Thermal Aging and Oxygen Permeation of Nylon-6 and Nylon-6/Montmorillonite Composites

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ABSTRACT: Nylon/clay nanocomposites are expected materials for the great improvement of various properties with small percent addition of clay; however, the degradation behavior and the long term stability of nanocomposites have been insufficiently studied. During the thermal aging in air atmosphere, Nylon is ordinarily affected by oxygen gas; therefore, the oxygen permeation under thermal aging condition is an important factor for considering the thermal degradation of Nylon. Moreover, to examine the relationship between the thermal degradation and the oxygen permeation, the oxygen permeation should be measured at the temperature higher than the temperature of respective T_g. According to the oxygen permeation measurement at the temperature of 65°C, the Nylon-6/MMT nanocomposites indicate lower permeability coefficient than that of neat Nylon-6 and Nylon-6/MMT composites. On the other hand, the solubility coefficients of the MMT contained Nylon-6 were similar to each other and the solubility coefficients were significantly higher than that of the neat Nylon-6. This characteristic is presumable to be closely related with the thermal degradation of Nylon-6. In case of the MMT contained Nylon-6, the permeation of oxygen gas is slower than the case of neat Nylon-6; however, it is conceivable that the oxygen gas permeates with some interactive influences on Nylon-6 matrix. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 928–935, 2010

Key words: nylon; montmorillonite; composites; gas permeation; degradation

INTRODUCTION

Nylon/clay nanocomposites are expected materials for the great improvement of mechanical properties, electric properties, and flame retardancy with small percent addition of clay; therefore, a lot of studies have been performed on various aspects.[1–4] However, the degradation behavior and the long term stability of nanocomposites have been insufficiently studied. These performances are not negligible in using the materials in practical products. Heretofore, some types of clays are used as filler for the rubber; the Kaolin and the Bentonite are ordinarily used for its purpose.[5,6] After the remarkable discovery of the nanocomposites technology, a lot of polymer/clay systems have been examined; however, the clay is relatively innovative filler for plastics and the montmorillonite (MMT) is one of the well-considered clay. The authors previously reported the thermal aging behavior of Nylon-6/MMT nanocomposites with use of spectrophotometer measurement.[7] However, this study was focused on the evaluation method of polymer degradation with use of color measurement; therefore, the degradation factors of the nanocomposites were only presumed based on the previous literatures.[8–12] During the thermal aging in air atmosphere, Nylon is ordinarily affected by oxygen gas; therefore, the oxygen permeation under thermal aging condition is an important factor for considering the thermal degradation of Nylon.[10] The improvement of gas barrier performance of the nanocomposites was previously well-examined; however, the correlation between the oxygen permeation and the degradation behavior of the nanocomposites has not been examined. In measuring the oxygen permeation, the dispersion state of the clay particles is an important factor. In case of the nanocomposites, the surface area of the clay particles is significantly larger than that of the simple mixed composites of the polymer and the clay. The larger surface area is presumable to be more interacted with permeated oxygen. Therefore, not only the neat Nylon-6 and Nylon-6/MMT nanocomposites but also the Nylon-6/MMT composites films were prepared to clarify the thermal aging behavior based on the oxygen permeation properties. Moreover, the gas permeation is ordinarily measured at the temperature lower than glass transition temperature (T_g); however, to examine the relationship between the thermal degradation and the oxygen permeation, the oxygen permeation should be measured at the temperature higher than the temperature of respective T_g.[13] Therefore, the oxygen permeation of prepared specimens was measured at the temperature of 65°C. In addition, the analyses of the ordinary

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TABLE I
Preparation of Specimens

Specimen	Type	Matrix serial number	Organic modified MMT (net MMT)	MMT (wt %)
A	Neat Nylon-6	1022B	0	0
B	Nylon-6/MMT	1022B/1022C2	1.15 (0.86)	0
C	Nanocomposites	1022C2	2.3 (1.72)	0
D	Nylon-6/MMT	1030B	0	0.86
E	Composites	1030B	0	1.51

polymer degradation, the tensile strength, the molecular weight, and the yellowness index were also performed to understand the degradation behavior of the prepared specimens.

