

Photo-oxidative degradation of nylon 66 under accelerated weathering

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The photo-oxidative degradation study of nylon 66 was carried out in a polychromatic irradiation chamber (Sepap 12/24, $\lambda \geq 290$ nm) at 60°C in air. The extent of photo-oxidation was monitored by Fourier transform infrared spectrometry. The sample underwent extensive changes in hydroxyl, carbonyl and amorphous region of infrared upon irradiations. The photo-products were characterized by i.r. and ultraviolet spectroscopy. The broadening of hydroxyl and carbonyl absorption bands indicated more than one species. The photo-oxidation mechanism implies the same intermediate photo-products. The kinetics of the photo-degradation also has been studied. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Degradation is a crucial factor, which causes deterioration of the useful properties of polymeric materials. Nylon 66 degradation has been studied widely during the past decades by several authors^{1–4}. It severely changes in chemical, physical and mechanical properties upon natural/artificial weathering. The degree of changes depends on the wavelength of the u.v. light, and the atmospheric conditions. Various techniques have been used to characterize the photo-degradation in nylon 66. Moore² compared photo-degradation products obtained from the model amides and polyamides and characterized them by several techniques like loss in tenacity, change in intrinsic viscosity, u.v. spectrophotometry and end group analysis. The hydroperoxide analysis and second derivative of u.v. spectroscopy are also important and have been used to characterize photo-degradation in polyamides^{5–8}. Allen *et al.*^{9–12} have studied the photochemistry of nylon polymers in details. Kinetics of photo-aging has been widely studied^{2,4,10,12} for nylon 66. Although a few workers have studied nylon photo-oxidation^{13–16} but the photo-oxidative kinetics is not well defined. Do *et al.*¹³ studied the photo-degradation and photo-oxidation in nylon films by FTi.r. spectroscopy. They also studied the evolution of gases and change in crystallinity with u.v. exposure.

To improve all aspects of the stability of polymers, a fundamental understanding of the degradation process involved is essential, therefore in the present study we have made an attempt to study the chemical and physical changes in nylon 66 with polychromatic irradiation ($\lambda \geq 290$ nm).

EXPERIMENTAL

Materials

Commercial samples of nylon 66 (Zytel 101 L NC 10) were received from M/s E.I. Dupont de Nemours (USA) and used without further purification.

Experimental procedure

Thin films (thickness ~ 50 μm) of commercial nylon 66 were prepared by pressing the polymers in a preheated Carver press at 270°C under ~ 14 kg/cm² pressure for 2 min. The films were quench cooled rapidly in the press. All samples were irradiated in a Sepap 12/24 (an accelerated photo-irradiation chamber $\lambda \geq 290$ nm) at 60°C for different time intervals. The details of this equipment are given elsewhere¹⁷. Photo-oxidative products and kinetics of photo-degradation were studied by FTi.r. (Fourier Transform Infrared 16 PC spectrometer). The ultraviolet absorption measurement for thin films (~ 50 μm) were carried out on a Hewlett-Packard 8452A Diode Array Spectrophotometer.

RESULTS AND DISCUSSION

FTi.r. spectroscopy was used to characterize the photo-oxidation in the polymer films. changes in hydroxyl region (3700–3200 cm⁻¹) during the photo-irradiation are quite different than that usually observed in polyolefines and styrenic polymers^{18,19}. *Figure 1*. shows that already formed hydroperoxides, which might have been generated during the melt processing of the polymer, are decomposed upon photo-irradiation. The rate of decomposition of the hydroperoxide/hydroxyl group is much faster than that of generation during the initial period of photo-oxidation, which leads to a decrease in the absorbance range of 3700–3200 cm⁻¹ in the initial 100 h irradiation, but subsequently there is no consistency in the changes, as shown in *Figure 2*. Decomposition of hydroperoxide/hydroxyl species can form imide or aldehyde, respectively²⁰

The i.r. spectral changes in the 1690–1800 cm⁻¹ region with exposure time are shown in *Figure 3*. The increase in the absorbance with irradiation time in this region indicates an increase in the imide group population. From *Figure 2*, it is also clear that there is a continuous increase in carbonyl absorption; moreover, the increase is more rapid during the initial period of exposure (up to 100 h), after which it continues to increase but at a slower rate. This observation gives perfect evidence about the decomposition of hydroperoxide/hydroxyl

