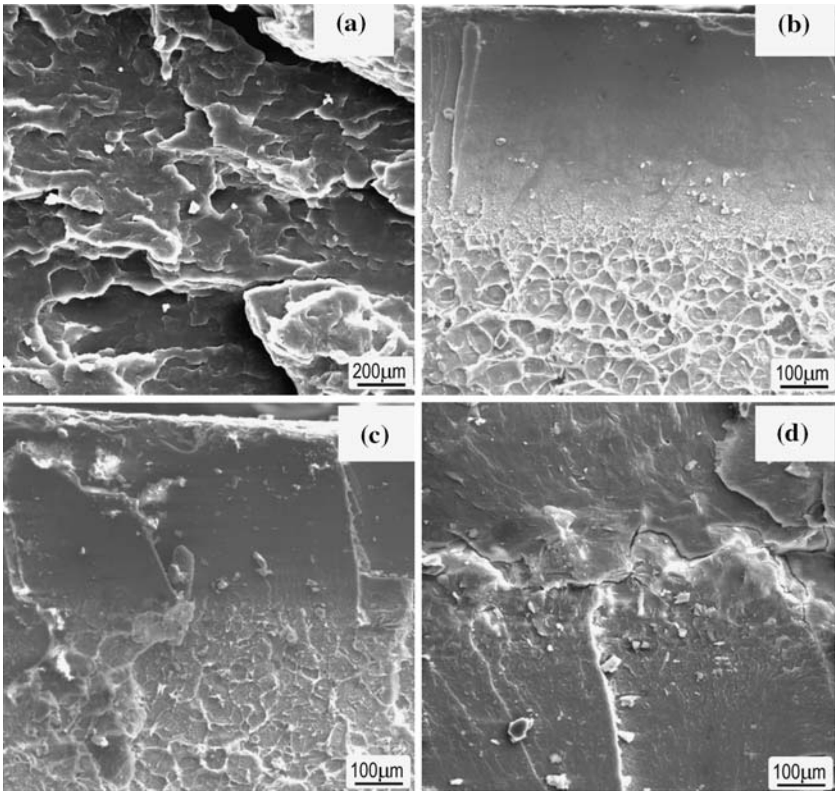

Fig. 9 Fracture surfaces observed by SEM in a region close to the exposed face of the test bar. (**a**) Unexposed; (**b**) 310 h; (**c**) 483 h; (**d**) 749 h. The samples were exposed under UVB at 60 °C

cracks formed at the surface are unable to propagate into the interior of the material and is the main reason for the partial recovery in tensile properties that is frequently observed in degraded polymers [9, 11]. The sample degraded for a more extensive period (Fig. 9d) showed a very brittle nature, with no ductile bands near the exposed surface.

Figure 10 shows the effect of exposure time on the elastic modulus for two different exposure conditions. At first glance it seems that there is not a consistent trend on the relationship between exposure time and Young modulus. However, a careful comparison between the various types of samples (shown here and elsewhere [23]) seems to indicate two distinct regions of behaviour: (i) at short exposure times the Young modulus seems to vary around an average value, but shows an increasing trend, that characterizes a structural arrangement due to molecular relaxation and other physical ageing effects; (ii) after a certain exposure time (e.g., 600 h), the modulus shows a sharp decrease with time. This change in the elastic modulus behaviour may be the combined effects of the changes caused by the increase in crystallinity and the decrease in molecular weight, as will be dealt with in the following section. The results shown here is, in fact, a summary of a much more extensive work done with PP and glass fibre reinforced PP exposed under many different conditions [23].

