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Mechanical properties of nylon 6 subjected to photodegradation

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The degradation of mechanical properties in nylon 6 films due to both oxidative and non-oxidative photodegradation is studied. It is shown that in a non-oxygen environment the rate of degradation is enhanced with rising temperature due to increases in quantum yield. Experimental results obtained on specimens exposed to natural weathering are found to be difficult to relate to those obtained by accelerated ageing. It is proposed and proven that the specific energy absorption in a tensile test (W_p) is an effective parameter for characterizing photodegradation in nylon.

1. Introduction

Nylon, like many other polymers, suffers considerable loss of mechanical properties due to photodegradation, i.e. the absorption of light in the visible and near-ultra-violet range. Although photodegradation can occur in the presence or absence of an oxygen environment, previous investigations [1–3] have been mainly concerned with oxidative degradation. There are fewer studies on the deleterious effects of non-oxidative degradation in nylon. Because of our particular interest in nylon as a parachute material, a research programme has been planned to determine the degradation of mechanical properties when nylon has been exposed to ultra-violet light both in air and in nitrogen. The degradation of nylon webbings, ropes and other structures is also of importance. Since temperature affects photodegradation in other polymers [4] this variable is included for study in the present research. Indeed George and Browne [5] have recently shown that thermal ageing at 80 ± 2° C in an oven has caused considerable strength loss in nylon 6,6 by an oxidation process which results in main chain scissions. However the interaction effects of heat ageing and light absorption, with or without oxygen, have not been firmly established and further work is needed. The present paper reports some preliminary experimental findings on the mechanical properties of nylon 6 which has been exposed to ultra-violet light ageing in air and in nitrogen respectively. To provide a basis of comparison and an indication of the equivalence of artificial ageing to natural ageing experimental results are also presented for nylon in the as-received condition and exposed to outdoor weathering.

Another purpose of the present study is to identify from these initial experimental results a more fundamental measure of strength than the commonly used parameters of elastic modulus (E) and ultimate tensile strength (σ_u), which would be sensitive to structural changes induced by photodegradation. In a recent study on composite propellants subjected to accelerated thermal ageing Marom *et al.* [6] suggested that the specific tearing energy (T_c) is independent of both test configurations and specimen geometries and thus would be a suitable candidate. The present authors cannot fully agree with the suggestion that T_c is specimen geometry independent although Anderton and Treloar [7] have shown that for polyethylene T_c obtained in a "trouser-leg" specimen is apparently the same as the cleavage specific fracture energy (G_c) determined from a double-cantilever-beam testpiece.* There is a clear difference between the modes of fracture in a

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*There are in fact some doubts as to whether linear elastic fracture mechanics concepts can be applied to some of the tougher polyethylenes studied in [7] using double-cantilever-beam specimens with beam depths of only 14 mm. Yielding in the beams could have occurred before cracking commenced.

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"trouser-leg" test, which is in predominantly a shearing mode, and that in a cleavage test, which is essentially in the opening mode. In ductile fracture, it is the deformation and fracture of the process zone that determines the specific fracture work [8, 9]. Our recent experiments on ductile fracture of nylon and polyethylene show that, in deep-edge-notched tension testpieces, after the process zone is fully developed across the ligament, it is cold-drawn as cracking proceeds. However, cold-drawing has not been observed to any significant extent in the "trouser-leg" tear tests. The thickness reductions on the section near the fractured surfaces confirm that tearing and cleavage are due to different mechanisms. Thus any agreement between G_c and T_c must be treated as simply fortuitous. In the present work, nevertheless, the suitability of T_c for characterizing the photodegradation of nylon is assessed. In addition an alternative fracture energy absorption parameter, W_p, defined as the area under the tensile stress–strain curve is studied. This is shown to be a more sensitive property to photodegradation in nylon than T_c which is suggested by Marom *et al.* [6]. If the fracture process zone width (d) can be identified as approximately equal to the film thickness (B) Hahn *et al.* [10] have shown that

$$G_c = W_p d \approx W_p B. \qquad (1)$$

This thus provides an indirect method of measuring G_c which is a fundamental material property.

