Evaluation of Degradation on Nylon-6 and Nylon-6/Montmorillonite Nanocomposite by Color Measurement

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Received 25 October 2007; accepted 17 December 2007
DOI 10.1002/app.27954
Published online 6 March 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: An evaluation of degraded level is an important subject for industrial products. Ordinarily, many kinds of polymer material changes its color through the degrading process by altering its chemical structure, and IR and UV are applicable to ensure the production of the functional groups. However, these methods are hardly applicable to measurements of product on site without the sample collection. A spectrophotometer is sufficiently lightweight, compact, and capable of measurements on site without the sample collection. With these backgrounds, the correlation of the color with the tensile strength and the molecular weight was studied by using the spectrophotometer. Through the thermal aging test at various temperatures, specimens became yellowish and the increase rate of color change was different between neat Nylon-6 and Nylon-6 nanocomposite. Such changes were closely related to the tensile strength and the molecular weight. As a method to evaluate the polymer degradation, the correlation of the difference of yellowness index (ΔYI) with the tensile strength and the molecular weight was sufficiently high and the ΔYI indicated a difference between neat Nylon-6 and Nylon-6 nanocomposite. From these results, it is found that the color measurement with the spectrophotometer is a practical method for evaluation of polymer degradation. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 3487–3494, 2008

Key words: nylon; nanocomposites; degradation; color measurement; spectrophotometer

INTRODUCTION

An evaluation of degraded level is an important subject for industrial products, in particular, for the long-term use products. Heretofore, ordinary test methods such as mechanical tests, measurement of pulse NMR, measurement of additive components, and other various measurements were applied to evaluate the degradation of polymer materials.[1,2] However, most of these methods were applied to the standard specimen forms, respectively; therefore, for evaluating the polymer degradation, some amounts of samples had to be collected from the aged products that were installed on site. In case of the product that covers a wide area, some kinds of damage were produced through the sample collection process; therefore, the damaged products had to be exchanged to brand new ones or repaired totally to be used for more lengthy periods. Such arrangement needs additional expenditure and is time-consuming. Furthermore, the mechanical strength of repaired part decreases as compared with the normal part; therefore, the repaired part becomes a weak point under aging conditions. With these backgrounds, an evaluation method that enables to measure the product on site without the sample collection is desirable for industrial products.

Ordinarily, many kinds of polymer material changes its color through the degrading process by altering its chemical structure, and IR and UV are applicable to ensure the production of the functional groups.[3] However, these methods are hardly applicable to measurements of product on site without the sample collection and IR is easily affected by measurement atmosphere. A spectrophotometer is sufficiently lightweight, compact, and capable of measurements on site without the sample collection. The spectrophotometer was applicable to the field for color matching of dental material[4,5]; however, there were a small number of researches concerning with the spectrophotometer in polymer material fields. The spectrophotometer enables to measure the color index directly; therefore, the spectrophotometer has an advantage of evaluating the color of polymer material under aging condition.

Nylon is a useful material in industrial as well as commercial fields and it becomes a remarkable material as nanocomposite in recent years.[6–8] Even in the railway field, Nylon is applied to many kinds of product such as track, vehicle, and electric parts. Heretofore, these products were maintained by visual inspection and easily exchanged with brand-new

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Journal of Applied Polymer Science, Vol. 108, 3487–3494 (2008)
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TABLE I
Preparation of Specimens

Specimen	Serial no	Mix ratio	Content of organic modified MMT (net MMT[a]) (wt %)
A	1022B	100	0
B	1022B/1022C2	50/50	1.15 (0.86)
C	1022C2	100	2.3 (1.72)

[a] Residue on ignition were measured in accordance with method A of ISO3451-4. Ashing temperature is 850°C.

products without a suitable evaluation of degraded level. On the other hand, the degradation mechanism of Nylon is relatively clear and Nylon becomes yellowish under thermal aging condition. The large number of researches has been carried out to identify the degradation mechanism of Nylon.[9–13] It is also found a lot of studies on the thermal degradation of Nylon nanocomposite.[14–17] In particular, Fornes et al. found the color formation after melt processing using a twin screw extruder.[17] However, this study was based on the melt processing circumstance; therefore, the temperature of the thermal degradation was more than melting point. Heretofore, it is unclear how the transition of the color is related with the mechanical strength under ordinary condition.

