Thermal Properties of Photo-Oxidized Nylon 6 Fibers

YASUHARU FUJIWARA* and S. HAIG ZERONIAN, *Division of Textiles and Clothing, University of California, Davis, California 95616*

Synopsis

Nylon 6 fiber begins to increase in weight at about 180°C when heated in oxygen. The increase is attributed to an uptake of oxygen resulting from thermal oxidation. A similar weight increase is not found in photo-oxidized nylon 6 on heating in oxygen. It appears that nylon 6 tends to form volatile compounds more easily on heating after photodegradation. Changes detected by differential thermal analysis and also by thermomechanical analysis after nylon 6 has been exposed to sunlight are discussed primarily in terms of the supramolecular structure of the fiber.

INTRODUCTION

On exposure to ultraviolet light, polyamides degrade and their physical and chemical properties change. The changes in such properties as tensile strength, molecular weight, degree of crystallinity, and density depend on the wavelength of the incident radiation,[1] the presence of fiber additives,[2] and the ambient conditions.[3] Photodegradation of nylon 6 fibers proceeds primarily by scission and crosslinking of the polymer molecules. Sunlight irradiation with wavelengths above 290 nm causes chain scission rather than crosslinking in nylon fibers. When irradiated in air, nylon 6 chains photooxidize initially and then cleave.[4] Photo-oxidation of polyamides is explained in terms of the formation and decomposition of hydroperoxides.[5]

In this work, the photo-oxidation of nylon 6 fibers exposed to sunlight was studied by differential thermal analysis (DTA) and thermogravimetry (TG). The effect of the photo-oxidative degradation on residual stress of the fibers was examined also.

EXPERIMENTAL

Materials

Nylon 6 filament yarn (660 denier/70 filaments) was supplied by Allied Chemical Co., Ltd. The samples were melt spun and drawn to four times their original length and were free of delustrant or additives. Before irradiation, the filaments were extracted with methanol to extract nylon 6 monomer and oligomers.[6]

---

* Present address: Department of Home Economics, Mukogawa Women's University, Nishinomiya 663, Japan.

Outdoor Exposure

The samples were exposed for one, two, and three months in midsummer at Davis, California. The filaments were placed in a quartz tube which was then stoppered to prevent accessibility of the samples to water or other contaminents during sunlight exposure. The tubes were mounted on an exposure support which was covered by an aluminum plate. The slope of the support was set at 45° to the horizontal and faced south. The quartz tubes were rotated at seven-day intervals.

CHARACTERIZATION OF PRODUCTS

Thermal Analyses

For all analyses, the samples were first dried in a desiccator over phosphorus pentoxide. For DTA and TG measurements, the filaments were cut into short segments ($\sim$ 1 mm).

DTA measurements were run on a Mettler TA 2000M thermal analysis system using 5-mg samples at a heating rate of 10°C/min in an atmosphere of either nitrogen or oxygen (flow rate 20 ml/min).

TG was measured with a Perkin–Elmer TGS-1 thermogravimetric analyzer in either a nitrogen or oxygen atmosphere. The initial sample weight was about 3.5 mg, and the heating rate was 10°C/min.

Thermomechanical analysis (TMA) was carried out with a Shimazu TMA-20 in an air atmosphere with a heating rate of 10°C/min, using a load of 100 mg/ filament.

RESULTS AND DISCUSSION

Thermogravimetry

On heating in oxygen, the weight of the starting unexposed (control) nylon 6 fiber was constant up to 180°C, then showed a slight increase before it began to decrease (Fig. 1). In nitrogen, a similar weight increase was not observed as the temperature was raised to above 300°C. The increase in weight of the control sample when TG was run in an oxygen atmosphere is attributed to an uptake of oxygen resulting from thermal oxidation. On exposure to sunlight for not less than one month, the nylon 6 samples lost weight on heating in oxygen, and the extent of the weight loss increased with the time of exposure to sunlight. The weight increase in the range about 180 to 270°C detected with the control sample was not found with the exposed samples. For nylon 6 fibers exposed to sunlight for three months, the weight loss started between 100 and 150°C, irrespective of whether the sample was heated in nitrogen or oxygen. Thus, it appears nylon 6 tends to form volatile compounds more easily on heating after it has been photodegraded, and this accounts for the weight of the irradiated samples not passing through a maximum during the TGA measurements in an oxygen atmosphere.
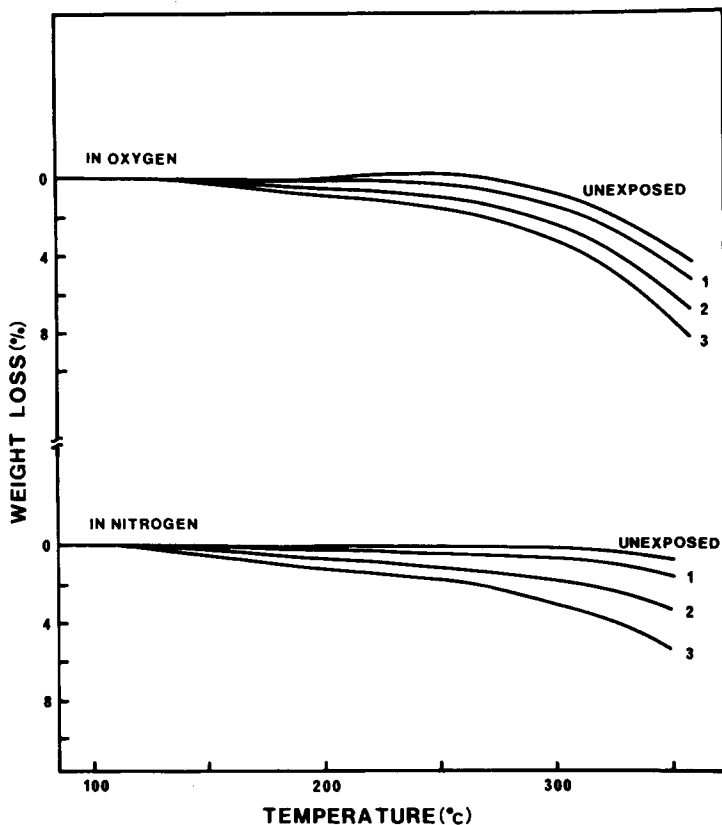
Fig. 1. TG curves in oxygen and in nitrogen of nylon 6 fibers unexposed to sunlight and of nylon 6 fibers irradiated in sunlight. Numbers by curves give lengths of exposures in months.