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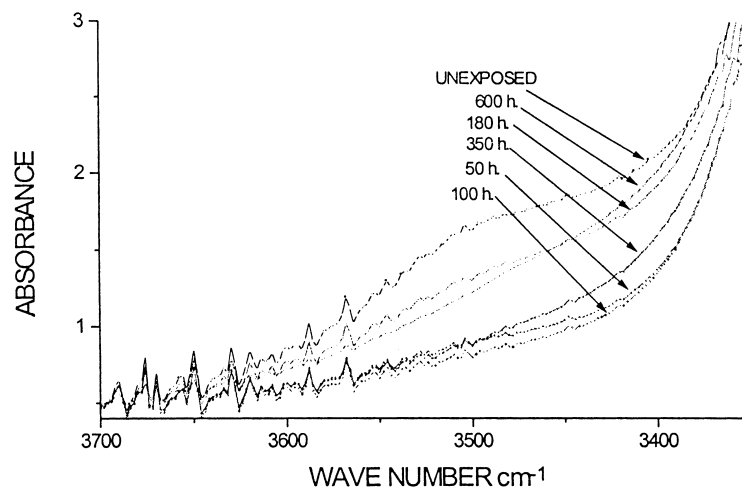


Figure 1 FTi.r. spectral changes in the hydroxyl region of polychromatic irradiated nylon 66 samples

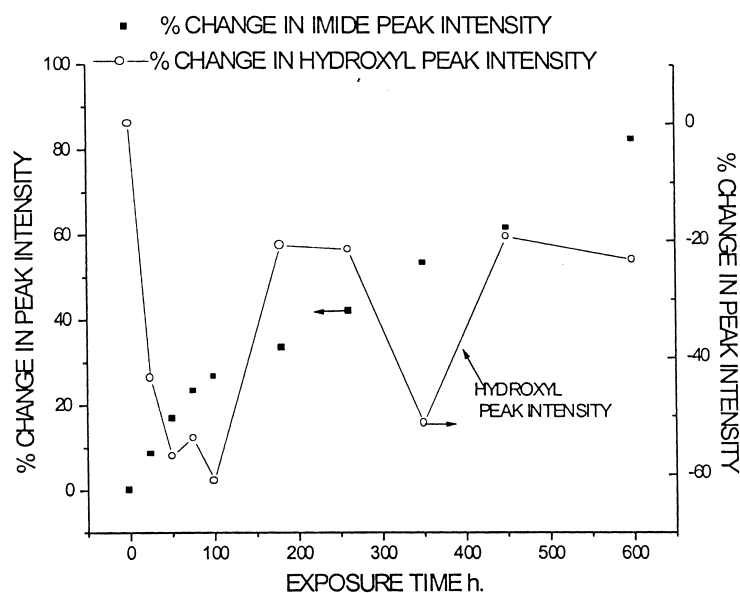


Figure 2 Rate of hydroperoxide decomposition/imide group formation with irradiation time

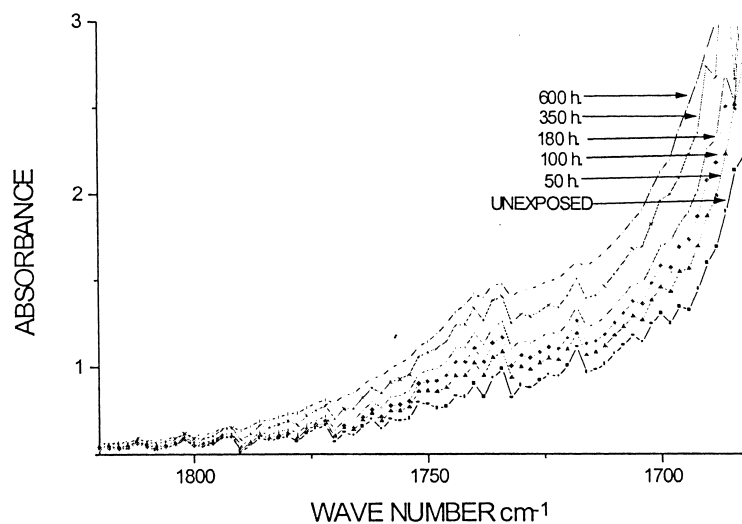
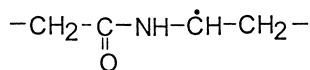


