

Colorimetric Evaluation of Thermooxidative Degradation of Nylon 6 Fibers

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SYNOPSIS

Nylon 6 fibers were annealed in air at 160°C for periods ranging from 1 to 10 h. Their spectral reflectance values were measured. Color parameters, including luminance factor, dominant wavelength, purity, and the color difference between annealed nylon 6 fiber samples and unheated ones were calculated. The observed variations in the colors of samples were assumed due to the thermal and oxidation degradations. The behavior of the color parameters with heating duration was compared with the general kinetic curve of thermooxidative degradation of polymers and the match between them is discussed. The color difference ΔE values is recommended for monitoring the thermooxidative degradation of nylon 6 fibers. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The logical need for color measurements can be classified under two categories: the visual quality of a color for its own sake, and using the color of an object as an indicator of other properties that it may possess.¹

Annealing is the most available technique to change the polymeric structure.²⁻⁶ Also, during the production of films, fibers, and engineered parts, a polymer is exposed to varying degrees of heat and humidity. The processing conditions have significant influence on the physical properties of the products. Annealing can be applied to polymers either under vacuum or in air. In both cases the polymeric structure suffers a chemical degradation associated with color variations.

The effect of high temperatures, where there is no access of oxygen, causes most polymers to degrade, i.e., their macromolecules break up into smaller molecules and even monomers. Thermooxidative degradation is the simultaneous effect of heat and oxygen and is the cause of rapid failure of polymeric articles. The rate of thermooxidative degradation of polymers is higher than the rate of their purely thermal degradation.⁷

Thermal stability of polymers is one of the important characteristics of their suitability for use. Therefore, the study of thermal degradation rate of polymers is worthy of being carried out with sufficient accuracy to improve their thermal stability by good selection of a method for inhibiting the associated thermal reactions.

By trademark definition, a nylon is any long-chain synthetic polymeric amide that has recurring amide groups as an integral part of the main polymer chain. Nylons are synthesized in many ways. These include the condensation of diamines with diacids, the polymerization of amino acids, and the ring-opening polymerization of lactams. The varied routes to synthesis lead to many different types of nylons whose structure and properties differ widely. The various aliphatic nylons are named by a numerical system based on the number of carbon atoms in the monomer(s) from which they are synthesized.

For convenience, nylons may be classified into six groups according to the number of CH₂ groups in the monomeric units. Nylon 6 (group F) from ω -amino acids with odd numbers of CH₂ groups (even numbers in the conventional expression).⁸

In the present work, colorimetric measurements were used to estimate the rate of thermooxidation of nylon 6 fibers when they are annealed for different times in air at 160 ± 1°C. As the annealing tem-