EXPERIMENTAL

Materials

The neat Nylon-6 (1022B, Ube Industries) (Specimen A), Nylon-6/MMT nanocomposites (1022C2, Ube industries) (Specimen B,C), Nylon-6/MMT composites (Specimen D,E) were molded in the form of 0.2 mm thickness film by using an extruder equipped with T-die. In case of the Nylon-6/MMT nanocomposites, the surface of MMT particles was organically modified by 12-aminolauric acid ammonium salt that is used as a surface active agent. The Nylon-6/MMT composites are prepared by mixing commercial grade Nylon-6 (1030B, Ube industries) and nontreated MMT with an extruder. Respective specimens are shown in Table I. Based on the microscopic observation, the MMT particles were detected unlike to the Nylon-6/MMT nanocomposites (1022C2, Ube industries) as shown in Figure 1.

Measurement of physical properties through thermal aging test

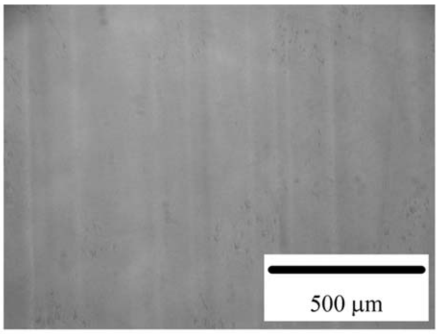
The thermal aging test was performed with use of ventilated oven (Yamato DN600). The test temperatures of the thermal aging test were, respectively, 80, 100, 120, and 150°C under an air condition. The specimens of approximately 200 mm × 150 mm × 0.2 mm were applied to the thermal aging test. After the thermal aging test, the specimens were preserved in an auto-desiccator for more than 72 h to control a specimen condition. The tensile properties, the molecular weight (MW), and the yellowness index (*YI*) were stepwise measured through thermal aging test in the same way as shown in the previous literature.[7]

Oxygen permeation measurement

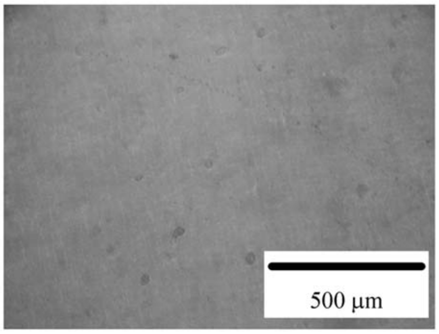
Oxygen permeation properties were determined using constant-volume variable-pressure method according to the previous literature.[13] The measurement temperature was 65°C, which was higher than the glass transition temperature (T_g) of Nylon-6, and the materials tested were at a rubbery state and it was suitable to estimate the gas permeation behavior through thermal aging test. The feed pressure was about 1 atm and the permeate side was maintained under vacuum. The permeability coefficient (P) was determined by

$$P = \frac{dp}{dt}\frac{273V}{760(273+T)}\frac{1}{A}\frac{1}{p_1}\ell$$

where *dp/dt* is the pressure increase over time at a steady-state; V is the permeate volume; T is the temperature; A is the permeation area of the sample; p_1 is the feed pressure; and ℓ is the sample thickness.

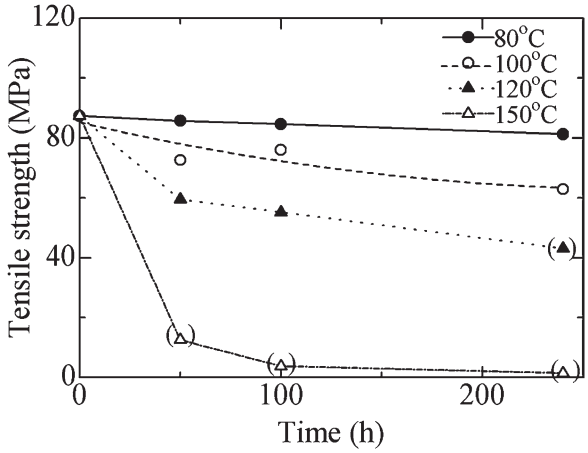


(a) 1022C2 (Nylon-6/MMT nanocomposites, Ube Industries Ltd.)
Organic modified MMT 2.3 wt% (net MMT 1.72 wt%)
(Specimen C)