Figure 3 FTi.r. spectral changes in the carbonyl region of polychromatic irradiated nylon 66 samples

groups in the carbonyl groups. A direct increase in carbonyl group concentration with irradiation time is an indication of the prevalence of a single photo-oxidation mechanism throughout the photo-oxidation process.

As per the mechanism suggested for photo-oxidation of model polyamides^{2,19,20}, it was observed that the primary free radical formed upon u.v. irradiation is



which suggests that there should be continuous decay of the $-\text{CH}_2-(\text{NH})-$ population. We also have tried to study the kinetics of $-\text{CH}_2-(\text{NH})-$ decomposition with exposure time. The absorption band at 1180 cm^{-1} is due to the $-\text{CH}_2-(\text{NH})-$ group, and we found that the population of the methylene group, vicinal to the $-\text{NH}-$ group, decreases linearly with irradiation time (Figure 4). This is an additional evidence to the mechanism suggested by Do *et al.*¹³ that decomposition of hydroperoxides leads to the formation of carbonyl groups:

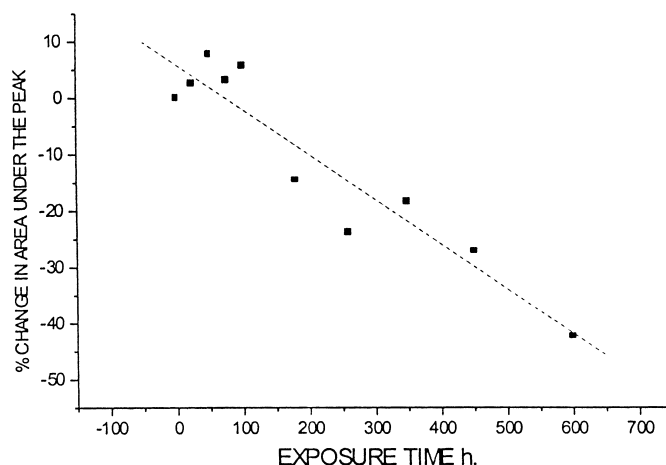
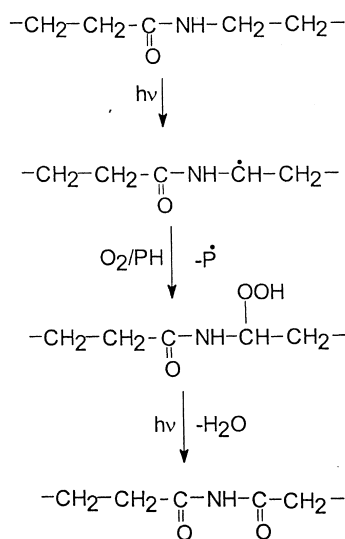


Figure 4 Change (%) in the methylene group adjacent to the $-\text{NH}-$ group with irradiation time

The nylon 66 absorption band at 1139 cm^{-1} is reported²¹ to be due to an amorphous region in the nylon matrix. Figure 5 shows that the amorphous region is the only site for photo-oxidation, and it decomposes continuously with exposure time. Somewhat similar results were observed by Do *et al.*¹³ during exposure of nylon 66 by short wavelength irradiation ($\lambda = 254\text{ nm}$). The reason for the exclusive decomposition of the amorphous region may be because of the lower oxygen diffusivity and permeability for nylon 66. This phenomenon might have limited photo-oxidation to the amorphous region only where oxygen diffusion would be sufficient to oxidize the polymer.

Exposure of nylon 66 films to polychromatic radiation led to the development of a u.v. band at $\sim 244\text{ nm}$. The spectra shown in Figure 6 are in the form of a spectral subtraction of the unexposed sample spectra from each of the spectra of the photo-oxidized sample at different times.