In this article, for the purpose of evaluating the polymer degradation, the authors studied the relationship between the color and the mechanical strength by using standard Nylon-6 and Nylon-6/montmorillonite nanocomposite. Based on the test results, the effectiveness of the color measurement was discussed in view of the evaluation of polymer degradation.

EXPERIMENTAL

Materials

Commercial grade Nylon-6 (1022B, Ube Industries), Nylon-6/montmorillonite nanocomposite (1022C2, Ube Industries), and the mixture of each of these materials were prepared as shown in Table I. These specimens were molded in the form of 0.2 mm thickness film by using extruder equipped with T-die.

Thermal aging test

A thermal aging test was performed with use of a Yamato ventilated oven (DN600) under an air condition. The test temperatures are 80, 100, 120, and 150°C. These test temperatures are selected based on the result of degradation behavior.[9] In the case of the thermal aging test performed at the temperature less than 100°C, the tensile strength hardly changed as compared with the initial strength. On the other hand, the thermal aging test performed at the temperature more than 120°C, the tensile strength dropped significantly at the early step.[9] Therefore, it is presumable that these varieties of test condition are sufficient for the study on thermal aging of Nylon. The specimens of ~ 200 mm × 150 mm × 0.2 mm were applied to thermal aging test. After thermal aging test, the specimens were preserved in an auto-desiccator for more than 72 h to control a specimen condition.

Measurement of tensile properties

The tensile properties were measured by a Shimadzu Autograph (AG-50kN) with a crosshead speed of 200 mm/min and No.5 dumb-bell specimen according to Japanese Industrial Standard JIS K 7127. The reported values are the average of five measurements on specimens and the specimens were taken from the same direction as the molded direction.

Measurement of molecular weight

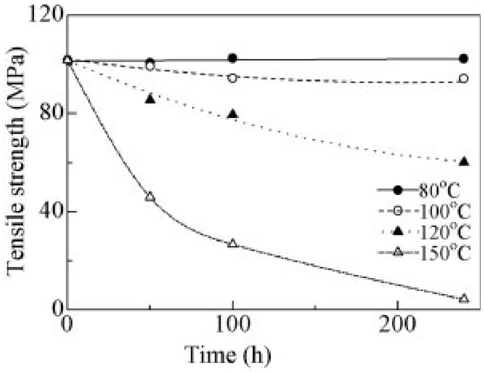
The molecular weight was measured with a GPC using a solvent of hexafluoro isopropanol (HFIP). The GPC system is consisted of a Waters U6K injector, a Waters 510 pump, and a Waters 410 differential refractometer. The concentration of Nylon-6 and Nylon-6/montmorillonite nanocomposite solution at 0.5 wt % was filtrated by Nihon Millipore PTFE membrane filter Millex-LH (ϕ0.45 μm) and injected to the system. The flow speed of the solution was 1 mL/min. The molecular weight was calibrated by standard polymethylmethacrylate.

Color measurement

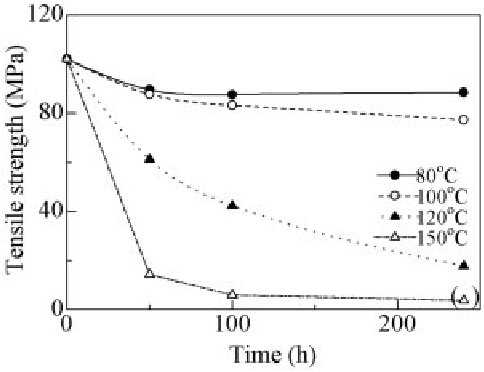
The color measurement was performed with Nippon Denshoku reflection spectrophotometer (NF 333) using standard light C (color temperature 6774 K) and a 2° standard observation angle. To measure the color of specimen, the detector was simply touched to the surface. The tristimulus value X, Y, and Z based on Commission Internationale de l'Eclairage (CIE) standard colorimetric system are measured. The yellowness index (YI) based on ASTM E313 was calculated from the function (1) by using X, Y, and Z. The ΔYI was derived from the YI by using the function (2). The YI of nondegraded specimen is defined as YI_0. The reported values are the average of five measurements on specimens.