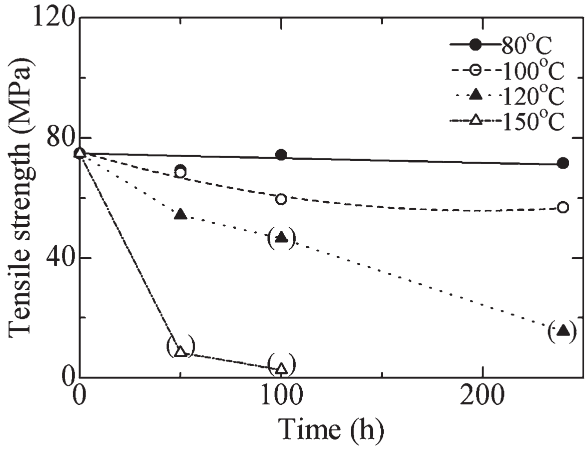


(b) 1030B (Nylon-6) mixed with MMT composites
MMT 1.51 wt% (Specimen E)

Figure 1 Microscope images of Nylon-6/MMT composites and Nylon-6/MMT nanocomposites. Respective specimens were molded by extruder.



(a) Specimen D



(b) Specimen E

Figure 2 The relationships between the tensile strength and thermal aging time. The number of measurement <5; the averaged results were shown with parenthesis.

The apparent diffusion coefficient (D) was determined by the following equation using the time-lag method.

$$D = \frac{\ell^2}{6\theta}$$

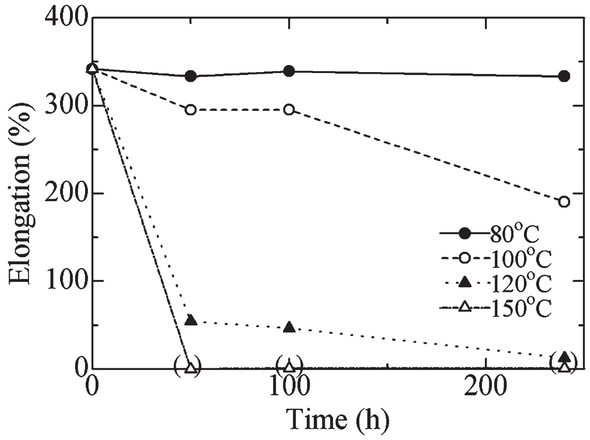
where ℓ is the membrane thickness and θ is the time lag. Based on the solution-diffusion mechanism, the apparent solubility coefficient (S) was estimated by dividing the permeability coefficient by the diffusion coefficient.

RESULTS AND DISCUSSION

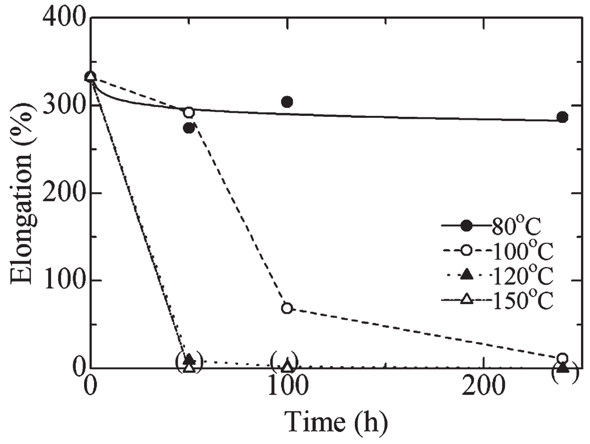
Tensile properties

According to the results of the tensile test of Specimen D and E, Figures 2 and 3 show the changes of the tensile properties with increase of the aging time. In performing the tensile test, five dumb-bell specimens were not taken from highly degraded specimens because of their brittleness. Therefore, in case the number of measurement less than 5, the averaged results are shown with parenthesis. Moreover, because of the serious brittleness, any dumb-bell specimen could not be taken from Specimen E after 240 h thermal aging at 150°C. For Specimen A–C, the results are shown in the previous literature.[7]

It is apparent that the tensile strength of nondegraded Nylon-6/MMT composites (Specimen D,E) indicates 75–85 MPa that is approximately 80% of neat Nylon-6 (Specimen A) and Nylon-6/MMT nanocomposites (Specimen B,C). Moreover, the initial strength of Specimen D was superior to that of Specimen E. In case of Nylon-6/MMT composites, unlike the Nylon-6/MMT nanocomposites, the surface of MMT particles was not modified by surface active agent. Therefore, the dispersion of MMT particles was heterogeneous as compared with



(a) Specimen D



(b) Specimen E

Figure 3 The relationships between the elongation and thermal aging time. The number of measurement was <5; the averaged results were shown with parenthesis.

