

The Effect of Ultraviolet Light on the Mechanical Properties of Polyethylene and Polypropylene Films

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Synopsis

Measurements were made of dynamic mechanical response spectra and stress-strain properties at room temperature on films of isotactic polypropylene and low-density polyethylene prior and after ultraviolet irradiation in a Xenotest 450 apparatus. The period of irradiation that caused a deep deterioration of ultimate mechanical properties influenced the dynamic mechanical properties only insignificantly. This is attributed to the heterogeneous nature of the photo-oxidative degradation process which is concentrated in a finite number of sites, thus forming crack precursors rather than changing the material properties in bulk. For a biaxially oriented tubular film of low-density polyethylene, anisotropic embrittlement after exposure in Xenotest 450 was observed. This even reversed the order of strain-at-break values in the two main directions of the film. This is remarkably similar to the effect of artificial incisions introduced into the specimens.

INTRODUCTION

Sunlight is the energetically richest component of weather effects during the outdoor aging of polymeric materials. In laboratory tests, the effect of natural daylight is simulated by the light of a xenon discharge lamp in a Xenotest apparatus. Even if the validity of laboratory results thus obtained for predicting the behavior of materials under conditions of natural weathering is questionable,¹ the obvious advantage of the Xenotest consists of an essential reduction in the exposure time needed for attainment of perceptible changes in the material under study. Interactions of photons with the polymer chain induce a complicated series of reactions. In the case of polyolefins, a sufficient detailed findings have been collected on photo-oxidative transformations of the polymer chain.² It has also been demonstrated that light-induced processes continue for some time even in the dark.³ Important for practical purposes are the effects of stabilization systems or, on the other hand, of sensitizers on the course of these reactions.⁴⁻⁶ The kinetics of photochemical changes of polyolefins is characterized by physicochemical methods^{7,8} and predominantly by infrared spectroscopy.^{7,8}

Photochemical degradation causes deterioration of mechanical characteristics, cracking, and eventually complete disintegration of the material. Ultimate mechanical characteristics (especially elongation at break) of polyolefins are more sensitive to irradiation than methods reflecting chemical changes,³ although, in fact, the deterioration of mechanical properties is a final consequence of the series of processes involved in the photochemical degradation. The obvious cause of such a somewhat peculiar behavior is localization of destructive processes in a finite number of sites, mainly on the sample surface on the one hand and sensitivity of the ultimate properties to most severe flaws on the other. The

ultimate behavior responds to localized structure irregularities and defects in a much more pronounced way than to the average properties of the material in the bulk. This is documented here on polyethylene and polypropylene films. The photodegradation process of the films was detected by means of two mechanical methods with different sensitivity to microstructural defects, i.e., by stress-strain test and dynamic mechanical spectroscopy.

EXPERIMENTAL

Materials

The types of polymer films obtained by different technologic procedures were used in this study. First, isotropic films of polypropylene and polyethylene were prepared in a heated press from pulverized polymers. The isotactic polypropylene HPF used had a tacticity index of 96% and a melt index of 9 g/10 min. The low-density polyethylene Bralen RA 2-19 had a density $\rho = 0.931 \text{ g/cm}^3$, a melt index of 2 g/10 min, and a Vicat softening point of 90. The thickness of the isotropic films was approximately 100 μm . Second, the biaxially oriented film was made of unstabilized low-density polyethylene Unifos DFDS 6600 by blow tubing technology by Celloplast AB, Norrköping, using the so-called adiabatic extruder produced by Reifenhäuser. The following characteristics of this product are given by the manufacturer: melt index MI = 0.3 g/10 min, density $\rho = 0.922 \text{ g/cm}^3$, number- and weight-average molecular weight determined by size exclusion chromatography $M_n = 22 \times 10^3$ and $M_w = 250 \times 10^3$, respectively, and degree of branching (long branches) determined according to Drotts $\lambda = 2.5 \times 10^{-4}$. The film was not stabilized and had a constant thickness of 0.06 mm. Biaxial orientation was introduced into the film by means of the blow technology, and the mechanical properties of the film were therefore characterized in two main directions of orientation, viz., in the machine direction (axially) and in the cross direction (transversally).