$$YI = \frac{100(1.28X - 1.06Z)}{Y} \tag{1}$$

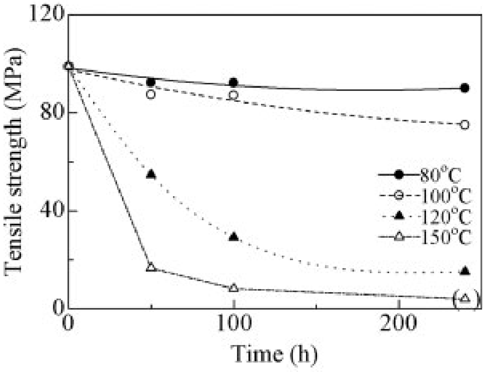
$$\Delta YI = YI - YI_0 \tag{2}$$



(a) Specimen A



(b) Specimen B



(c) Specimen C

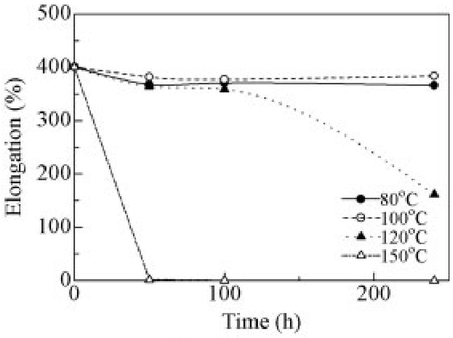
Figure 1 The relationships between the tensile strength and thermal aging time. The number of measurement was less than five; the averaged results were shown with parenthesis.

RESULTS AND DISCUSSION

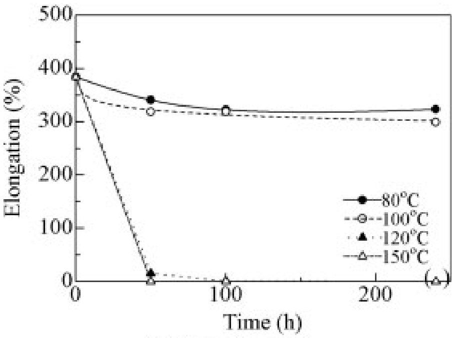
Tensile properties

Based on the results of the tensile test, Figures 1 and 2 show the changes of the tensile properties with an increase of the aging time. In performing the tensile test, five dumb-bell specimens were not taken from highly degraded specimens because of its brittleness. Therefore, in case the number of measurement was less than five, the averaged results were shown with parenthesis.

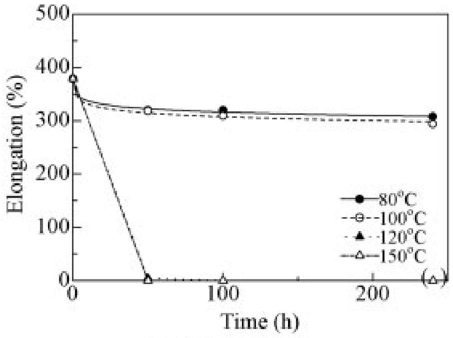
It is apparent that the significant difference of the initial tensile strength between neat Nylon-6, Specimen A and Nylon-6 nanocomposite, Specimen B and C was not indicated. In former research, the mechanical strength of Nylon-6 was greatly improved by the compounding and the dispersion of the organic modified montmorillonite (MMT).[8] However, the former result was measured based on the specimen prepared by injection molding; therefore, the result of the tensile strength based on the film specimen indicates the difference from the mechanical strength of the molded specimen.



(a) Specimen A



(b) Specimen B



(c) Specimen C

Figure 2 The relationships between the elongation and thermal aging time. The number of measurement was less than five; the averaged results were shown with parenthesis.