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

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
D	0.033	0.295	0.558	1.496
E	0.112	0.129	0.411	1.329
				(MPa/h)

nanocomposites as shown in Figure 1. It is presumable that the MMT particles acted as a stress concentration point at the tensile test.

Through the thermal aging test, the tensile strength decreased gradually as shown in Figure 2, and the decrease rate of the tensile strength became faster in accordance with an increase of test temperature. The initial decrease rate of the tensile strength ($-dT_B/dt$) was calculated according to the result between nondegraded specimen and 50 h thermal aged specimen. As shown in Table II, most of the decrease rate of Nylon-6/MMT composites, Specimen D and E, was seemed to be the middle between neat Nylon-6, Specimen A, and Nylon-6/MMT nanocomposites, Specimen B and C. In case of the Specimen D at the temperature of 100°C, this decrease rate was the only exception of the above mentioned behavior; however, the difference of the resulted decrease rate was not remarkable.

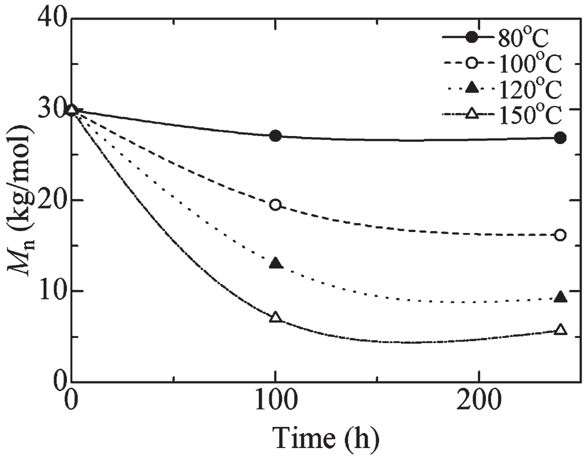
As described in the previous literature, the tensile strength presumably decreased with the decrease of the molecular weight.[7] The thermal aging condition was closely related with the change of the molecular weight of Nylon-6. The changes of the molecular weight will be discussed elsewhere.

On the other hand, with respect to the elongation, it reduced as shown in Figure 3. In case of neat Nylon-6 and Nylon-6/MMT nanocomposites, the tensile strength through the thermal aging test at 80 and 100°C were not changed remarkably and the changes at these temperatures were similar to each other.[7] However, in case of Nylon-6/MMT composites, through the thermal aging test at the temperature higher than 100°C, the elongation decreased significantly with an increase of the aging time. These changes were different from the case of neat Nylon-6 and Nylon-6/MMT nanocomposites. In case of Nylon-6/MMT composites, the MMT particles acted as a stress concentration point at the tensile test; therefore, the elongation was presumed to be more sensitive than the case of neat Nylon-6 and Nylon-6/MMT nanocomposites.

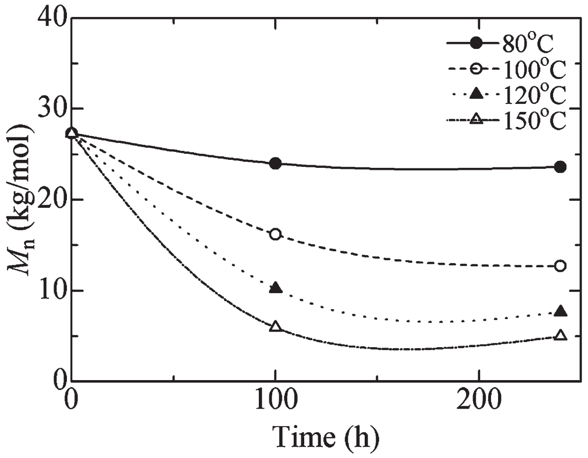
Molecular weight

According to the test of the molecular weight of Specimen D and E, the number average molecular weight (M_n) changes with an increase of the aging time. As shown in Figure 4, the molecular weight decreased gradually with an increase of the aging time and became to form a clear plateau. It is apparent that the molecular weight comes to be saturated for each of test temperature. The initial decrease rate of the molecular weight became larger in accordance with an increase of test temperature. It is presumable that the degradation reaction is accompanied with the decrease of the molecular weight and that reaction is accelerated by the increase of the test temperature. These results are closely related with the results of the tensile strength.