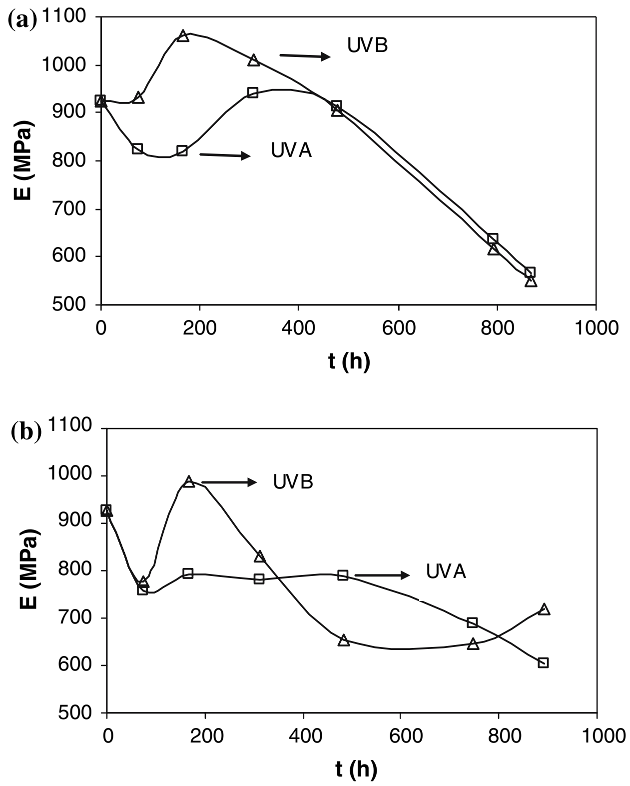

Fig. 10 Elastic modulus of PP exposed to UVA and UVB at 50 °C (**a**) and 60 °C (**b**)

Figure 10 also shows a comparison between the two types of light sources. As occurred with chemical degradation, there is little effect of total irradiance upon the elastic modulus of the exposed samples, especially on the second stage of the curve (i.e., above 600 h).

Combined effect of crystallinity and chemical degradation on elastic properties

A comparison between Figs. 5 and 6 indicates that while the degree of crystallinity varies with time since the very beginning of exposure, i.e., from $t = 0$, the carbonyl index (CI) shows an induction time in which it is modified above $t = t_{\mathrm{ind}}$. This observation is consistent with the concept that the variation in the modulus before it reaches its maximum value (in the first stage of the behaviour) is due to a structural rearrangement caused by molecular relaxation and an increase in crystallinity, and not due to a consequence of the degradation process.

In an attempt to correlate the three parameters $\mathrm{CI}(t)$, $X_{\mathrm{C}}(t)$ and $E(t)$, where t is the exposure time, dimensionless quantities were introduced. The relative elastic modulus E_{R} was defined as:

$$E_{\mathrm{R}} = \frac{E(t)}{E(0)} \tag{1}$$

where $E(0)$ is the modulus of the unexposed sample. The reduced dimensionless elastic modulus will be given by

$$E^{*} = \frac{E_{\mathrm{R}} \,.\, t_{\mathrm{E\,max}}}{t} \quad \forall t > 0 \tag{2}$$

where t_{Emax} is the estimated exposure time where the elastic modulus reaches its maximum value.

In the same way, the reduced crystallinity will be given by

$$X_{\mathrm{C}}^{*} = \frac{X_{\mathrm{C}}(t) \,.\, t_{\mathrm{Emax}}}{t} \quad \forall t > 0 \tag{3}$$

Since the characteristic time of CI is the induction time (t_{ind}), here defined as the last exposure time where $\mathrm{CI}(t)$ is the same as the unexposed sample, the reduced CI will be given by

$$\mathrm{CI}^* = \frac{\mathrm{CI}(t)\ .\ t_{\mathrm{ind}}}{t} \quad \forall t > 0 \tag{4}$$

A plot of the dependence of E^* with CI* and X_C* is shown in Fig. 11. Since E^* decreases with increasing CI* and it increases with increasing X_C*, it is reasonable to conclude that the resultant behaviour of the elastic modulus with exposure time is expected to be the summation of the influences of both the extent of degradation (i.e., carbonyl index) and crystallinity at each exposure time. This approach considers that chain scission is the only significant degradation event during photodegradation of polypropylene (i.e., crosslinking reactions do not occur or are much less frequent than chain scission) [15].

