

Notes

Oxidative and Nonoxidative Photodegradation of Nylon 6

In a previous paper¹ we have studied the effects of photodegradation on the mechanical properties of nylon-6 films. We suggest that, if used independently, the common mechanical properties such as yield (σ_y) and ultimate (σ_u) tensile strengths, elastic modulus (E), and elongation to break (ϵ_f) are not suitable parameters for characterizing the damages caused by photodegradation. To incorporate the combined effects of these properties, we have shown that the area under the tensile stress-strain curve (W_p) provides a better index of photodegradation.¹ W_p may also be related approximately to a fundamental material property, $G_c (=W_p B$, where B is the specimen thickness), which is the specific fracture resistance. It has been previously suggested by others² that the specific tear resistance (T) determined from the "trouser" test is independent of both test configurations and specimen geometries and is thus a good measure of polymer degradation. Supporting evidence is given for composite propellants subjected to accelerated thermal aging where *bulk* changes in the material have occurred.² However, we have shown¹ that T is, in theory, geometry-dependent and that it is not very sensitive to photodegradation of nylon 6 since any degradation effects will be confined to the first few μm on the surfaces and the inside thickness material is relatively undegraded. The tearing work done on the degraded surface layers cannot affect to any significant extent the total tearing work (T) for the full thickness. In a tensile test, however, the embrittled surfaces can provide enough constraint on the deformation of the middle layer^{3,4} so that "brittle" fracture of varying degree depending on the aging period occurs in the nylon-6 specimens.

It was not possible in the previous work¹ to assess the relative effects of oxygen (oxidative) and nitrogen (nonoxidative) on photodegradation because the test temperatures were not comparable. We have since rebuilt the test chamber equipped with an air conditioner so that oxidative and nonoxidative photodegradation experiments can be conducted at the same temperature, thus avoiding the thermal aging effect which is known to occur in nylon.⁵ The test temperature may be varied between 30°C and 70°C by varying the thermostat control. Silica gel was placed inside the chamber as desiccant to eliminate any hydrolysis effect. In this note we report some preliminary results on photodegradation of nylon 6 due to oxygen and nitrogen at 30°C. The effect of thermal aging in nitrogen is also discussed. The nylon-6 material, the irradiation equipment, and the test procedures for the tensile and "trouser" tear experiments (ASTM 882-756 and ASTM 1938-67) were the same as those described in our previous paper.¹

Figure 1 shows the variation of the ultimate tensile strength (σ_u) and the elongation to break (ϵ_f) with sunlamp exposure time at 30°C. The relative effects of oxygen to nitrogen are obvious from these results. Oxidative photodegradation leads to main chain scissioning, which in turn reduces the strength of the polymer. However, as shown in Figure 1, the ultimate tensile strength is independent of exposure time up to 800 h. Evidence of oxidative degradation is, nevertheless, available through the ultimate elongation results. In nonoxidative photodegradation both main chain scissioning and crosslinking can occur by photon absorption. From the results shown in Figure 1 it seems that, for the time scale of the experiments, crosslinking is the more effective mechanism, thus increasing σ_u with exposure time. The ultimate elongation is not significantly affected by nonoxidative photodegradation. It is, however, possible that with longer exposure to the sunlamp crosslinking gives way to main chain scissioning so that both σ_u and ϵ_f will eventually decrease.

The specific tear resistance (T) are rather independent of aging period in the presence of oxygen and vary within $\pm 10\%$ of the mean value of 120 kJ/m² for the as-received material. In the nitrogen environment the mean T value increases slightly with aging time to a maximum of 140 kJ/m² at approximately 500-h sunlamp exposure. This can be explained in terms of the crosslinking having taken place in the surface layers. However, the variation is not large enough to provide a sensitive degradation index to photon absorption. Indeed, "degradation" is a misnomer here since there is no reduction in T . Therefore, as explained previously,¹ it is better to use W_p to characterize the light-induced degradation of the polymer.

The specific energy absorption (W_p) for both oxidative and nonoxidative photodegradation of nylon 6 is shown as a function of exposure time in Figure 2. Clearly, there is not much difference in W_p for exposure periods less than 400 h. For longer times of exposure, oxidative photodegradation is more severe than in a nitrogen atmosphere. This indicates without doubt that at isothermal conditions oxygen enhances photodegradation of this polymeric material.