2. Experimental work

The material used in this work was nylon 6 supplied by Cadillac Plastics Pty. Ltd. (Australia) in the form of 1 mm thick films. The nylon 6 had no u.v. stabilizers or any other additives. For photodegradation experiments rectangular sheets measuring 500 mm × 1000 mm were erected in racks exposed to tungsten mercury sunlamps (Philips model MLU 300W) at a distance of 500 mm. The relative spectral energy distribution, at 500 mm is given in Table I. For oxidative photodegradation the irradiation experiments were conducted in the open atmosphere of the laboratory at 25 ± 2° C. But for non-oxidative photodegradation, the irradiation of the nylon sheets was carried out in an airtight sealed chamber filled with nitrogen gas at 45 and 65° C respectively. The temperature was varied by means of a small radiator and fan. Nylon sheets were also exposed to natural weathering mounted on frames at 45° to the horizontal and placed on the rooftop of the Mechanical Engineering Building facing north so as to receive the maximum possible amount of sunlight (Standards ASTM D1435, As CK24.1).

TABLE I U.v. radiation at 500 mm from the lamp

	Wave length (nm)	Radiation (mW cm^{-2})
UV–A	400–315	1.69
UV–B	315–280	0.88
UV–C	< 280	0.01

Random samples were retrieved from the nylon sheets at regular intervals during the various ageing processes and were identified and then placed in separate black plastic bags before they were tested. Both tensile and "trouser-leg" tear experiments were performed on these samples according to the standards ASTM 882-75b and ASTM 1938-67 respectively in an Instron machine. The cross-head speed for the tensile tests was 10 mm min^{-1} and that for the tear experiments was 20 mm min^{-1}. From the tensile tests the Young's modulus (E), elongation-to-fracture (ϵ_f) and ultimate tensile strength (σ_u) are obtained. From the "trouser-leg" tear tests, typical records of which are shown in Fig. 1, the specific tear resistance at crack initiation (T_i) and at maximum load (T_m) are given by

$$T_i = 2P_i/B \qquad (2)$$

and

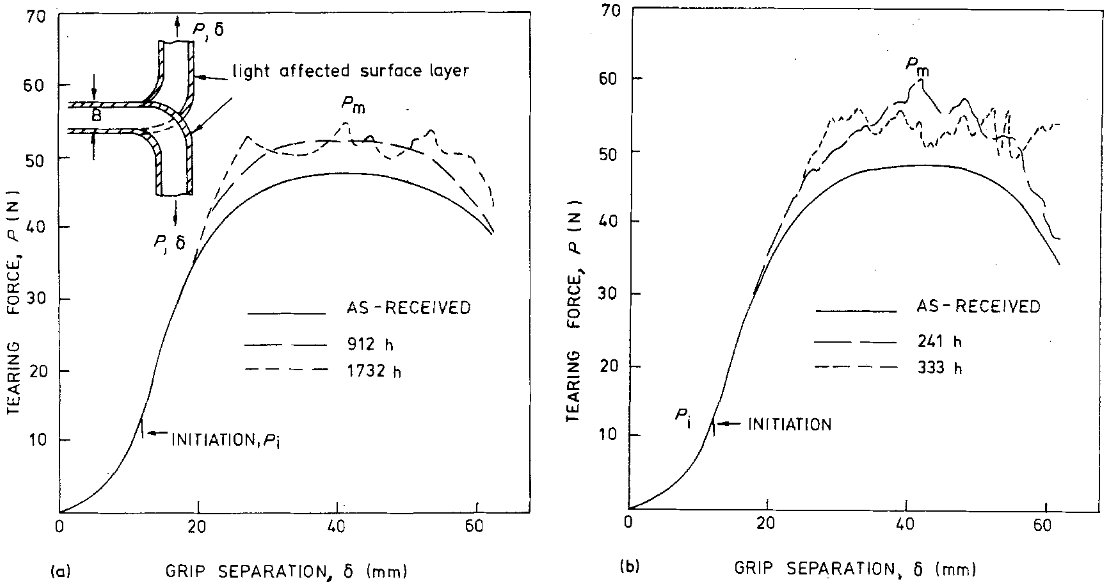
$$T_m = 2P_m/B, \qquad (3)$$

where P_i and P_m are the initiation and maximum loads respectively. In addition the average specific tear resistance (T_c) defined as the ratio of the total work required to completely tear the specimen (i.e. the work area under the load–displacement diagram as shown in Fig. 1a to c) and the newly created fracture surfaces is obtained.