TABLE II
Decrease Rate of the Tensile Strength ($-dT_B/dt$) (MPa/h)

Specimen	80°C	100°C	120°C	150°C
A	0.022	0.051	0.325	1.117
B	0.250	0.287	0.818	1.756
C	0.133	0.232	0.886	1.648

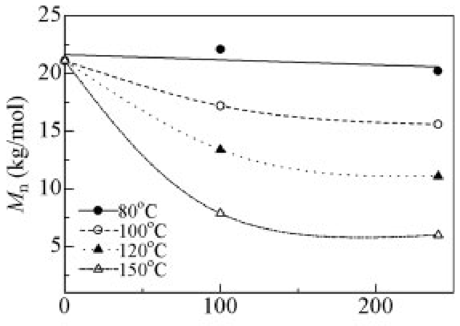
Through the thermal aging test, the tensile strength decreased gradually as shown in Figure 1 and the decrease rate of the tensile strength became faster in accordance with an increase of test temperature. Furthermore, the decrease rate of the tensile strength was different between neat Nylon-6 and Nylon-6 nanocomposite. The initial decrease rate of the tensile strength ($-dT_B/dt$) was calculated by the result between nondegraded specimen and 50 h thermal-aged specimen. As shown in Table II, the decrease rate of Nylon-6 nanocomposite, Specimen B and C, was faster than that of neat Nylon-6, Specimen A. It is apparent that the organic modified MMT has close relation with this result. The decrease rate of Specimen B and C were very similar to each other in spite of the difference of MMT content. Based on the result, it is presumable that these compounds performed as initiation reagents in the degradation reaction.

The tensile strength was affected by a number of factors. In particular, the molecular weight closely related to the degree of entanglement of molecular chain and the van der Waals forces, each of factors affect the tensile strength.[18] From the test results, the degradation reaction of Nylon-6 through the thermal aging test was found to be related with the decrease of mechanical strength. Some of the degradation reaction, such as crosslinking and annealing, reinforced the mechanical strength of the polymer materials. With these backgrounds, it is predictable that the molecular weight of Nylon-6 decreases through thermal aging test. The changes of the molecular weight will be discussed elsewhere.

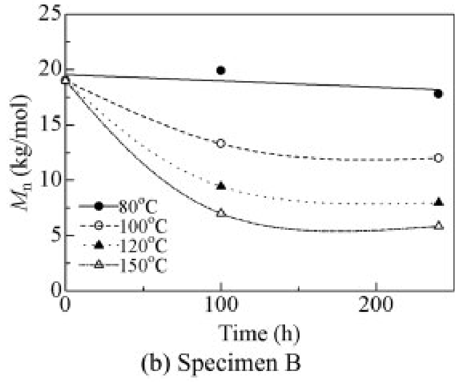
On the other hand, with respect to the elongation, it reduced as shown in Figure 2. The transition of the elongation was similar to that of the tensile strength through the thermal aging test at 80 and 100°C; however, through the thermal aging test at the temperature more than 120°C, the elongation decreased remarkably.

Molecular weight

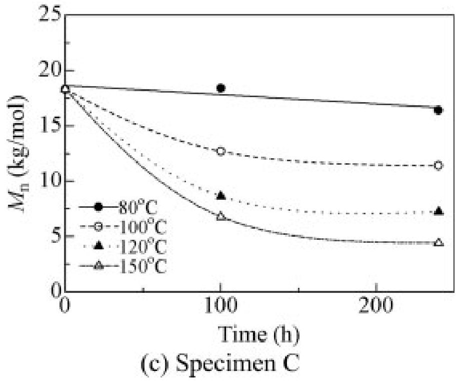
Based on the test result of the molecular weight, Figure 3 shows the changes of the number average molecular weight (M_n) with an increase of the aging time. Through the thermal aging test, the molecular weight decreased gradually and become to form a clear plateau. It is shown that the molecular weight come to be saturated at each of test temperature. The initial decrease rate of the molecular weight became faster in accordance with an increase of test temperature. It is presumable that the degradation reaction accompany with the decrease of the molecular weight was accelerated by the increase of the test temperature. These results were closely related with the results of the tensile strength. It is apparent that the decrease of the tensile strength was closely related with the decrease of the molecular weight. However, the decrease rate of the molecular weight was similar between neat Nylon-6 and Nylon-6 nanocomposite. This point was inconsistent with the results of the tensile test. Ordinarily, the molecular