Irradiation

The polymer films were irradiated in the Xenotest 450 apparatus (Original Hanau, FRG) in air, without wetting the film.

Dynamic Mechanical Measurements

The temperature dependence of the real (E') and imaginary (E'') components of the complex Young modulus $E^* = E' + iE''$ between about -190 and 80°C was determined by means of a Rheovibron DDV II apparatus at a frequency of 110 Hz. The test pieces were strips 4 mm wide; gauge length was 35 mm. After fixation of the specimen in the clamps of the apparatus, the thermostating chamber was cooled with liquid nitrogen; the measurements were performed at increasing temperatures (approx. $1^\circ\text{C}/\text{min}$) in intervals of 5°C .

Stress-Strain Measurements

The stress-strain curves were recorded with an Instron tensile tester at a test rate of 10 cm/min and 25°C. The test pieces were strips 5 mm wide; gauge length was 12.5 mm. The tensile strength σ_b , strain at break ϵ_b , and the form of the stress-strain curves were determined as the average of several (usually five) measurements.

RESULTS AND DISCUSSION

Isotropic Samples

The temperature dependences of the real and imaginary (loss) components of the complex Young's modulus of the isotropic polypropylene and polyethylene samples are plotted together in Figure 1. In the case of polypropylene [Fig. 1(a)], a distinct loss maximum⁹ can be identified at a temperature of about 20°C. The simultaneous decrease in the modulus E' by one order of magnitude indicates that the relaxation corresponds to the glass transition of the amorphous regions. Due to the relatively high frequency of measurements, the temperature thus determined is much higher (by some $30 \pm 5^\circ\text{C}$) than the glass transition temperature T_g (determined, e.g., dilatometrically). The secondary relaxation at about -50°C , assigned in the literature⁹ to local motions of the main chains, was not seen distinctly in our samples.

Generally, polyethylene exhibits three loss relaxation maxima,⁹ of which the high-temperature loss maximum (α), usually assigned to the onset of molecular motions in crystalline regions, lies above the temperature range of our mea-

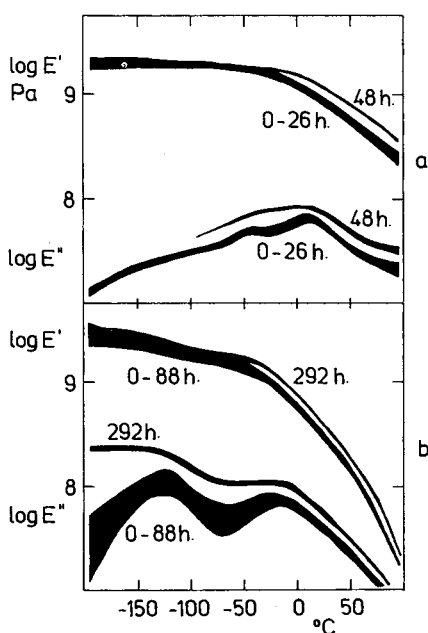


Fig. 1. Effect of UV exposure on temperature dependences of the real E' and imaginary E'' components of the complex Young's modulus of elasticity for isotactic polypropylene (a) and low-density polyethylene (b). Numbers at curves indicate irradiation time (h).

surements. The relaxation maximum at -15°C (β) is related to long branches and is characteristic of low-density polyethylene, while it is absent in high-density polyethylene.⁹ The low-temperature γ -relaxation of polyethylene, situated approximately at -125°C , is due to rotational motions of short sequences of the main chains. With increasing polymer density, the intensity of this relaxation decreases, but its temperature position remains unchanged.

It can be seen (Fig. 1) that irradiation in Xenotest 450 affected the course of the dynamic mechanical response spectra only insignificantly. In most cases, the observed differences between the curves lie almost within the limits of experimental scatter. However, owing to the systematic shift of curves (or their parts) with irradiation time, it can be assumed that changes in the curves, particularly at the longest irradiation times, are real both for polypropylene and polyethylene. Irradiation for 48 h in the case of polypropylene and for 292 h in the case of polyethylene caused a perceptible rise in mechanical losses within the whole temperature range studied and an increase in the real part of the Young's modulus in the higher-temperature range.