On the other hand, the changes of the polymer disperse index (PDI = M_w/M_n) with an increase of the aging time of Nylon-6/MMT composites (Specimen D,E) were as shown in Figure 5. In the case of Nylon-6/MMT composites, the PDI did not indicate a significant change at the test temperature lower

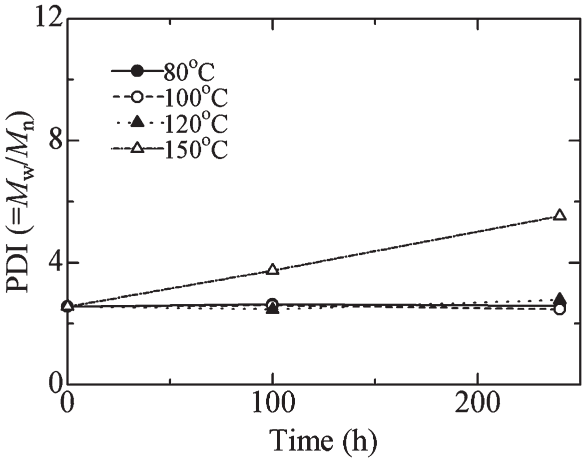


(a) Specimen D

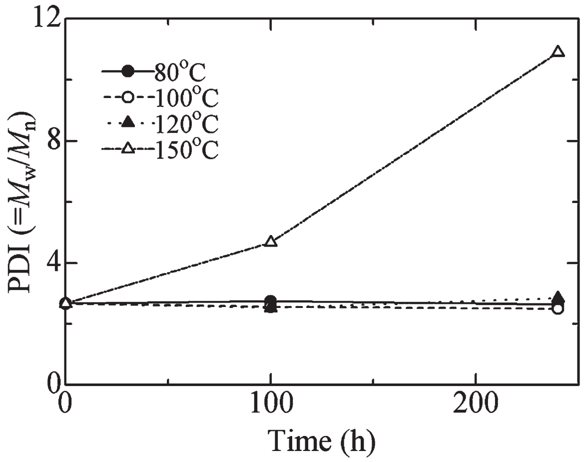


(b) Specimen E

Figure 4 The relationships between the M_n and thermal aging time.



(a) Specimen D



(b) Specimen E

Figure 5 The relationships between the polymer disperse index (PDI = M_w/M_n) and thermal aging time.

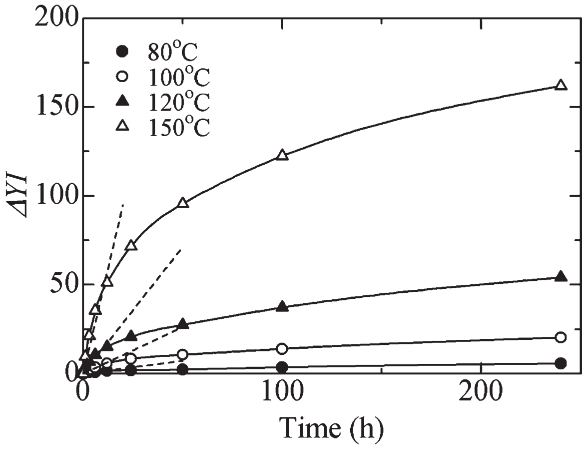
than 120°C; however, the PDI linearly increased at the test temperature of 150°C. These behaviors are similar to those of Nylon-6/MMT nanocomposites (Specimen B,C). It is presumable that the degradation reaction proceeds depending on a distribution of the molecular weight at the test temperature lower than 120°C. However, it is assumable that the degradation reaction proceeds independently of a distribution of molecular weight at the test temperature of 150°C, 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 change