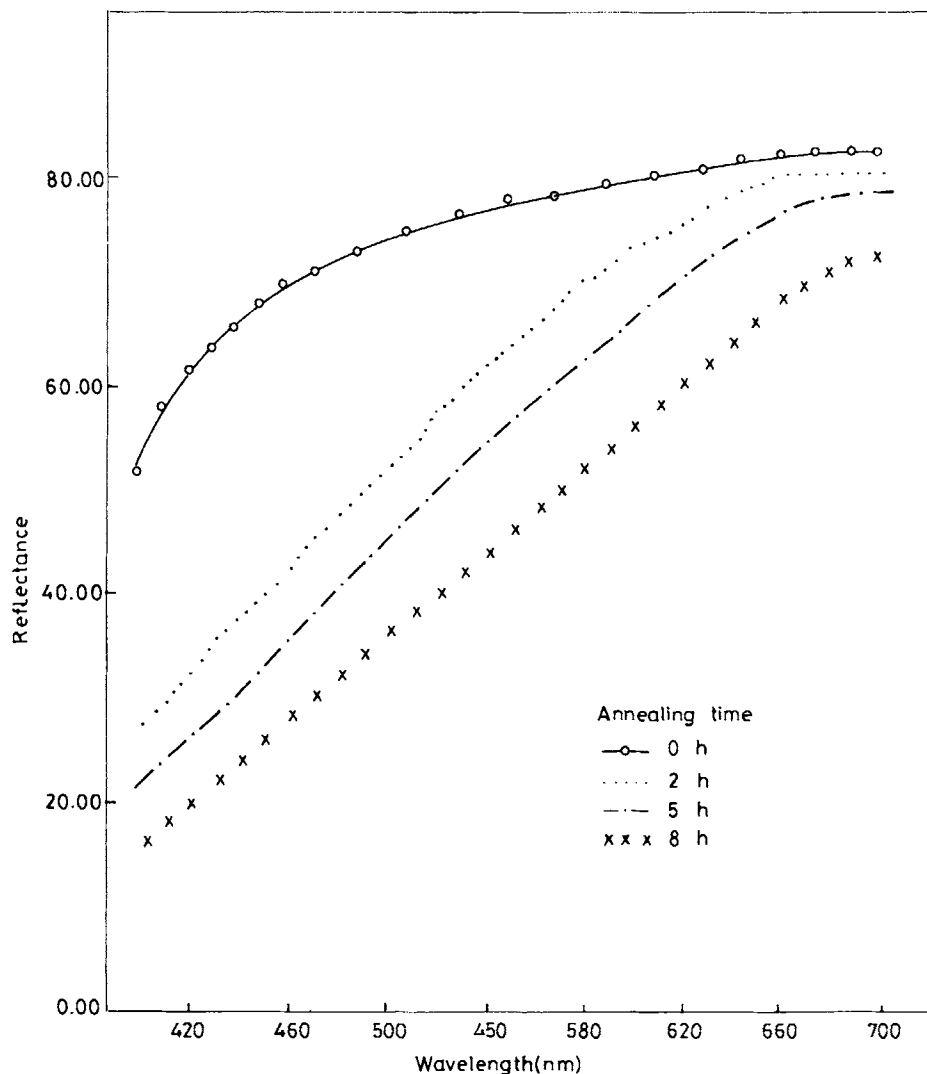


Figure 1 The spectral reflectance curves of annealed nylon 6 fibers in the visible range of the spectrum at different annealing times.

perature and time were increased, the fiber become more brittle (at 185°C for 6 h) due to the partial productions of ash on the samples.⁶ So nylon 6 can be heated at $160 \pm 1^{\circ}\text{C}$ without embrittlement.

EXPERIMENTAL

Preparation of Samples

Long bundles of nylon 6 fibers (Amilan, Morubeni Co., Japan) were loosely folded in a cocoon form with free ends. Several samples were left in an electric oven and heated at $160 \pm 1^{\circ}\text{C}$ for different annealing times ranging from 1 to 10 h. The samples were then left to cool at the room temperature. The

samples were free from any additives (delustrant and or stabilizer).

Measurement of Color Parameters

The spectral reflectance curves for unheated sample (substrate) and for all annealed samples were carried out using the Acs600 color control system of Applied color Systems, USA. The reflectance values were measured in the visible range of the spectrum from 400 to 700 nm. The reflectance curves of substrate and some annealed nylon 6 fiber samples are shown in Figure 1.

The X, Y, Z tristimulus values of the substrate and annealed samples were used in the calculation

of the chromaticity coordinates x , y using the relation⁹:

$$x = X/(X + Y + Z), \quad y = Y/(X + Y + Z).$$

The dominant wavelength λ_d , and the purity P_e of each annealed sample were determined by the graphical method using the large area (10°), CIE 1964 chromaticity diagram.

Visual evaluation of the depth of color is not accurate. In this case, small color differences cannot be detected adequately. Measurements with a spectrophotometer or any other colorimetric equipment are more accurate and the reproducibility is better. These measurements can be used to establish and control color tolerances in industry.

The CIE system of colorimetry does not plot chromaticities that refer to equal perceptible differences at equal spaces on the chart.¹⁰ It is recommended to transform this system into another one where the chromaticities are located at equal distances corresponding to the visual perceptible differences. Many authors¹¹⁻¹³ experimentally investigated the magnitude of the visual color difference and color appearance thresholds.

Many color difference formulas are known. In this work we used two of them.