In order to evaluate the influence of CI and X_C upon the deterioration of the elastic properties of the exposed samples, a new elastic quantity, named global compliance spectra, $\phi(t)$, is introduced. This parameter indicates the propensity of the sample to be instantaneously deformed by an imposed static stress, and it depends on the changes in both carbonyl index and crystallinity during exposure. The global compliance spectra is given by

$$\phi(t) = \frac{D_R\ .\ \mathrm{CI}}{X_C} \quad \forall t \geq t_{\mathrm{ind}} \tag{5}$$

where $D_R = E_R^{-1}$ is the relative elastic compliance.

By definition, $\phi(t) = 0$ for $0 < t < t_{\mathrm{ind}}$ indicating that the material did not have any kind of negative modification in its main elastic characteristics, when it is not exposed to a degradation process. The results for global compliance as a function of exposure time are given in Fig. 12. The parameter increased sharply after the induction time for degradation. This occurs due to: (i) the increasing scission of the tie chain molecules and (ii) formation of oxidation products. Even though the first process promotes a rise in crystallinity, the second one causes a decrease in the crystal perfection and crystallinity of the exposed sample.

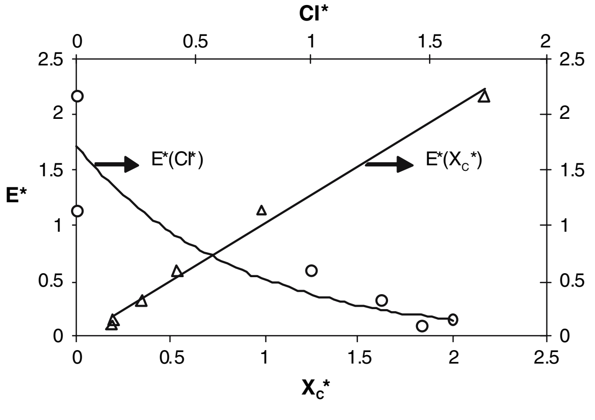

Fig. 11 Relationship between the reduced values of E, CI and X_C for samples exposed to UVB

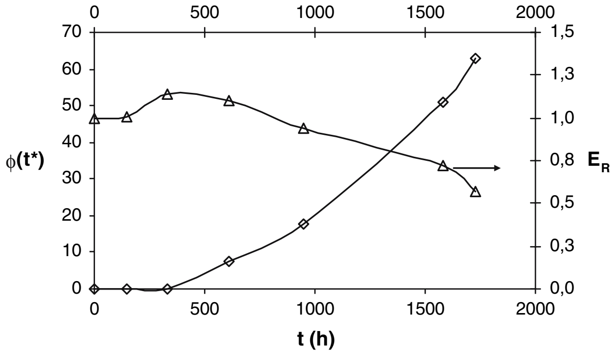

Fig. 12 Relative elastic modulus and global elastic compliance for samples exposed to UVB

A fact that should be taken into consideration in the analysis of the variation of the elastic modulus of degraded polypropylene is the contribution of sample thickness. It is well known that in thick samples, the chemical degradation is concentrated at the exposed surface and a depth profile of degradation is obtained. The relationship between the modulus and the degradation effects was done here based on the results of carbonyl index and crystallinity taken from a depth of 0.2 mm from the exposed surface. Previous results showed the most of the degradation process occurs within this layer, but some degradation still takes place in deeper positions [9]. We believe that the contribution of modulus variation due to changes in molecular weight and crystallinity in deeper layers is small in comparison to the contribution of surface layers but a thorough analysis would be better conducted with data taken from different depth positions. Since the modulus is a property obtained from the whole section, the approach used here must be understood in a semi-quantitative basis. Another observation that must be made refers to the contribution of the detached surface layer in the modulus measurements. Even though the cracked surface is unlikely to be load bearing, this layer was not eliminated in the calculations of the cross sectional area since in practical situations the load bearing capacity of the whole product must be considered.

Conclusion

In this paper, the analysis of the effects of ultraviolet exposure parameters in polypropylene Young modulus was conducted. A non-uniform behaviour of elastic modulus with exposure time was observed for all applied conditions and an interpretation was offered based on the combined effects of crystallinity and chemical degradation. A new elastic parameter, called global compliance, was defined and shown to depend on the observed elastic behaviour.

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