Differential Thermal Analysis

A large exothermic peak at about 200°C, followed by a small endothermic peak and another large exothermic peak at about 330°C, was found on the DTA curves, run in oxygen, of the control nylon 6 sample (Fig. 2). The endothermic peak is due to the melting of the sample. The exothermic peaks are attributed to oxidation reactions.[7] These exothermic peaks were entirely absent when DTA was performed in nitrogen.

For DTA conducted in oxygen, the thermal oxidation exothermic peak prior to melting shifted to lower temperature and also became smaller when the sample had been exposed to sunlight. The temperature at which thermal oxidation began for the control fibers and the two- or three-month sunlight-exposed samples was about 180 and 100°C, respectively. A lowering of the temperature at which the exothermic reaction begins indicates that the thermal oxidation occurs more easily after the nylon 6 sample has been exposed to sunlight. Since the size of the first exothermic peak decreased when the nylon 6 sample had been exposed to sunlight, it appears that photo-oxidation results in a decrease of thermal oxidation as indicated by DTA. However, the extent to which the size of the peak might be affected by the loss of volatile compounds, as noted in the TG data, is not known at this time. The same decrease in the size of the exothermic peak has been observed in the thermograms of the nylon 6 fibers irradiated in air with ultraviolet light from a mercury lamp.[8]
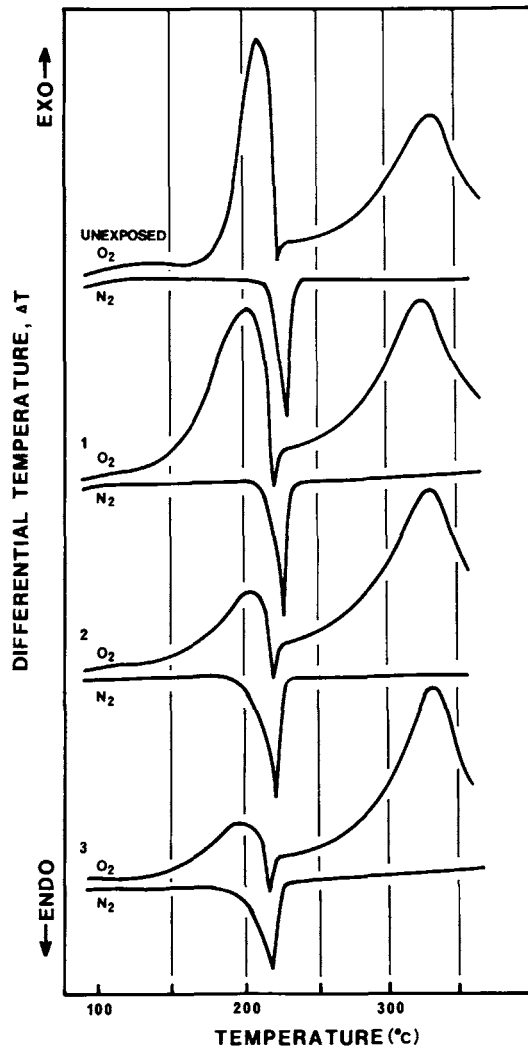
Fig. 2. DTA curves in oxygen and in nitrogen of nylon 6 fibers unexposed to sunlight and of nylon 6 fibers irradiated in sunlight. Number by curves give lengths of exposures in months.

The second exothermic peak at about 330°C in the thermograms run in oxygen of the nylon fibers did not show much change in size and height when the samples had been exposed to sunlight. This exothermic reaction is attributed to a pronounced oxidative decomposition accompanied by weight loss. Since it occurs after the crystalline portions of the fiber have melted, we speculate that polymer from the crystalline regions is primarily involved in the reactions which result in the second exothermic peak. Since the crystallinity of the fiber would not have changed markedly after irradiation, this would explain, at least in part, why the size of the second exothermic peak remains approximately constant.