The changes in the mechanical relaxation behavior just described can be explained by two possible structural modes, viz., crosslinking and additional crystallization.³ Both these structural changes could affect the mechanical behavior mainly in the main transition region and above the glass transition temperature. For polypropylene, crosslinking due to UV radiation is highly unlikely. On the other hand, crosslinking of polyethylene, which generally contains vinylidene groups, should be considered. The effect of crosslinking may also be supplemented by that of additional crystallization, especially at longer irradiation times. Secondary "chemocrystallization" due to UV radiation has already been discussed for both polypropylene and polyethylene.³ This is explained by assuming that chain segments resulting from photo-oxidative scissions of the chains which originally were present in amorphous regions can additionally crystallize owing to their sufficient mobility above 50°C during the exposure to the Xenotest. The higher crystallinity of xenotested samples of polypropylene and polyethylene is indicated not only by the more moderate decrease in the real part of the modulus in the higher temperature range but also by a relative decrease of loss maxima within the generally raised background level of mechanical losses. It is to be noted that UV irradiation affects the loss modulus E'' more than the storage modulus E' . Therefore, it seems likely that degraded regions of the material themselves can contribute to energy dissipation along with the mechanism mentioned above.

The effect of UV irradiation at room temperature on the stress-strain curves of isotropic films is shown in Figures 2 and 3. It can be seen that the nonlinear tensile behavior to break is much more sensitive to structural changes in the polymer caused by UV light than the dynamic mechanical behavior in the linear region. The ultimate mechanical properties, and particularly strain at break of various polymer systems, react to the photo-oxidative degradation much earlier and in a more pronounced way^{3,10} than in the usual physicochemical analytic methods. Thus strain at break can be utilized in practice as a sensitive indicator of the degree of degradation.

This is of course useful for timely detection of early stages of photo-oxidative degradation. But even more important from a practical point of view is the embrittlement of polymers due to the ultraviolet component of sunlight, which

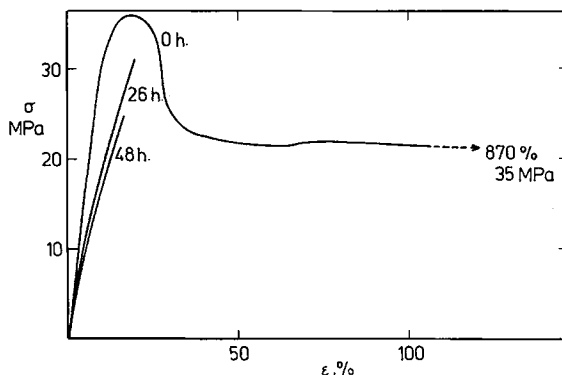


Fig. 2. Effect of UV exposure on stress-strain curves of isotropic film of isotactic polypropylene at room temperature. Numbers at curves indicate irradiation time (h).

may completely deteriorate the utility of polymeric products, especially of films. However, the fundamental physical effect of the irradiation is the change from a situation in which fracture stress is higher than yield stress to the reverse situation. This implies only a decrease of fracture stress from 36 MPa to 31 and 24 MPa for exposure times of 26 and 48 h, respectively.

There are two reasons for the sensitivity of the ultimate properties in photo-oxidative degradation. One is the key role of defects or cracks in the fracture behavior of materials already expressed theoretically in the classical Griffith concept and in the statistical weakest link hypothesis. Another reason is the heterogeneous character of the degradation process itself. One should bear in mind that photodegradation proceeds preferentially in a comparatively localized region near the initiation site (such as, e.g., photosensitive impurity, a structural element in the polymer or additive). Such a localization of the process is a consequence of the low molecular mobility both of the polymer and of the photoactive site in the solid state. Chemical reasons are also involved here, e.g., the zip mechanism of degradation along the polymer chain. The probability of the occurrence of these degradation sites is higher in the surface layer of the body, in particular in the case of polypropylene, but such sites may also lie inside the bulk of the material.⁷ When the body is subjected to mechanical stress, the