(a) Specimen A

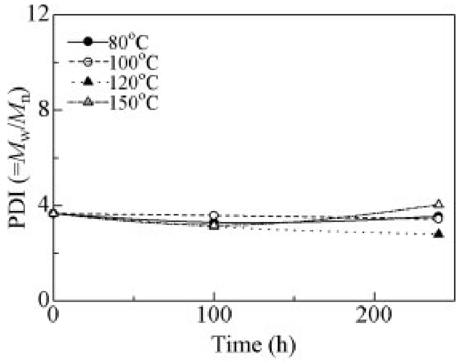


(b) Specimen B

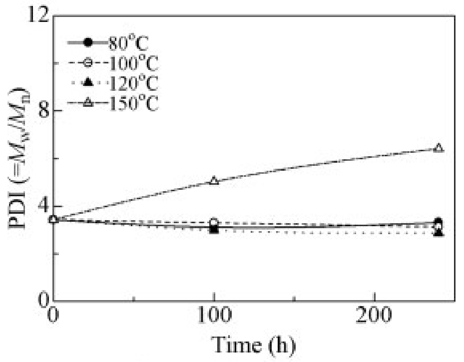


(c) Specimen C

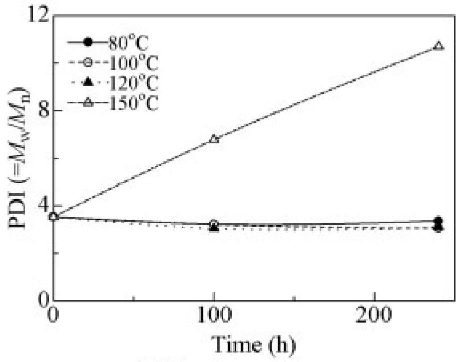
Figure 3 The relationships between the M_n and thermal aging time.



(a) Specimen A



(b) Specimen B



(c) Specimen C

Figure 4 The relationships between the polymer disperse index (PDI = M_w/M_n) and thermal aging time.

weight has some discrepancies; therefore, the molecular weight was sometime discussed in a logarithm scale.

Furthermore, as described earlier, the degree of entanglement of molecular chain and the van der Waals forces affect the tensile strength. In addition, the energy of the hydrogen bond also relates to the tensile strength. On the other hand, the results measured by the GPC indicate the distribution of the molecular weight. It is obvious that the degree of the entanglement of molecular chain and the van der Waals forces were closely related to the molecular weight. However, in measuring the GPC, the conformation of the molecular chain and the interaction between the molecular chain and the organic modified MMT were not detected generally. Accordingly, it is presumable that the molecular weight did not indicate the difference between neat Nylon-6 and Nylon-6 nanocomposite.

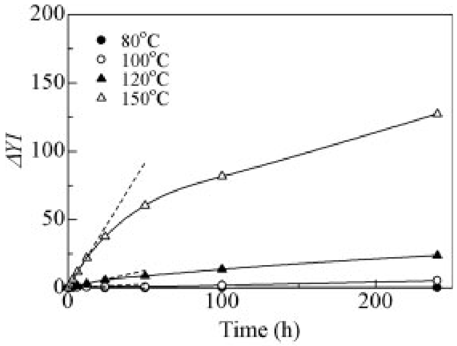
On the other hand, the changes of the polymer disperse index (PDI = M_w/M_n) with an increase of the aging time were shown in Figure 4. Some differences were indicated between neat Nylon-6 and Nylon-6 nanocomposite. The PDI indicates little change even with an increase of test temperature and aging time in case of neat Nylon-6. In case of Nylon-6 nanocomposite, the PDI indicates a change similar to neat Nylon-6 at the test temperature less than 120°C; however, the PDI linearly increased at the test temperature of 150°C. These results mean that the degradation reaction was different among the respective cases. It is presumable that the degradation reaction proceeds depending on a distribution of the molecular weight in case of both neat Nylon-6 and Nylon-6 nanocomposite at the test temperature less than 120°C. However, in case of Nylon-6 nanocomposite at the test temperature of 150°C, it is assumable that the degradation reaction proceeds independently of a distribution of molecular weight, because of the sufficient thermal energy to promote the degradation reaction. It is also presumable that the content of MMT was influenced as an accelerated factor in the degradation reaction.