Figure 7 shows that the peak height increases continuously with exposure time. Increase in peak height with exposure time is due to the formation of imide groups. The nature of the kinetic curves in Figures 2, and 7 is similar, as already reported²² for open chain imides, which show a tail which extends out to 280 nm and points of inflection in the region of 250 and 230 nm . Allen *et al.* reported¹² peaks at ~ 230 and 294 nm in u.v. spectra (due to α,β -unsaturated carbonyl species), but we did not observe the same in our studies.

CONCLUSION

The presence of hydroperoxide groups in melt-processed films was found in quite a high concentration; this, according to us, is the main driving force for the higher rate of photo-oxidation during the initial period of exposure. The continuous increase in carbonyl group concentration indicates the existence of a single photo-oxidation mechanism throughout the oxidation process. The primary photo-oxidation process in polyamide is the oxidation of the methylene group adjacent to the $-\text{NH}-$ group. Physical changes in the polymer matrix, such as the disappearance of the amorphous phase with exposure time, is the main evidence for the effectiveness of photo-oxidation in the amorphous phase. Finally, the u.v. absorption study suggests that the increase in u.v. absorption at 244 nm is due to imide formation.

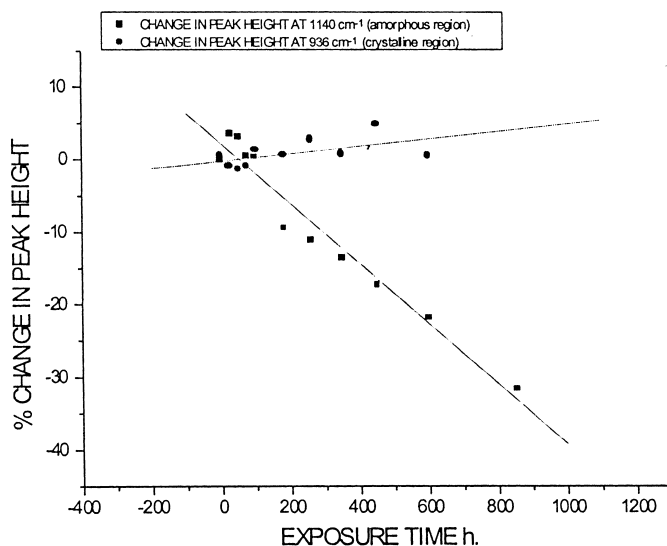


Figure 5 Variation in amorphous (1139 cm⁻¹) and crystalline (936 cm⁻¹) regions upon irradiation

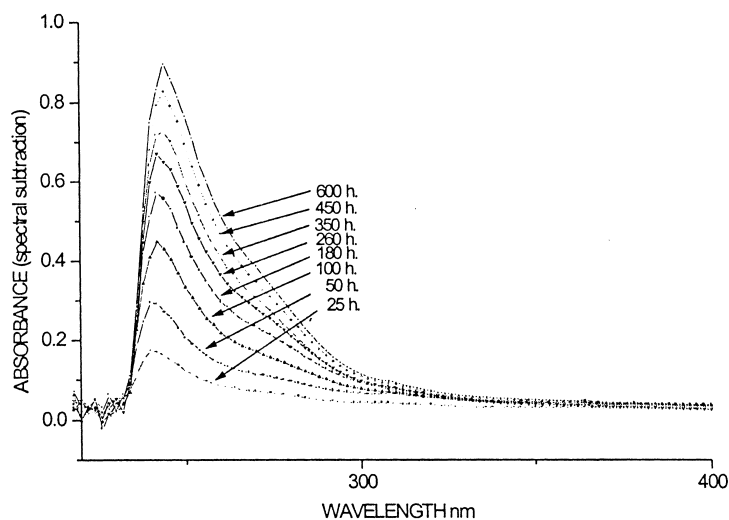


Figure 6 Variation in u.v. absorbance spectra of nylon 66 upon polychromatic irradiation