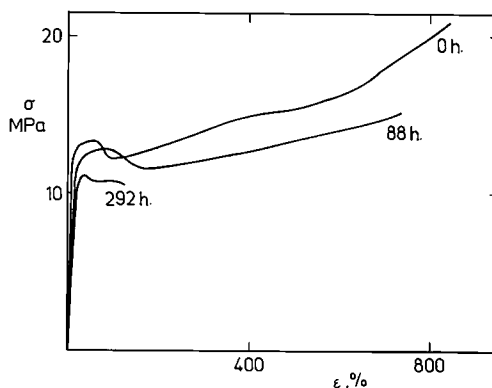


Fig. 3. Effect of UV exposure on stress-strain curves of anisotropic blown film of low-density polyethylene at room temperature. Numbers at curves indicate irradiation time (h).

degraded weak sites act as stress concentrators and crack nuclei. The macroscopic fracture behavior of the test piece is then determined by the most severe defect or crack, in agreement with the weakest link hypothesis. The overall embrittlement of the material is a result of the formation of cracks which act qualitatively similarly to macroscopic incisions introduced into the test piece. Hence, according to this model, it can be assumed that the subsequent effects of light and mechanical stress transform the molecular heterogeneity into a mechanically active form of microstructural defect and, eventually, into an initiator of total failure. This is illustrated by Figure 4.

While the ultimate behavior is governed by a single extreme defect, spectral analytic methods yield integral characteristics of the material in bulk. For this reason, the latter methods reflect structural changes caused by photo-oxidative degradation in a less sensitive way. This is especially true for the first stage of photodegradation, where the process is still localized only in a finite number of very small regions (or sites).

Biaxially Oriented Polyethylene Film

The dynamic mechanical response spectra measured in the two main directions of orientation of the blown tubular film are shown in Figure 5. The dynamic behavior of the film in the axial and cross directions differed only little; moreover,

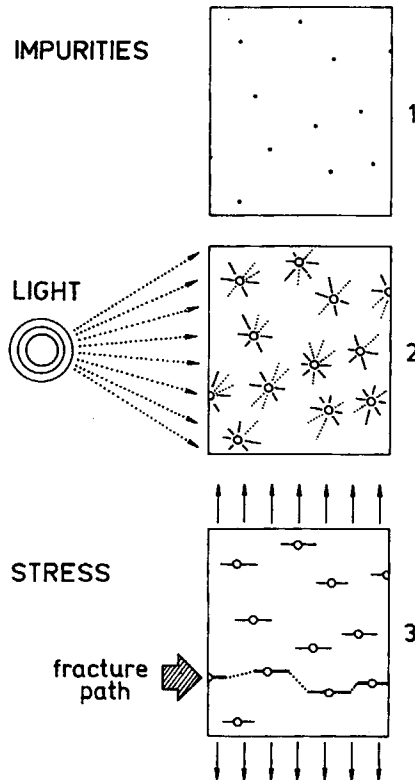


Fig. 4. Schematic diagrams illustrating the subsequent effects of UV radiation and mechanical stress on the formation of weak centers and microcracks in sites of initial chemical heterogeneities. Arrow indicates the direction of final fracture progress along the most weakened cross section of the test piece.

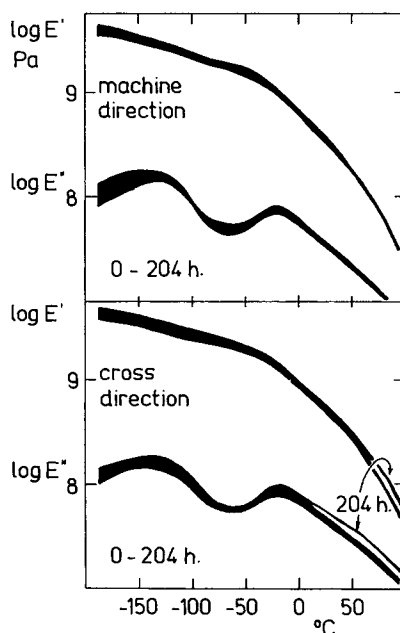


Fig. 5. Effect of UV exposure on temperature dependences of the real E' and imaginary E'' components of the complex Young's modulus of elasticity for a biaxially oriented blown film of low-density polyethylene. Numbers at curves indicate irradiation time (h).

contrary to the conclusions of Ref. 11, the values of both components of the complex Young's modulus are somewhat higher in the cross direction than in the machine direction. Although such a behavior is reproducible in the film under investigation, its structural interpretation still remains somewhat unclear. Similarly to the case of isotropic films, two characteristic loss maxima, β and γ , can be seen on the loss modulus vs. temperature dependence curve. As the maximal irradiation time used for tubular film (204 h) was shorter than that for isotropic film, changes in the dynamic mechanical characteristics of degraded samples do not distinctly exceed the limits of experimental scatter. (The small shift of the experimental curves toward lower values of the moduli in the lower-temperature range cannot be regarded as significant.)