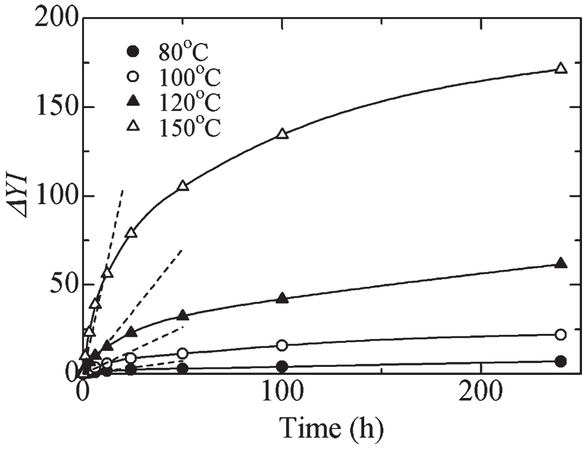
Table III summarizes the test results of nondegraded specimens including the results of the tensile properties and the molecular weight of Specimen A–E. According to the result of color measurement, the *YI* of nondegraded specimen (YI_0) shows an increase with an increase of MMT content, because the MMT particles have a slight yellowness. In case of the Nylon-6/MMT nanocomposites, Specimen B and C, the YI_0 significantly increased with an increase of MMT content as compared to the case of Nylon-6/MMT composites. The Nylon-6/MMT nanocomposites contain the surface active agent, which is used for organic modification of MMT. The organic modified MMT become yellowish as compared with nontreated MMT; therefore, the content of the organic modified MMT was closely related to the YI_0 of Nylon-6/MMT nanocomposites. The changes of the ΔYI with an increase of the aging time of Specimen D and E are as shown in Figure 6. In this article, the ΔYI was calculated based on the YI_0 of respective specimen. Each of the specimens indicated the similar transition, namely, the ΔYI of entire specimens shows a gradual increase with an increase of aging time. In addition, the initial increase rate of the ΔYI becomes larger according to an increase of test temperature. As described earlier, the decrease of the molecular weight occurred according to the degradation reaction. It is assumable that many kinds of degradation reaction such as a scission and hydrolysis of molecular chain occurred. Furthermore, these reactions were activated by a higher temperature. The resulted compounds produced by these degradation reactions were closely related with the yellowness of specimen. It is assumable that the color change is the result of various kinds of degradation reactions; however, it is evident 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 the activation energy, the reaction rate constant K (h^{-1}) of respective specimen was estimated based on the dotted line as shown in Figure 6. The calculated activation energies are shown in Table IV. The activation energies of Nylon-6/MMT composites are the smallest among those of the Specimens. These results indicate that the Nylon-6/MMT composites easily change its color as compared with neat Nylon-6 and Nylon-6/MMT nanocomposites.

TABLE III
Properties of Nondegraded Specimens

Specimen	Tensile strength (MPa)	Elongation (%)	M_n (kg/mol)	YI_0
A	101.7	400	21.1	1.4
B	102.1	380	19.0	2.6
C	99.0	380	18.3	4.0
D	87.4	340	29.9	2.2
E	74.8	330	27.3	2.5



(a) Specimen D



(b) Specimen E

Figure 6 The relationships between the Δ*YI* and thermal aging time. Dotted lines are used to make an Arrhenius plot.

Moreover, according to the color measurement, the neat Nylon-6, Specimen A, indicated the highest activation energy among those of the Specimens. It is presumable that the contained MMT seems to have some relation with the thermal degradation. The relationship between the contained MMT and oxygen was subsequently discussed based on the results of the oxygen permeation measurement.

In case of Nylon-6/MMT composites, Specimen D and E, the correlation of the ΔYI with the tensile strength and the molecular weight are shown in Figures 7 and 8. Similarly to the case of neat Nylon-6 and Nylon-6/MMT nanocomposites, the results are well correlated.