3. Results and discussion

3.1. Tensile properties and photodegradation

The change in the tensile properties, E, σ_u and ϵ_f with sunlamp exposure time up to 1700 h in air and in nitrogen are shown in Figs 2 to 4. It was not possible to retrieve samples from the nylon sheets exposed at 65° C in nitrogen exceeding 400 h because upon cutting the sheet it shattered indicating that significant embrittlement had occurred. In the non-oxygen environment light-induced degradation is not an oxidative but rather



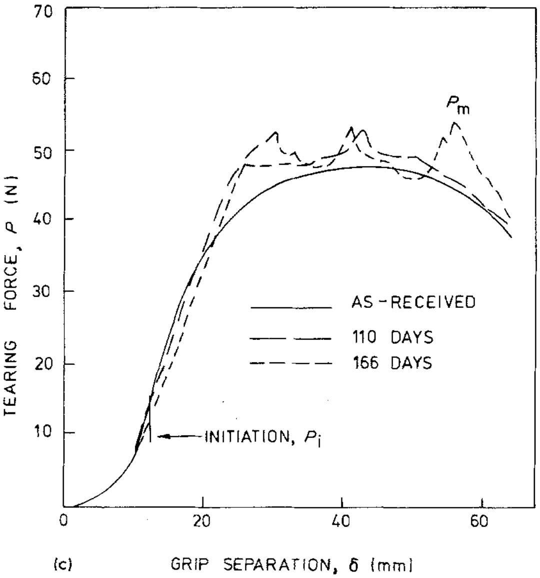


Figure 1 Typical load–displacement records for tear tests on nylon 6 subjected to sunlamp exposure (a) in air at 25° C, (b) nitrogen at 65° C and (c) natural weathering.

a photolytic effect. It is possible for nylon 6 to undergo structural changes by cross-linking or by main chain scissioning by photon absorption, the effectiveness of which can be measured by the quantum yield. From the results shown in these figures it is clear that at 45° C in nitrogen both the ultimate tensile strength and Young's modulus increase with exposure time up to 1000 h due to a plausible light-induced cross-linking mechanism. However there is a tendency for these mechanical properties to decrease for exposure periods over 1000 h as the main chain scission mechanism assisted by thermal effects becomes predominant. The elongation-to-fracture decreases continuously with ageing time, a phenomenon compatible with polymer embrittlement. As the temperature was raised to 65° C the photodegradation effect became more obvious. Young's modulus (E) intitially increased to twice its original value at about 300 h exposure time and then decreased; σ_u and ϵ_f both decreased significantly with ageing period when compared with the corresponding results at 45° C. Since temperature does not affect light absorption rate [4], but light-induced degradation is worse at higher temperatures, it seems that the quantum yield for chain scission must have increased with temperature. This suggestion is certainly not new as Guillet [11] has shown previously that in the photolysis of MMA–MVK (3%) co-polymer and indeed in some other polymers the rate of degradation by chain scissioning increases with temperature.

In an oxygen environment the ultra-violet light acts as an initiator to an oxidation process that occurs in nylon as a free-radical chain reaction [2, 5]. Oxidation leads to chain scissioning which in turn lowers the molecular weight and reduces the strength of the polymer. If ultra-violet radiation is excluded, the degradation process is slowed down [3]. As shown in Figs 2 and 3, the Young's modulus remains essentially constant and there is only a slight trend for σ_u to decrease with irradiation time in the laboratory. However the