The stress-strain curves of a biaxially oriented unstabilized film before and after irradiation are plotted in Figure 6. This plot contains some new features compared with the analogous Figure 3 (for isotropic polyethylene film). At the beginning of the exposure (88 h), the yield point and stress at break increased, while the ultimate strain decreased in both main directions of the film. This behavior is obviously a consequence of the secondary chemocrystallization mentioned above, and probably also of the crosslinking process after irradiation. Moreover, additional crosslinking is also suggested (though with less evidence) by the more gradual decrease in the real part of the complex Young's modulus of the film after UV exposure. Only after prolonged irradiation time (204 h) do defects in the material originate via the mechanism of localized degradation. Macroscopically, this is reflected in the reduction of breaking stress and embrittlement of the material (reduced strain at break).

However, in the two main directions of the biaxially oriented film, the em-

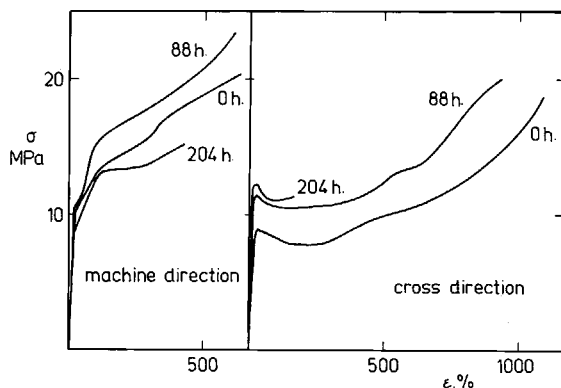


Fig. 6. Effect of UV exposure on stress-strain curves of a biaxially oriented blown film of low-density polyethylene at room temperature. Left: test pieces cut out along the machine direction; right: test pieces cut out in the cross direction. Numbers at curves indicate irradiation time (h).

brittleness was not of the same intensity. Strikingly enough, a drastic reduction in the tensile strength occurred in the cross direction, while in the longitudinal direction (in the machine direction of the film) the effect of irradiation was only weak. Owing to this anisotropic embrittlement, even a reversal in the order of strain-at-break values in the both main directions, ϵ_b , occurred: originally, a higher strain at break appears in the transverse direction of the film, while after irradiation for 204 h a relatively higher ϵ_b value corresponds to the machine direction. A qualitatively similar influence on the stress-strain behavior of the tubular film is observed if small single-edge incisions are introduced into the test piece.¹²

The ultimate mechanical properties in both main directions of the blown tubular film as received, after UV irradiation, and after the introduction of single-edge incisions¹² are compared in Table I. Our preceding articles¹²⁻¹⁴ report a detailed experimental investigation of the effect of incisions of various lengths on the ultimate elongation. An assumption was derived that the tubular film contained an "intrinsic" system of small elongated defects, the longer axis of which is oriented along the machine direction. These intrinsic structural defects then interact with a growing macroscopic crack and either facilitate its progress (if parallel to its axis) or, on the contrary, blunt its tip and impede its propagation (if perpendicular). The same mechanism can be assumed also for the tubular film after irradiation, with the only difference that the critical (catastrophic) crack does not propagate from an incision artificially introduced into the edge

TABLE I
Tensile Strength σ_b and Strain at Break ϵ_b of Biaxially Oriented Blown Polyethylene Film

Sample history	Machine direction		Cross direction	
	σ_b , MPa	ϵ_b , %	σ_b , MPa	ϵ_b , %
As received ^a	24.4	630	20.6	1091
With incision 0.1 mm ^b	17.1	107	10.9	88
UV exposure 88 h ^a	27.9	616	24.2	936
UV exposure 204 h ^a	18.5	425	12.2	172

^a Specimen width 5 mm, gauge length 12.5 mm.