TABLE IV
Calculated Activation Energy of Specimens

Specimen	Activation energy (J/mol)
A	99.76
B	78.03
C	78.67
D	63.93
E	65.31

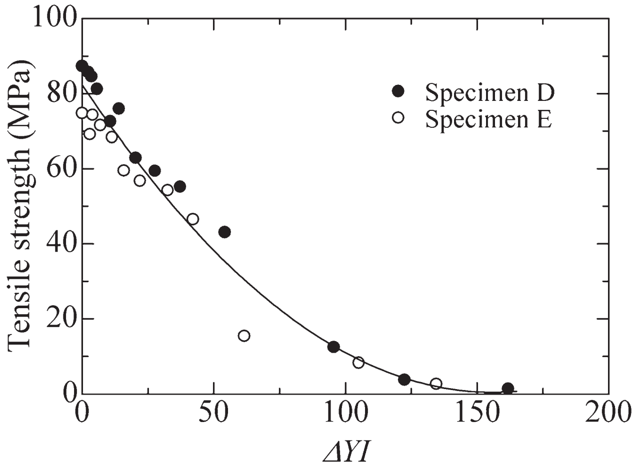


Figure 7 The relationships between the Δ*YI* and the tensile strength.

Oxygen permeation at the temperature of 65°C

The results of oxygen gas permeation at the temperature of 65°C were shown in Figure 9. The Nylon-6/MMT nanocomposites, Specimen C, indicate the lowest permeability coefficient of 4.33 ± 0.10 ($\times 10^{-12}$ (STP)cm/cm^2 s cmHg) among three specimens, which corresponds to the ordinary results measured at the temperature lower than T_g.[14,15] In addition, the solubility coefficients of the Specimen C and the Nylon-6/MMT composites, Specimen E, which are similar to each other, are significantly higher than that of the neat Nylon-6, Specimen A. The solubility coefficients of Specimen A, C, and E were 5.03 ± 0.97, 15.0 ± 3.0, and 14.3 ± 3.9 ($\times 10^{-4}$ cm^3 (STP)/cm^3 cmHg), respectively. The Specimens C and E contain approximately 2 wt %

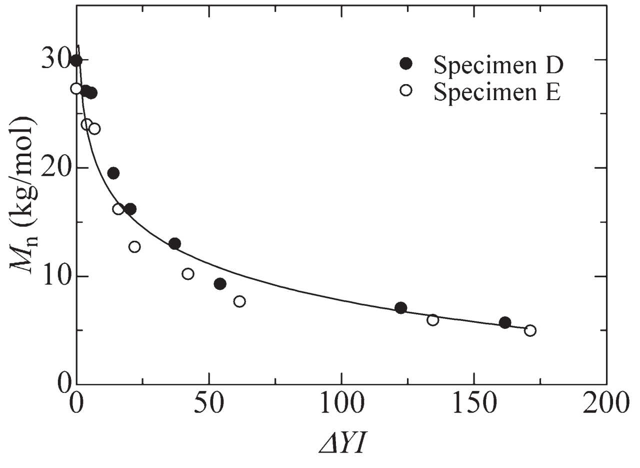
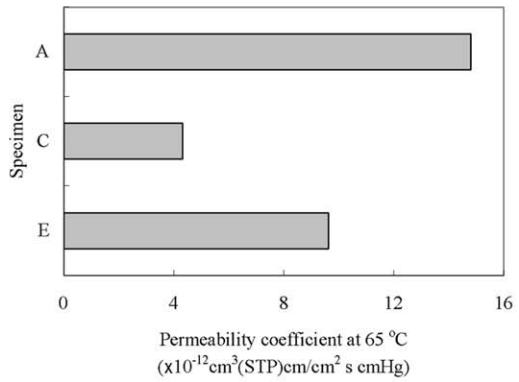
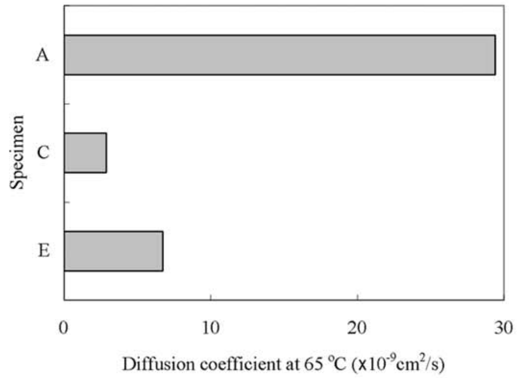