1964 CIE Color-Difference Equation

The color differences ΔE_{CIE} between the annealed samples (U_2, V_2, W_2) and the unheated nylon 6 sample (U_1, V_1, W_1) were calculated using the transformation form^{14,15}:

$$\Delta E_{\text{CIE}} = [(U_2 - U_1)^2 + (V_2 - V_1)^2 + (W_2 - W_1)^2]^{1/2}$$

where $W = 25Y^{1/3} - 17$; $U = 13W(u - u_0)$; $V = 13W(v - v_0)$.

As alternative equations to those above:

$$u = 4X/(X + 15Y + 3Z)$$

and

$$v = 6Y/(X + 15Y + 3Z)$$

and u_0, v_0 are the values of u and v for the nominally achromatic color in the (U, V) coordinate system. This means that for surface colors, u_0 and v_0 will be the coordinates corresponding to the color of the illuminant.

Cube-Root Color Difference Formula

The color difference is given as¹⁶:

$$\Delta E(L^*a^*b^*) = [(\Delta a^*)^2 + (\Delta b^*)^2 + (\Delta L^*)^2]^{1/2}$$

where $L^* = 25(100Y/Y_0)^{1/3} - 16$ ($1 \leq Y \leq 100$); $a^* = 500[(x/x_0)^{1/3} - (Y/Y_0)^{1/3}]$; $b^* = 200[(Y/Y_0)^{1/3} - (Z/Z_0)^{1/3}]$. In these equations, the tristimulus values X_0, Y_0, Z_0 define the color of the nominally white object color stimulus.

RESULTS AND DISCUSSION

Figure 2 shows the variation of both the luminance factor Y and the color purity $P_e\%$ with the duration (in hours) of the heat set. It is clear that the mac-

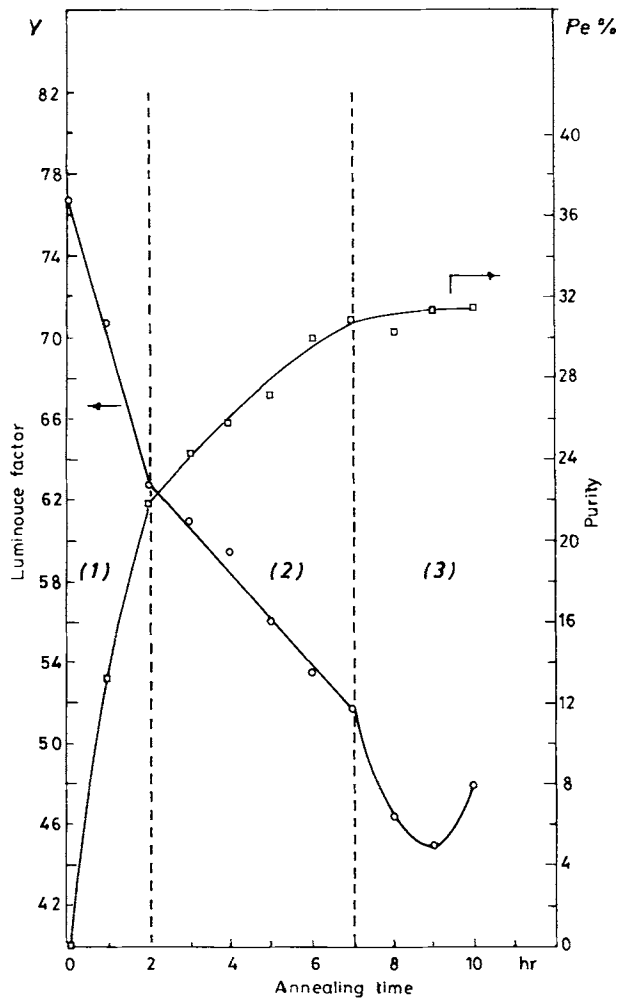


Figure 2 The variation of luminance factor Y and the percentage color purity $P_e\%$ of nylon 6 fibers annealed at 160°C in air for different times.