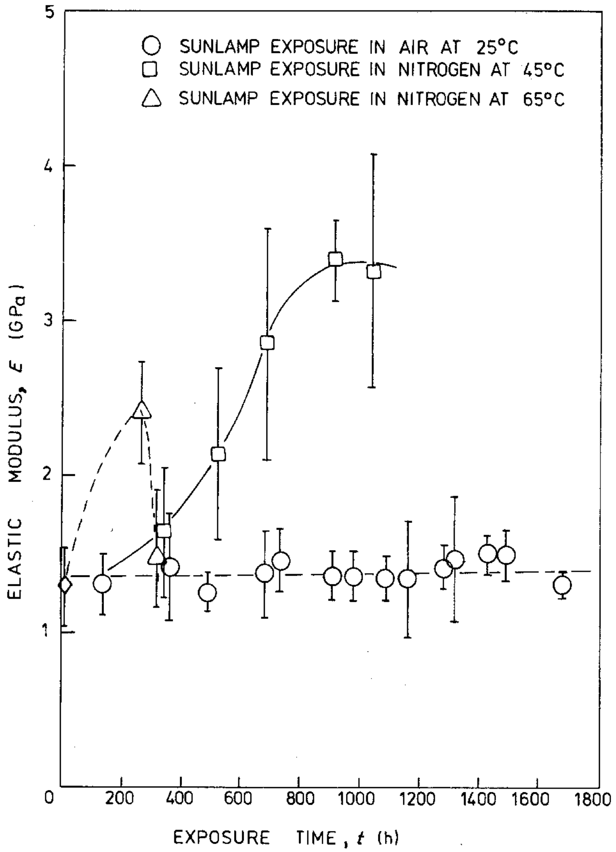


Figure 2 Variation of elastic modulus with sunlamp exposure time. Bars indicate one standard deviation, sample size of 8.

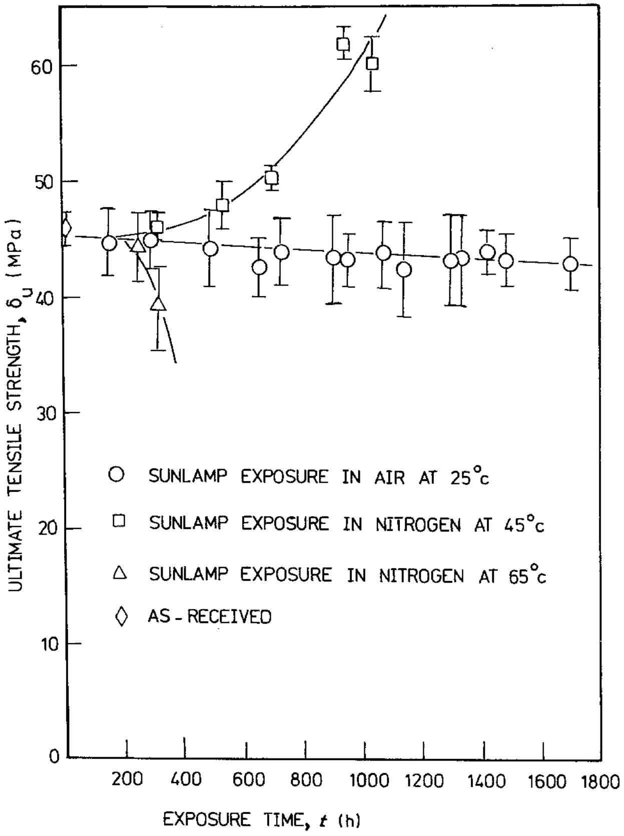


Figure 3 Variation of ultimate tensile strength with sunlamp exposure time. Bars indicate one standard deviation and sample size of 8.