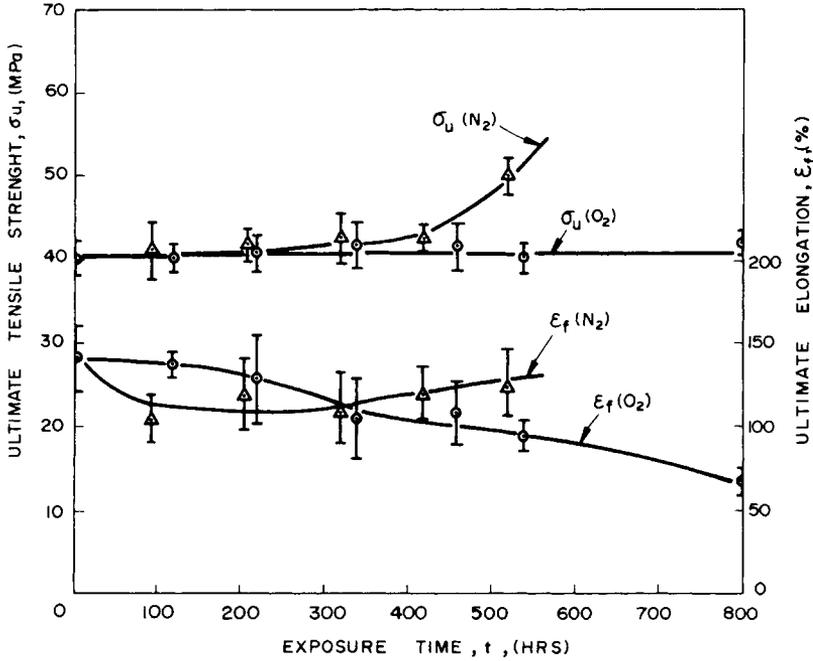


Fig. 1. Variation of ultimate tensile strength (σ_u) and elongation to break (ϵ_f) with sunlamp exposure time at 30°C. Bars indicate one standard deviation, sample size of 5. (Δ) Nitrogen; (\odot) oxygen.

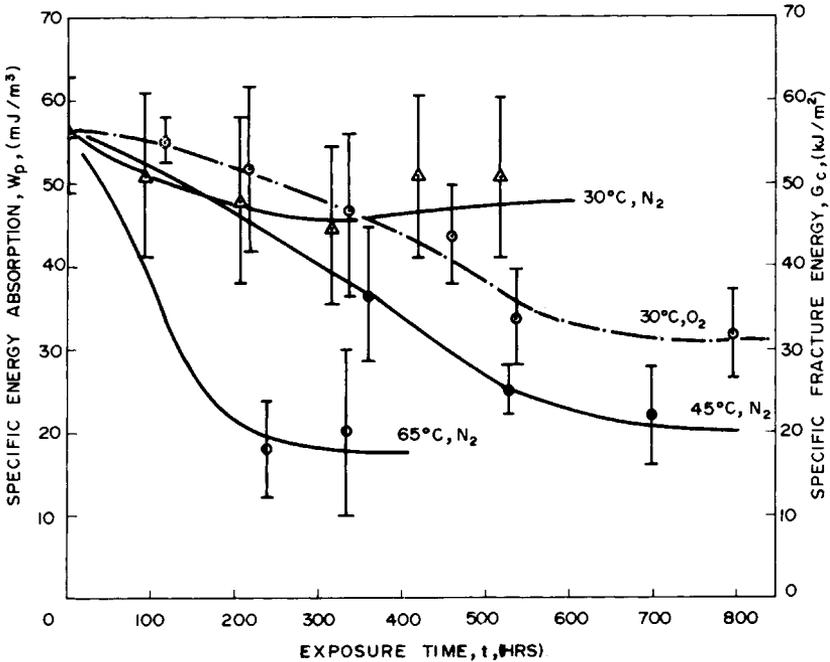


Fig. 2. Variation of specific energy absorption (W_p) with sunlamp exposure time. Bars indicate one standard deviation, sample size of 5. (\odot) Oxygen at 30°C; (Δ) nitrogen at 30°C; (\bullet) nitrogen at 45°C; (\bullet) nitrogen at 65°C.

To study the effect of temperature in nonoxidative photodegradation, the specific energy absorption results at 45°C and 65°C are superimposed in Figure 2. Since temperature does not affect light absorption rate, these data indicate that the quantum yield for chain scissioning must have increased with temperature so that photodegradation is worse at higher temperatures. Chain scissioning is known to be enhanced at or above the glass transition temperature of the polymer. For nylon 6 this is about 50°C. It is therefore not unexpected that at 65°C the embrittlement is the most severe (Fig. 2) and the ultimate strength always decreases with exposure time,¹ indicating that crosslinking does not take place at this high temperature.

Although the deleterious effect of oxygen on photodegradation of nylon 6 at 30°C is clearly demonstrated here, we are not in a position yet to assess the oxygen effect at higher temperatures until such data are obtained.

We wish to thank Mr. D. Head and Mr. N. Yates for experimental assistance in the course of this work.

References

1. Y. W. Mai, D. R. Head, B. Cotterell, and B. W. Roberts, *J. Mater. Sci.*, **15**, 3057 (1980).
2. G. Marom, E. Harel, and J. Rosner, *J. Appl. Polymer Sci.*, **21**, 1629 (1977).
3. A. G. Atkins and Y. W. Mai, *Int. J. Fract.*, **12**, 923 (1976).
4. O. F. Yap, Y. W. Mai, and B. Cotterell, *Proceedings of the International Conference on Analytical and Experimental Fracture Mechanics*, G. C. Sih and M. Mirabile, Eds., Sijthoff and Noordhoff, Netherlands, pp. 919-930.
5. G. A. George and N. McM. Brown, "Non-Destructive Evaluation of the Degradation of Nylon 6,6 Parachute Materials," Report No. MRL-R-691, Materials Research Laboratories, Department of Defence, Melbourne, Australia, June 1977.

Y. W. MAI
B. COTTERELL

Department of Mechanical Engineering
University of Sydney
Sydney, N.S.W. 2006 Australia

Received April 5, 1982
Accepted July 14, 1982