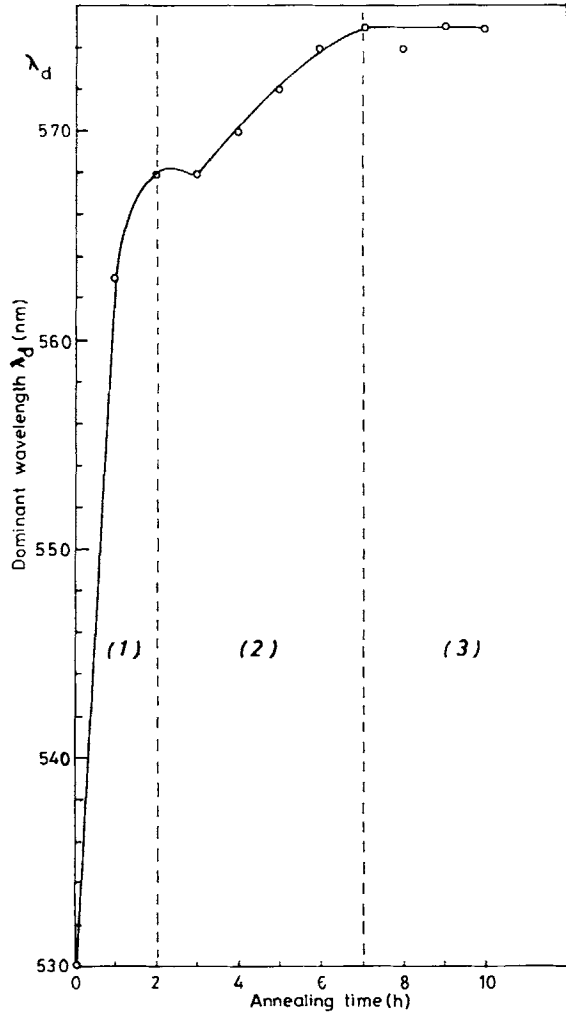


Figure 3 The dominant wavelength λ_d of nylon 6 fibers annealed at 160°C in air as a function of the annealing time.

romolecular structure of nylon 6 went through at least three different mechanisms before it reached the thermally stable state after 7 h preheating at 160°C. This phenomenon is supported also by the behavior of the dominant wavelength λ_d and the total color difference ΔE with preheating duration in Figures 3 and 4, respectively.

To identify the presage of each region in Figures 2 and 4, it was suitable to assume that the observed color variations may be due to thermal oxidation of the polymeric samples. This assumption may be accepted by recalling the general kinetic curve of polymer oxidation during a thermooxidative degradation process⁷ (Fig. 5).

The kinetic curve of polymer oxidation shows that a polymer undergoing a thermooxidative degradation obeys four sequential processes:

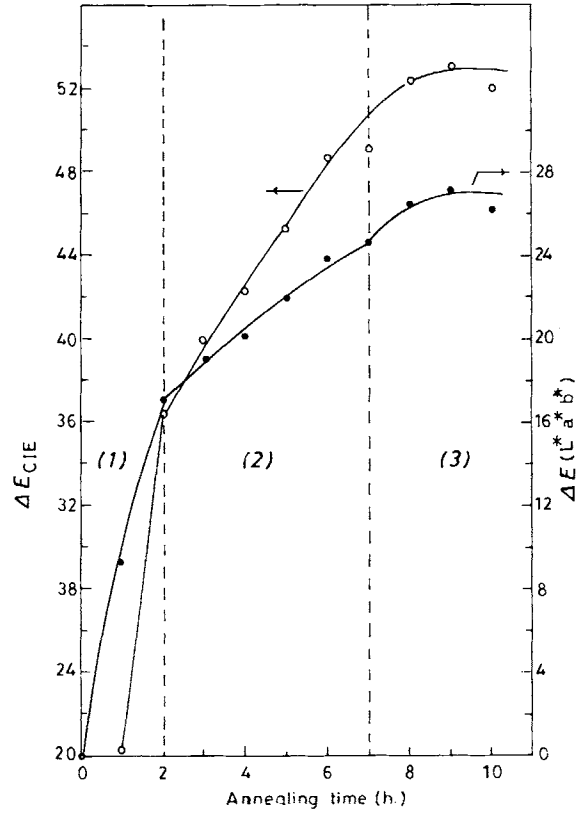


Figure 4 The variation of ΔE_{CIE} and $\Delta E(L^*a^*b^*)$ with the annealing time of nylon 6 fibers.