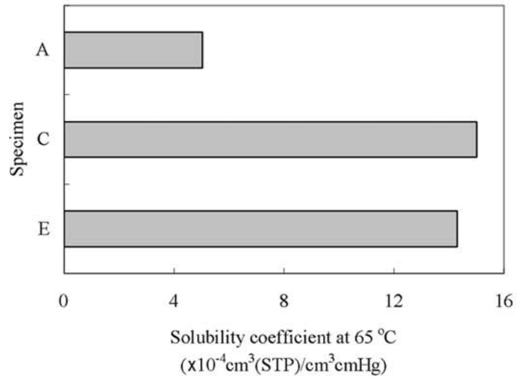
Figure 8 The relationships between the Δ*YI* and the M_n.



(a) Permeability coefficient at 65 °C



(b) Diffusion coefficient at 65 °C



(c) Solubility coefficient at 65 °C

Figure 9 Oxygen permeation properties of specimens at 65°C.

of MMT; therefore, it is presumable that the MMT seemed to have a close affinity with oxygen gas as compared with Nylon-6 matrix and to relate to solubility coefficient. Moreover, the Specimen C also contains the surface active agent; however, the surface active agent did not indicate significant relation with the solubility coefficient. According to the results of the yellowness index, the neat Nylon-6 indicated the highest activation energy among the Specimens in spite of the highest permeability coefficient of oxygen gas. The solubility coefficient was assumable to be more influential in the degradation reaction of the Nylon-6 than the permeability coefficient.

In case of the neat Nylon-6, the permeation of oxygen gas was relatively rapid as compared with Nylon-6/MMT nanocomposites and Nylon-6/MMT composites; therefore, it is conceivable that the oxygen gas permeated through the neat Nylon-6 with a slight interactive influence. On the other hand, in case of the Nylon-6/MMT nanocomposites and the Nylon-6/MMT composites, the permeation of oxygen gas was slow and roundabout as compared with neat Nylon-6; therefore, it is conceivable that the oxygen gas permeated with some interactive influences on Nylon-6 matrix. According to the oxygen permeation result, in case of the Nylon-6/MMT nanocomposites and the Nylon-6/MMT composites, respective time lags are significantly longer than that of neat Nylon-6 as shown in Table V. In the oxygen permeation through the MMT contained Nylon-6, it is presumable that the oxygen gas permeated slowly and had a longer time to react with Nylon-6 matrix; therefore, the Nylon-6/MMT nanocomposites and the Nylon-6/MMT composites are easily degradable as compared with the neat Nylon-6 under the thermal aging condition.

CONCLUSIONS

The mechanical performance of Nylon/clay nanocomposites was improved by adding small amounts of clay; however, Nylon was easily affected by oxygen gas under the thermal aging condition. To understand the thermal aging behavior, the oxygen permeation properties of neat Nylon and the MMT contained Nylon were clarified. According to the oxygen permeation measurement at the temperature of 65°C, the Nylon-6/MMT nanocomposites indicate a lower permeability coefficient than those of neat Nylon-6 and Nylon-6/MMT composites. On the other hand, the solubility coefficients of the MMT contained Nylon-6, Nylon-6/MMT nanocomposites, and Nylon-6/MMT composites, were similar to each other and their solubility coefficients were significantly higher than that of the neat Nylon-6. It is presumable that the contained MMT seems to have a close affinity with oxygen gas as compared with

TABLE V
Time Lags of Specimens at 65°C

Specimen	Time lag θ ($\times 10^3$ sec)
A	2.71 ± 0.54
C	25.0 ± 2.7
E	10.6 ± 0.8

Nylon-6 matrix. This characteristic is presumable to be closely related with the thermal degradation of Nylon-6. On the other hand, the surface active agent which is contained in Nylon-6/MMT nanocomposites did not indicate significant relation with the solubility coefficient. The activation energies of the MMT contained Nylon-6 were lower than that of neat Nylon-6. This result indicates that the MMT contained Nylon-6 was easily degraded under the thermal aging condition. It is conceivable that the oxygen gas permeated through the neat Nylon-6 with a slight interactive influence. In case of the MMT contained Nylon-6, the oxygen gas slowly permeated as compared to the case of neat Nylon-6; however, it is conceivable that the oxygen gas permeated with some interactive influences to Nylon-6 matrix.

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