^b Specimen width 10 mm, gauge length 25 mm.

of the test piece, but originates in a site weakened by the localized photo-oxidative degradation. Figure 7 illustrates this structural model. Thus, the observed anisotropy of the effect of UV radiation on the mechanical behavior of the tubular film is the linchpin which joins the concept of elongated microdefects in the film with that of localized photodegradation to create a uniform structure.

However, alternatively to the above explanation based on anisometric voids, it is possible to consider the crack growth from isometric voids into an anisotropic material under uniaxial stress. Besides, Akay, Tinger, and Aydin⁸ report that the increasing degree of orientation (draw ratio) slows down the kinetics of photo-oxidative degradation in the bulk of the material as reflected by the carbonyl index. It is known that extremely oriented polyethylene exhibits an extraordinarily good resistance to photodegradation. In spite of this, the results reported by Akay et al.⁸ were obtained at an irradiation time longer by an order of magnitude than those used in this study. The carbonyl index method employed by them does not indicate any pronounced differences between samples oriented to various degrees up to 200 h of irradiation time. Thus, the volume and the localized effects of orientation on the degradation kinetics do not rule each other out, and both effects may even act simultaneously within a certain time interval.

Generally, a characteristic feature of the ultimate properties is their sensitivity to the presence of flaws in the material. This leads on the one hand to a considerable scatter of ultimate data, while on the other hand the possibility is provided to use just the ultimate properties in the detection of early stages of

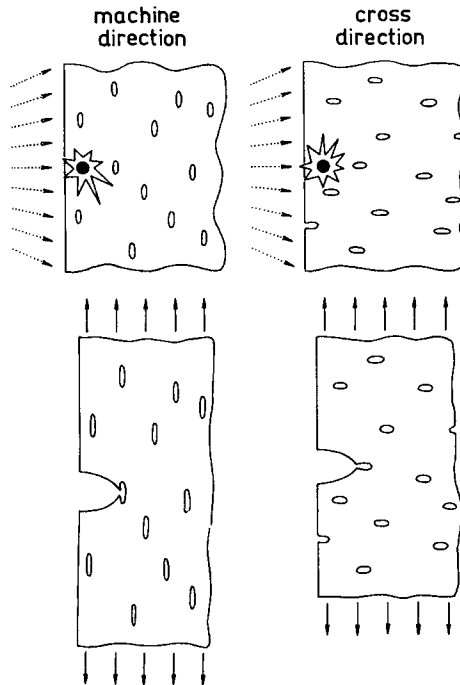


Fig. 7. Schematic model explaining the anisotropic embrittlement of a biaxially oriented blown film. In the site of localized photo-oxidative degradation, a crack develops which later interacts with an intrinsic system of elongated microdefects oriented by their longer axis along the machine direction.

those processes which occur localized in certain sites. This is, the case in stress corrosion, but especially in photodegradation. In the latter case, in particular, the stress-strain tests are a simple but very sensitive detection method, much more sensitive than the usual analytic spectral methods.

According to the weakest link hypothesis, it is the single, extreme, and most severe defect which decides the conditions of failure of the body. A considerable difference may exist, however, between this critical defect in a certain volume and an "average" defect, as revealed, e.g., by microscopic methods investigating some more or less randomly chosen regions of the material. It is just the weakest link mechanism that underlies the special position occupied by ultimate mechanical methods, not only among mechanical test, but in a more general sense in the whole system of physicochemical methods of characterization of polymeric materials. Ultimate mechanical methods are irreplaceable for the prediction of the behavior of materials under service conditions, while also providing valuable structural information which cannot be obtained by other methods. On the other hand, the ultimate mechanical data alone are usually insufficient for reliable structural interpretation; they must be combined with further mechanical or physicochemical characteristics. As indicated in this report, such a parallel use of different methods in the field of photo-oxidative degradation of polymers can still bring new useful information.

The authors are indebted to Mr. Gerth Jonsson, AB Celloplast, Norrköping, Sweden, and Dr. Arne Holmstöm, Swedish National Authority for Testing, Inspection and Metrology, Borås, Sweden, for the supply of polyethylene film and its basic characteristics; and to Mrs. L. Sladká, Institute of Macromolecular Chemistry, Prague, for technical assistance.

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Received August 21, 1981

Accepted December 28, 1981