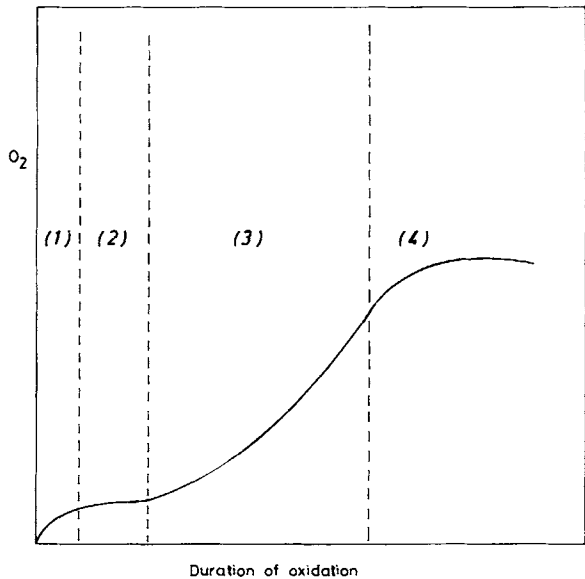


Figure 5 The general kinetic curve of polymer oxidation (after Kuleznev and Shershnev⁷).

1. rapid initial addition of oxygen at the active centers of the macromolecules in addition to the free radical formation;
2. an induction period whose magnitude may grow in the presence of an inhibitor (with elevation of the temperature, the induction period diminishes, while the rate of oxidation grows);
3. a sharp growth in the rate of oxygen addition due to the development of chain radical reactions (autocatalysis);
4. drop in the oxidation rate due to exhaustion of the active centers.

On the basis of the kinetic curve of polymer oxidation and the above processes, one may interpret the obtained variations in Figures 2 and 4. The behaviors in the three regions in these figures are in good agreement with behaviors in regions 1, 3, and 4 in Figure 5, respectively. The samples of nylon 6 fibers were annealed in air at relatively high temperature (160°C) with respect to its polymer structure. These samples were pure nylon 6 and free from any oxidation inhibitors. Therefore, the data in Figures 2 and 4 are found free from the induction period.

Among the four color parameters present in this work, the authors recommend the total color difference ΔE as a factor that can be used to determine the concentration of the oxidized centers in a polymer undergoing a thermooxidative degradation. This recommendation is based on the following findings:

1. ΔE is a relative quantity, i.e., it is measured, with respect to some substrate reference; therefore, it is free from any effect due to the initial color of the oxidized samples.
2. ΔE is determined numerically; λ_d and P_e are found graphically; therefore, ΔE possesses higher accuracy.
3. There are different forms through which the color difference of a set of samples can be calculated,^{11,16} hence, ΔE can be obtained irrespective of the darkness of the substrate sample.

So, recalling Figure 4 and assuming that the slope of any curve segment represents the rate of a certain mechanism, one may explain the process of thermooxidative degradation in nylon 6 fibers when heated in air at 160°C.

CONCLUSION

From the previous discussion and notations, the following conclusions may be drawn:

1. The visual color of nylon 6 fibers is changed remarkably due to different annealing conditions. Thus the changes occurring in nylon 6 are expected.
2. The observed changes in the color parameters of annealed nylon 6 fibers can be related to the thermooxidative degradation process.
3. Applying color measurement to annealed polymers is a useful tool for explaining the degree of thermal stability of polymers.
4. ΔE is a well-established method for characterizing small differences in color between fibers, carpets, fabrics, etc. So changes in the color difference ΔE are the most suitable color parameters directly related to comparing the efficiency of different variations.
5. One would expect any fiber discoloration process to plateau on prolonged exposure, as all surface sites become attacked (Figs. 1–4). This does not necessarily mean that there are no ongoing changes in mechanical properties. This needs further study.
6. The annealing process affects other physical properties (melting temperature, water sorption, density,⁶ electrical, etc.) of nylon 6 as well as its color parameters. This is possibly due to changes in the cohesive forces between adjacent molecules.

So, we recommend color measurement as a suitable nondestructive technique to follow the oxidation rate of polymeric films, fibers, and bulks. For most polymers, color measurement is a promising technique to follow the rates of radiolysis, and thermal, oxidative, and chemical degradations. It should be useful in the future to have further studies in an oxygen free atmosphere, because it impossible to test at this time.

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Received October 3, 1994

Accepted December 22, 1994