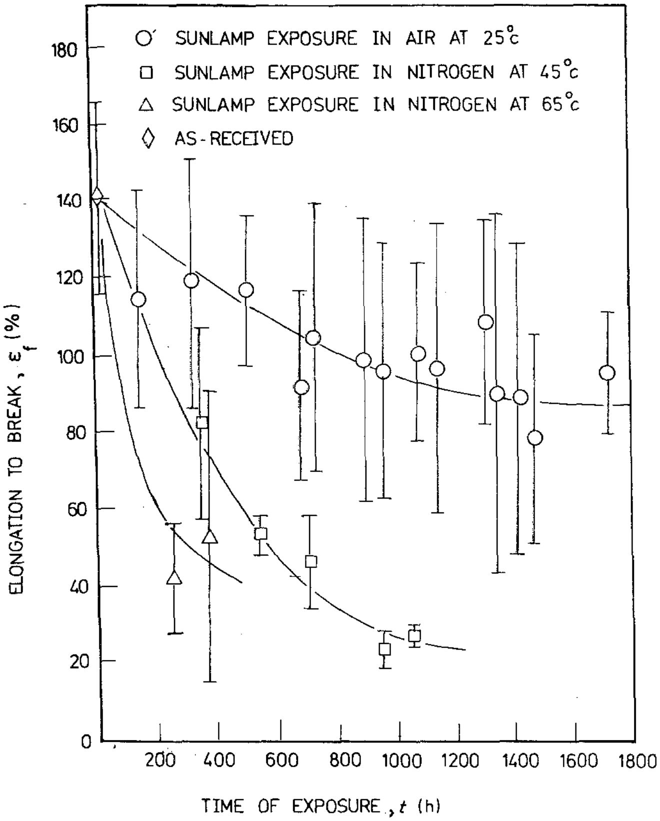


Figure 4 Variation of elongation to break with sunlamp exposure time. Bars indicate one standard deviation and sample size of 8.

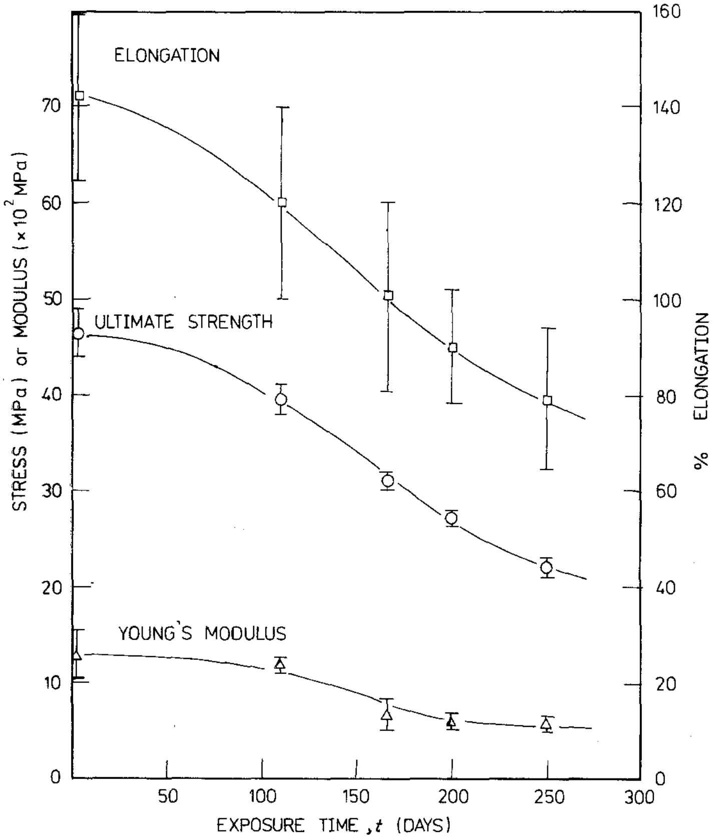


Figure 5 Variation of elastic modulus, ultimate tensile strength and elongation to break with natural ageing time. Bars indicate one standard deviation and sample size of 8.

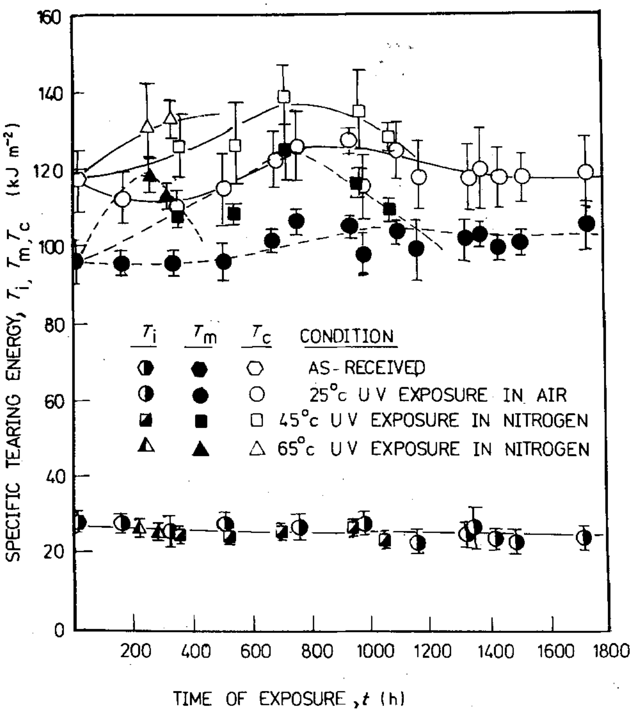


Figure 6 Variation of specific tearing energy at initiation (T_i), maximum load (T_m) and work of fracture (T_c) with sunlamp exposure time. Bars indicate one standard deviation and sample size of 5.

elongation-to-break (ϵ_f), Fig. 4, has provided some definite evidence of degradation in the material. We have not yet completed experiments at other elevated temperatures but it is expected that the oxidation induced chain scission effect will be enhanced.