Color measurement

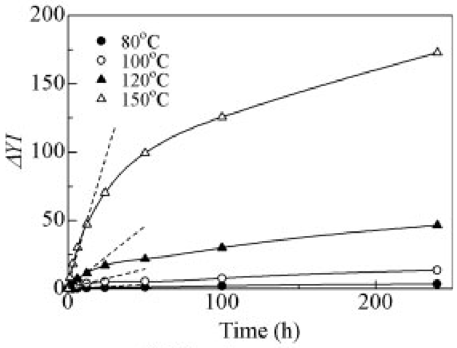
For the result of color measurement, Table III summarizes the test results of nondegraded specimens including the results of the tensile properties and the molecular weight. According to the result, the YI_0 shows an increase with an increase of MMT content, because MMT has a little yellowness. The changes of the ΔYI with an increase of the aging time as shown in Figure 5. In this article, the ΔYI was calculated based on the YI_0 of respective specimen. Each of the

TABLE III
Properties of Nondegraded Specimens

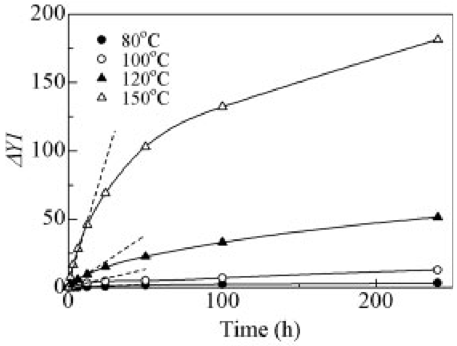
Specimen	Tensile strength (MPa)	Elongation (%)	M_n (kg/mol)	YI_0
A	101.7	400	21.1	1.38
B	102.1	380	19.0	2.55
C	99.0	380	18.3	3.96



(a) Specimen A



(b) Specimen B



(c) Specimen C

Figure 5 The relationships between the *ΔYI* and thermal aging time. Dotted lines are used to make an Arrhenius plot as indicated in Figure 6.

specimens indicated the similar transition, namely, the *ΔYI* of every specimens shows a gradual increase with an increase of aging time. In addition, the initial increase rate of the *ΔYI* becomes larger in accordance with an increase of test temperature. As described earlier, the decrease of the molecular weight occurred based on the degradation reaction of molecular chain. It is presumable that many kinds of degradation reaction such as a scission and hydrolysis of molecular chain occurred.[10] Furthermore, these reactions were activated by a higher temperature. The resulted compounds produced by these degradation reactions were closely related with the color of specimen. However, the increase rate of the *ΔYI* was different between neat Nylon-6 and Nylon-6 nanocomposite. The increase rate of the *ΔYI* of Nylon-6 nanocomposite became significantly larger as compared with neat Nylon-6. It is presumable that the color change was the result of various kinds of degradation reaction; however, it is found that the initial increase rate of the *ΔYI* shows a linear relationship with the aging time. Therefore, these degradation reactions were approximated to the first-order reaction. To calculate activation energy, the reaction rate constant K (h^{-1}) of respective specimen was estimated based on the dotted line as shown in Figure 5.[19] Based on the result, an Arrhenius plot was obtained as shown in Figure 6. The calculated activation energies of Specimen A, B, and C were, respectively, 99.76, 78.03, and 78.67 kJ/mol. This result indicates that Nylon-6 nanocomposite easily changes its color as compared with neat Nylon-6. Under a pyrolysis condition, the activation energy of Nylon-6 nanocomposite was a little higher than that of neat Nylon-6.[20] It is presumable that the activation energy closely relates with the binding energy between MMT and Nylon-6 molecular chain under pyrolysis condition. However, Nylon-6 nanocomposite contains low molecular weight compounds, such as tetraalkylammonium that is applied as a surface active agent in organic modification of MMT; therefore, these compounds affect the degradation reaction under thermal aging condition.[21] Furthermore, the activation energies of Specimen B and C were very similar to each other in spite of the difference of the MMT content. This result was closely related with the result of the tensile strength. These results support the effect that the surface active agent in organic modification of MMT performed as initiation reagents in the degradation reaction.