It can be deduced from the thermograms run in nitrogen that on exposure to sunlight, the initiation and zenith of the melting peak shift to lower temperatures. This lowering of the melting temperature could be due to the following factors: (a) Scission of tie molecules connecting microfibrils causes an increase in surface

energy and thus lowers the melting temperature.[9]   (b) It is speculated that if the nylon 6 fibers oxidizes solely in the amorphous regions during sunlight exposure, then the increased bulk of the oxidized chains suppresses reconstruction of the crystalline regions and the samples melt at a lower temperature than that of the nonoxidized fibers.   It has been reported that polyolefins, such as isotactic polypropylene and polyethylene,[10] oxidize in the amorphous region when treated in the solid state.   (c) Crosslinking occurs and lowers the melting point.   It is known that nylon 6 fiber which has been crosslinked in the amorphous regions melts at 190°C (11).   The crosslinking suppresses reorganization as the sample is heated during thermal analysis.

Thermomechanical Analysis

The control fiber, which had been drawn to four times of its original length during manufacture, shrank initially as the temperature was raised and then elongated just below its melting point (Fig. 3).   In contrast, undrawn nylon 6 fiber only elongated when measured under the same conditions.   There might be more strained interfibrillar tie molecules in the drawn fibers than in undrawn fibers.[12]   Relaxation of such strained tie molecules on heating would result in shrinkage in the length of the fibers.

The degree of shrinkage of the sunlight-exposed fibers decreased with exposure time, and with the three-month exposed sample only elongation occurred above 150°C.   We suggest that the chain cleavage, caused by sunlight irradiation taking place in amorphous regions, reduced the fraction of strained tie molecules connecting the adjacent crystallites and that any chain scission which occurred in the crystalline regions caused imperfections in the crystallites.   These structural changes are reflected in a decrease in shrinkage (Fig. 3) and in the lowering of the melting temperature (Fig. 2).   The rate of increase of elongation with temperature increases markedly as the melting point of the fiber is approached.   It will be noted that the temperature at which the rate increases markedly shifts
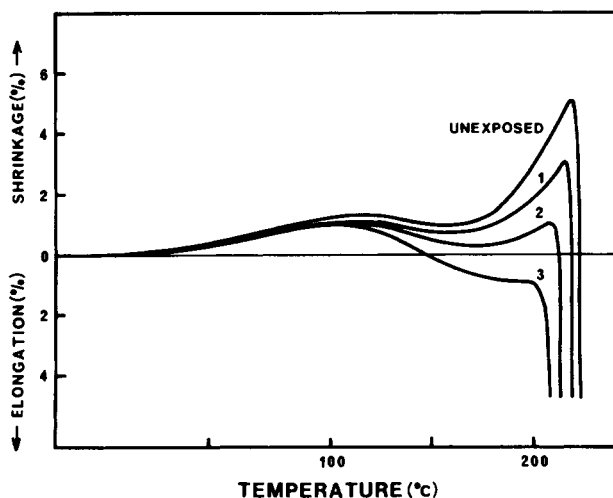

Fig. 3.   TMA curves in air of nylon 6 fibers unexposed to sunlight and of nylon 6 fibers irradiated in sunlight.   Numbers by curves give lengths of exposures in months.

to lower temperatures as the sunlight exposure time of sample increases. This observation agrees with the melting behavior found in the DTA thermograms.

References

1. H. A. Taylor, W. C. Tincher, and W. F. Hamner, *J. Appl. Polym. Sci.*, **14**, 141 (1970).
2. L. M. Lock and G. C. Frank, *Text. Res. J.*, **43**, 502 (1973).
3. S. H. Zeronian, K. W. Alger, and S. T. Omaye, *Text. Res. J.*, **43**, 228 (1973).
4. R. V. R. Subramanian and T. V. Talele, *Text. Res. J.*, **42**, 207 (1972).
5. B. Ranby and J. F. Rabek, *Photodegradation, Photo-oxidation and Photostabilization of Polymers*, Wiley–Interscience, New York, 1975.
6. Y. Fujiwara and S. H. Zeronian, *J. Appl. Polym. Sci.*, **23**, 3601 (1979).
7. R. F. Schwenker, Jr. and L. R. Beck, Jr., *Text. Res. J.*, **30**, 624 (1960).
8. Y. Fujiwara and T. Yasuda; *Sen-i Gakkaishi*, **30**, T434 (1974).
9. P. Blais, D. J. Carlsson, F. R. S. Clark, P. Z. Sturgeon, and D. M. Wiles, *Text. Res. J.*, **46**, 641 (1976).
10. N. C. Billingham, P. Prentice, and T. J. Walker, *J. Polym. Sci.*, *Symp.*, **No. 57**, 287 (1976).
11. M. Todoki and T. Kawaguchi, *Kobunshi Ronbunshu*, **31**, 427 (1974).
12. D. C. Prevorsek, P. J. Harget, and R. K. Sharma, *J. Macromol. Sci. Phys.*, **B8**, 127 (1973).