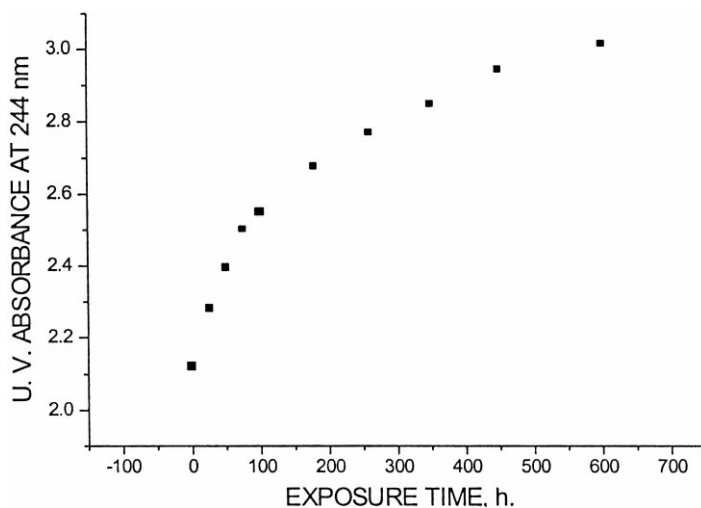


Figure 7 Rate of imide group formation with irradiation time

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REFERENCES

1. Sharkey, W.H. and Mochel, W.E., *J. Am. Chem. Soc.*, 1959, **81**, 3000.
2. Moore, R.F., *Polymer*, 1963, **4**, 493.
3. Jellinech, H.H.G. and Chaudhari, A.K., *J. Polym. Sci. A1*, 1972, **10**, 1773.
4. Fornes, R.F., Cilberts, R.D., Stowe, B.S. and Cheek, G.P., *Text. Res. J.*, 1973, **43**, 714.
5. Tang, Ly, Lamaire, J., Sallet, D. and Mery, J.-M., *Makromol. Chem.*, 1981, **182**, 3467.
6. Tang, Ly., Sallet, D. and Lamaire, J., *Macromol.*, 1982, **15**, 1437.
7. Roger, A., Sallet, D. and Lamaire, J., *Macromol.*, 1985, **18**, 1771.
8. Roger, A., Sallet, D. and Lamaire, J., *Macromol.*, 1986, **19**, 579.
9. Allen, N.S., Homer, J., McKeller, J.F. and Phillips, G.O., *Br. Polym. J.*, 1975, **7**, 11.
10. Allen, N.S., McKeller, J.F., Moghaddam, B.M. and Phillips, G.O., *J. Photo. Chem.*, 1979, **11**, 101.
11. Allen, N.S., Harrison, M.J., Follows, G.W. and Mathews, V., *Polym. Deg. Stab.*, 1987, **19**, 77.
12. Allen, N.S., Ledward, M. and Follows, G.W., *J. Photochem. Photo-biol.*, 1990, **A53**, 373.
13. Do, C.H., Pearce, E.M., Bulkin, B.J. and Reimschnessel, H.K., *J. Polym. Sci. Part A Polym. Chem.*, 1987, **25**, 2301.
14. Allen, N.S., Harrison, M.J., Follows, G.W. and Mathews, V., *Polym. Deg. Stab.*, 1987, **19**, 77.
15. Allen, N.S., Harrison, M.J., Follows, G.W. and Mathews, V., *Polym. Deg. Stab.*, 1988, **21**, 251.
16. Allen, N.S., *Polym. Deg. Stab.*, 1994, **44**, 357.
17. Mani, R., Singh, R.P., Sivaram, S. and Lacoste, J., *Polym. J.*, 1994, **26**, 1132.
18. Singh, R.P., Mani, R., Sivaram, S., Lacoste, J. and Valliant, D., *J. Appl. Polym. Sci.*, 1993, **50**, 1871.
19. Israeli, Y., Lacoste, J., Lamaire, J., Singh, R.P. and Sivaram, S., *J. Polym. Sci. Part A Polym. Chem.*, 1994, **32**, 485.
20. Burnett, G.M. and Reches, K.M., *J. Chem. Soc. B*, 1966, **12**, 1229.
21. Starkweather, H.W. Jr. and Moynihan, R.E., *J. Polym. Sci.*, 1956, **22**, 363.
22. Mazzocchi, P. H., in *Organic Photochemistry*, vol. 5, ed. A. Padwa. Marcel Dekker, New York.