Correlation of the color change with the tensile properties and the molecular weight

The color change occurred based on the degradation reaction of molecular chain; therefore, it is presum-

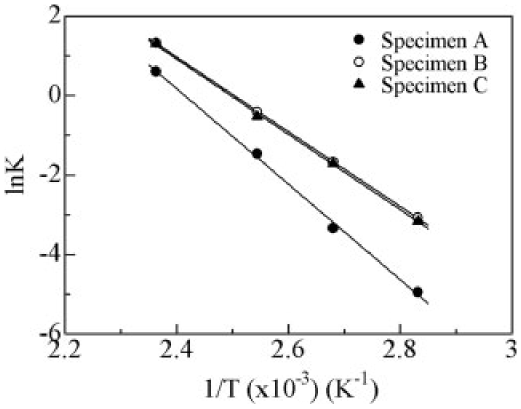


Figure 6 Arrhenius plot of *ΔYI* on thermal aging.

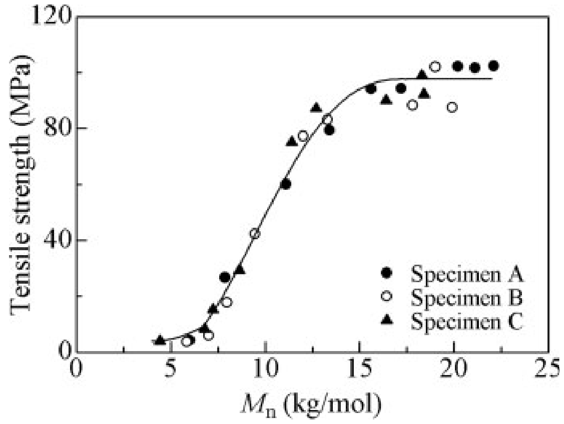


Figure 7 The relationships between the M_n and the tensile strength.

able that the color change was closely related with the mechanical properties and the molecular weight.

The correlation between the M_n and the tensile strength was shown in Figure 7. The tensile strength decreased as the decrease of the molecular weight. However, the tensile strength indicates little change for Nylon-6 with more than 15 kg/mol of the molecular weight, furthermore, the entire plots were approximated by one correlation line, namely, the difference between neat Nylon-6 and Nylon-6 nanocomposite were not indicated.

The correlation of the *ΔYI* with the tensile strength was shown in Figure 8. The tensile strength was decreased gradually as the increase of the *ΔYI*; however, the transition of respective specimen was different. The neat Nylon-6, Specimen A, decreased gradually and became to saturate to a lower level. On the other hand, the transition of Nylon-6 nanocomposite, Specimen B and C, was approximated by two separated correlation lines depending on the range of *ΔYI*. For the range of more than 50 of the *ΔYI*, the slope of the correlation line was gentle; on the other hand, for the range of less than 50 of the *ΔYI*, the slope was relatively sharp. Each of approximate expressions calculated by the least squares method is as shown in the following:

$$\text{Specimen A: } T_B\ (\text{MPa}) = 4.04 \times 10^{-3}(\Delta YI)^2 - 1.24(\Delta YI) + 99.2 \quad (0 \leqq \Delta YI < 130)\ (R^2 = 0.98)$$

$$\text{Specimen B,C: } T_B\ (\text{MPa}) = -1.70(\Delta YI) + 96.0 \quad (0 \leqq \Delta YI < 50)\ (R^2 = 0.98)$$

$$T_B\ (\text{MPa}) = -1.06 \times 10^{-1}(\Delta YI) + 22.9 \quad (50 \leqq \Delta YI < 180)\ (R^2 = 0.81)$$

The squared multiple correlation coefficient of respective approximate expression was sufficiently high to estimate the tensile strength from the result of the *ΔYI*. Based on the result, it is apparent that the sensitivity of the *ΔYI* has the advantage to indicate the difference between neat Nylon-6 and Nylon-6 nanocomposite as compared with the result of the molecular weight.