Fig. 5 shows the results for nylon samples subjected to natural weathering during the period

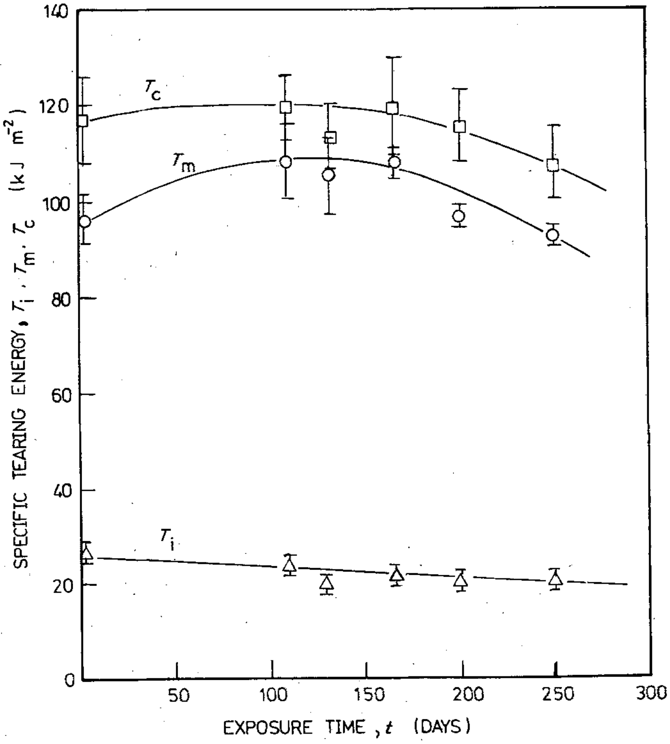


Figure 7 Variation of specific tearing energies, T_i, T_m and T_c, with natural ageing time. Bars indicate one standard deviation and sample size of 5.

April to December. Clearly all the tensile properties, E, σ_u and ϵ_f, decrease with exposure period as a direct consequence of chain scission.

No records were kept of temperature or humidity for the naturally weathered samples and thus only very general comparisons can be made. For example, sunlamp exposure in the open atmosphere of the laboratory at 25° C for 1730 h gives E and σ_u values equivalent to approximately 100 days natural ageing but ϵ_f values equivalent to 170 to 200 days natural weathering. Another complicated effect is the differential moisture contents in the samples aged in the laboratory under controlled conditions and those naturally aged where moisture absorption from precipitation is uncontrolled. In the light of these difficulties, it seems that the non-destructive technique of phosphorescence spectroscopy developed by George and Browne [5] provides the best solution to the problem of predicting strength loss from accelerated ageing test results. It would however be useful to confirm whether the technique gives the correct predictions for other mechanical properties such as ϵ_f, E and T_c.

3.2. Specific tear energy and photodegradation

The specific tearing energies, T_i, T_m and T_c, for the nylon samples subjected to photodegradation of various means are given in Figs 6 and 7 respectively. These results seem very high but they are of the same order of magnitude as those reported for polyethylenes [7] and polypropylenes [12]. Within experimental limits T_i is independent of ageing period, whether exposed to sunlamp in air or in nitrogen. Under laboratory conditions, both T_m and T_c are rather independent of sunlamp exposure period. However in the nitrogen environment, these quantities show an initial increase with ageing time to maximum followed by a decrease for longer periods (see Fig. 6) in agreement with the variation of Young's modulus shown in Fig. 2. When subjected to natural weathering, Fig. 7, T_i shows a 25% reduction after 250 days when compared with the as-received material, however, T_c only shows an 8% decrease.