The correlation of the *ΔYI* with the molecular weight was shown in Figure 9. The molecular weight decreased as the increase of the *ΔYI*. The change of the M_n indicates a significant decrease initially and became to saturate to a lower level; furthermore, the entire plots were approximated by one correlation line. As described earlier, the molecular weight hardly indicates the difference between neat Nylon-6 and Nylon-6 nanocomposite. On the other hand, based on the result, it is also apparent that the *ΔYI* is closely related to the molecular weight. The approximate expression calculated by the least squares method is as shown in the following:

$$\text{Specimen A–C: } M_n\ (\text{kg/mol}) = -2.65\ln(\Delta YI) + 19.1 \quad (0.2 \leqq \Delta YI < 180)\ (R^2 = 0.95)$$

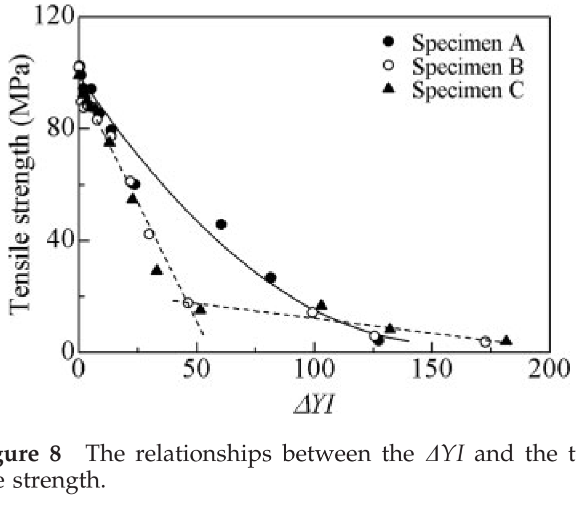


Figure 8 The relationships between the *ΔYI* and the tensile strength.

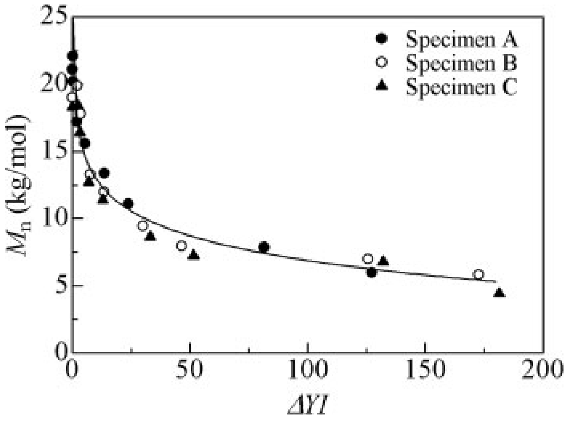


Figure 9 The relationships between the *ΔYI* and the M_n.

The squared multiple correlation coefficient of the approximate expression was sufficiently high to estimate the molecular weight from the result of the ΔYI.

CONCLUSIONS

Many kinds of polymer material change its color through the degrading process by altering its chemical structure. The color change occurred based on the degradation reaction of molecular chain; therefore, it is presumable that the color change was closely related with the mechanical properties and the molecular weight. Moreover, the color measurement is easy enough and the measurement was performed without the sample collection. With these backgrounds, the correlation of the color with the tensile strength and the molecular weight was studied. Through the thermal aging test at various temperatures, specimens became yellowish and the increase rate of color change was different between neat Nylon-6 and Nylon-6 nanocomposite. Such changes were closely related to the tensile strength and the molecular weight. As a method to evaluate the polymer degradation, the correlation of the ΔYI with the tensile strength and the molecular weight was sufficiently high and the ΔYI indicated a difference between neat Nylon-6 and Nylon-6 nanocomposite. From these results, it is obvious that the color measurement with the spectrophotometer is a practical method for evaluation of polymer degradation.

The authors thank UBE Industrial Co., Ltd. for the manufacture of the specimens used in this research.

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