It may be useful to point out some interesting features of the tearing tests and to explain why the tearing energies, whether T_i, T_m or T_c, as shown in Figs 6 and 7 are not as sensitive to structural changes due to photodegradation as would for example ϵ_f given in Fig. 4. Since light absorption does not penetrate deeply past the surface it follows that any structural changes and thus degradation effects will be mainly confined to the first few μm. The inside thickness material may be considered as relatively undegraded. In the "trouser-leg" tests, the tearing work as shown in the inset of Fig. 1a is the sum of those required to tear the light affected surface layers and the middle undegraded layer. If there is cross-linking in the surface layers the tearing force is increased and if chain scissioning predominates the force is reduced. However since the light affected layers are so thin compared with the undegraded middle layer the tearing energies, T_i, T_m and T_c, are therefore not expected, as shown in this work, to vary considerably with light ageing or natural weathering period. This conclusion is confirmed upon noting that all fractured surfaces show similar thickness reductions after the tear tests are completed. It seems therefore that the suggestion by Marom *et al.* [6] to use T_c or T_m as a material parameter to characterize the extent of photodegradation in nylon 6, is inapplicable. In their work on propellant composites the ageing effect is throughout the specimen thickness so that both T_c and T_m are useful material parameters.

As shown in Fig. 1a to c there are two forms of tearing force curves, one is "smooth" and the other is "stick–slip". In the "smooth" case the cracking is continuous and occurs for nylons in the as-received condition and for short periods of light exposure. In the "stick–slip" case cracking proceeds in a series of unstable jumps presumably caused by the intermittent fracture of the photodegraded surface layers. The magnitude of "stick–slip" appears to increase with ageing period.

3.3. Specific energy absorption as an index of photodegradation

In the previous section it is shown that T_c and T_m are not sensitive to photodegradation in nylon 6 although they are physically much more appealing parameters than E, σ_u and ϵ_f. Inspection of Figs 2 to 4 suggests that ϵ_f is the most effective measure of photodegradation. However in order to incorporate the two other tensile properties E and σ_u it is proposed here to use the area under the stress–strain curve (W_p) (strictly speaking true stress–strain curves should be used in Equation 1, as an effective index of photodegradation. As shown in Figs 8 and 9 this seems promising. Another advantage of this parameter (i.e. W_p) is

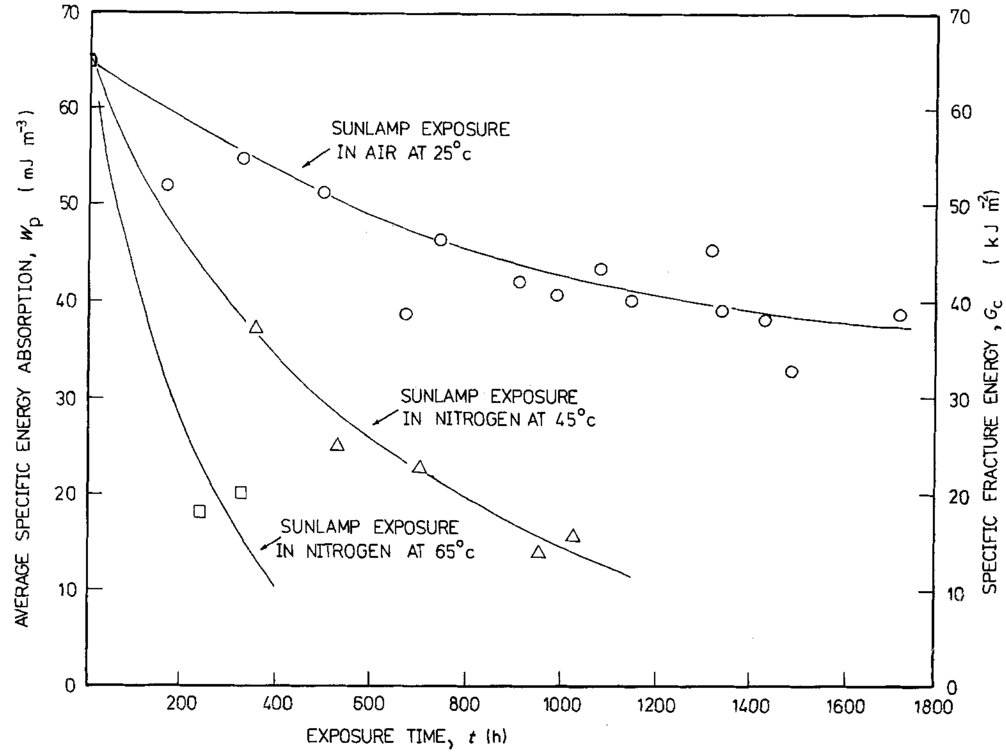


Figure 8 Variation of specific energy absorption with sunlamp exposure time.

that G_c can be approximately calculated from Equation 1* if the fracture process zone width is taken as about 1 mm, the sheet thickness. Thus Figs 8 and 9 also represent the variation of fracture surface energies (G_c) with ageing period. Clearly, G_c decreases with photodegradation.

Two points must be mentioned here. Firstly, $G_c \neq T_c$, e.g. in the as-received condition G_c ($65\,\mathrm{kJ\,m^{-2}}$) $\div$ $1/2T_c$ ($120\,\mathrm{kJ\,m^{-2}}$). This means that fracture surface energies in ductile materials such as nylon 6 studied here, are geometry dependent because as discussed in Section 1 the process zone

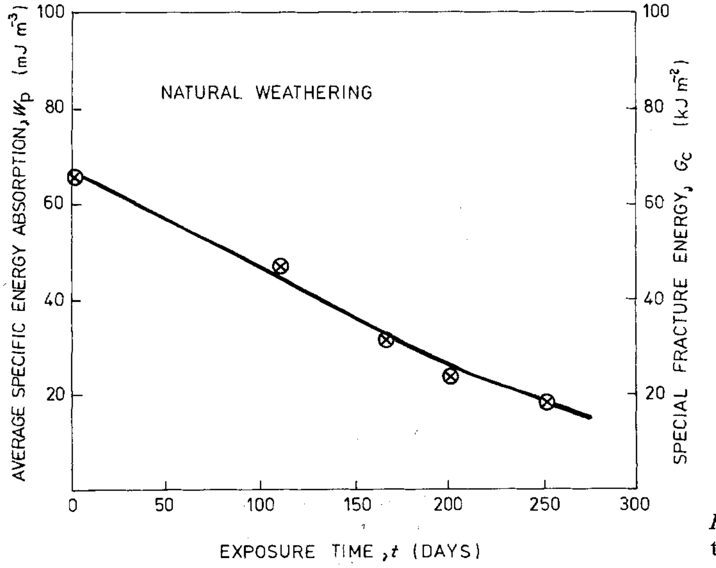


Figure 9 Variation of specific energy absorption with natural ageing time.

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*An exact method of estimating the work absorbed in the fracture process zone is given in [9]. For the present study since fracture mechanics experiments have not been thoroughly carried out Equation 1 although approximate, will be used here.

size depends on the specimen geometry. Secondly, the surface layers that are photodegraded behave differently in a tensile test to a "trouser-leg" test. In a tensile test the specimen is like a layered composite with two embrittled outside layers and a middle tough layer of undegraded material. It has been shown theoretically by Atkins and Mai [13] and proven experimentally by Guild *et al.* [14] and Yap [15] that brittle fracture can occur in such a composite system. It is thus suggested that, because of the constraints of the photodegraded layers exerted on the middle layer, depending on the ageing period, "brittle" fracture of varying degrees occurs in nylon 6 specimens. "Brittle" is used here to mean reduction in ductility or toughness. In fact all tensile tests fail beyond the yield strength.

4. Conclusions

The loss of mechanical properties in nylon 6 due to oxidative and non-oxidative photodegradation has been studied in this paper. At the time of writing it has not been possible to assess the effects of oxygen on photodegradation from these preliminary experiments because the temperatures are not comparable. In the non-oxygen environment it is however shown that photodegradation increases with rising temperature. Experimental results are also obtained on nylon specimens subjected to natural weathering but it is not possible to relate them to those by accelerated ageing. The specific tearing energy, T_c or T_m, is not a suitable candidate for characterizing photodegradation in nylon. Instead it is proposed and shown that W_p, the specific energy absorption given by the area under the tensile stress–strain curve, provides a better index of photodegradation.

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