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Study on the Long-Term Acid Rain Aging Behaviour of Polyamide 6

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The long-term acid rain aging behavior of polyamide 6 (PA6) was studied in aqueous solution with pH = 1 at 40°C in comparison with a stabilized sample (Stabilizer: 0.2wt% Irganox 1010, 0.2wt% Irgafos 168, 0.3wt% Tinuvin 770 and 0.3wt% Tinuvin 234). The aging can be described as a succession of three stages. The first one corresponded to the physical absorption of water until equilibrium while the chemical degradation can be neglected resulting in a drop of the mechanical strength and an increase of the toughness of the sample of PA6. The hydrolysis reaction of the amido link of PA6 predominated during the middle and last stage of aging, resulting in a decrease of all the mechanical properties. The reduced viscosity of PA6 decreased monotonically during the whole aging process. The end amine group concentration could not be detected due to its reaction with acid. The carboxylic acid came not only from the carboxylic acid end group produced by the degradation of the sample, but also from the acid rain. The stabilizers didn't have any effect of the anti-acid rain degradation of PA6.

Keywords   acid rain aging, mechanical properties, polyamide, structure

Introduction

Polyamide, as one of the most common engineering plastics, has a wide range of applications in industry due to its excellent mechanical properties. Usually, the carbon-hydrogen bond on the methylene group adjacent to nitrogen is considered to be the weakest bond, with an oxidation reaction proceeding on this carbon when subjected to heat, oxygen, light and water.[1] It leads to the decrease of the molecular weight, subsequent deterioration in physical and mechanical properties, increased yellowing, and eventually embrittlement.[2–6]

Considerable research has been concentrated on the thermal-oxidative and ultraviolet-oxidative aging behavior and mechanism of PA6.[7–11] Due to its properties of strong polarity and water absorption, the hydrolysis, ammonolysis and acid hydrolysis under high temperature all have detrimental influences on its properties. However, little work has been reported on the acid hydrolysis of polyamide, except that the aging of polyamide 11 in acid solution was studied in terms of the water absorption property, viscoelasticity and surface morphology.[12]

The long-term acid rain aging behavior of PA6 was studied in this work in order to provide valuable results for its industrial applications, especially in areas with heavy acid

rain. The aging behavior and mechanism of PA6 stabilized with several commonly used stabilizers were also studied for the purpose of comparison with the pure sample.

Experimental

Materials

The pure sample of polyamide 6 used in this work was a commercial grade granular product (YH800) without any additives, supplied by Yueyang Petrochemical Co., Ltd (Hunan, China), with relative viscosity of 2.85 ± 0.03 in formic acid. The stabilizers, with analytical purity, included Irganox 1010 as the hindered phenolic main antioxidant, Irgafos 168 as the phosphorous-based secondary antioxidant, Tinuvin 770 as the hindered amine light stabilizer and Tinuvin 234 as the benzotriazol ultraviolet absorbent, all obtained from Ciba-Geigy Co. The composition of stabilizers applied in the sample of the stabilized PA6 was 0.2wt%Irganox 1010, 0.2wt% Irgafos 168, 0.3wt%Tinuvin 770 and 0.3wt%Tinuvin 234.

Preparation of the Samples

The materials used in our work were pure PA6 and stabilized PA6. The stabilized PA6 was prepared by mixing the pure sample in dry form with stabilizers (Irganox 1010, Irgafos 168, Tinuvin 770 and Tinuvin 234) at room temperature in a high-speed mixer, and then extruding them with a TSSJ-25/03 twin-screw extruder from Chenguang Co. (Chengdu, China) at a rotational speed of 70 rpm. The temperature of the barrel was in the range of 210~250°C. The extrudates were pelletized and dried. For comparison purposes, pure PA6 was extruded, pelletized and dried by the same technique. Some of the granules were injected, then molded into standard dumb-bell and rectangular splints (length: 155 mm, thickness: 4.2 mm), and some of the granules were hot compression molded to form round plates with 3 mm thickness.

Acid Rain Aging

Immersion of PA6 samples was done in a solution with pH = 1 at 40°C for up to 28 days. The solution was prepared with HCl, HNO_3, and H_2SO_4, with molar ratio 1:2:12.

Measurement

Mechanical Pproperties. The tensile and bending performance of the samples were measured with a 4302 material testing machine from Instron Co. (U.S.A.) according to the ISO 527-1993 and ISO 178-1993 standards, respectively. The tensile test speed was 50 mm/min, and the sample length between benchmarks was 50 ± 0.5 mm. The bending test speed was 2 mm/min.

The notched Charpy impact strength of the samples was measured with a ZBC-4A impact testing machine from Xinsansi Co. (Shenzhen, China) according to the ISO 180 standard.

Reduced Viscosity. Samples of PA6 of about 0.5g were dissolved in 100mL of formic acid (88 wt%). The time of outflow of the solution was measured in a Ubbelohde viscometer

in a water bath at 25°C, according to ISO 307-1984. Then the reduced viscosity can be calculated with the following formula.

$$\eta = \left(\frac{t}{t_0} - 1\right) \times \frac{1}{C} \tag{1}$$

where t is the time of outflow of the PA6 solution (s), t_0 is the time of outflow of the solvent (s), and C is the concentration of the PA6 solution (g/mL).

End Group Analysis[13].

Carboxylic acid groups. Samples of PA6 of about 0.3 g were dissolved in 20 mL of phenylcarbinol at 150°C. Three milliliters of propyl alcohol were added and the hot solution was titrated with NaOH (about 0.02 mol/L), using phenolphthalein as the indicator. The content of the carboxylic acid can be calculated with the following formula

$$X = \frac{(a - b)n}{W} \times 10^{-3} \tag{2}$$

where a is the volume of NaOH solution used by sample (mL), b is the volume of NaOH solution used by the solvent (mL), n is the molar concentration of NaOH solution (mol/L), and W is the weight of the sample (g).

Terminal amine groups. Samples of PA6 of about 0.3 g were dissolved in 25 mL of a mixed solution of phenol-methyl alcohol (volume ratio 1:1) at 55°C. The solution was titrated with HCl (about 0.005 mol/L), using thymol blue as the indicator. The content of the terminal amine groups can be calculated with the following formula.

$$Y = \frac{(A - B)n}{W} \times 10^{-3} \tag{3}$$

where A is the volume of HCl solution used by the sample (mL), B is the volume of HCl solution used by the solvent (mL), n is the molar concentration of HCl solution (mol/L), and W is the weight of the sample (g).

Yellow Index. The yellow index (YI) was measured with a DC-P3 full automatic chromatic aberration meter from Xingguang Instrument Co. (China). According to GB 2409-80 of China, a few points on the plate were selected, and the relevant stimulus values (X, Y, and Z) were measured. Then YI could be calculated according to the following formula given in GB 2409-80:

$$YI = 100(1.28X - 1.06Z)/Y \tag{4}$$

The YI of the samples was the average value of YI for all the points measured on the plate samples.

Ultraviolet Absorption. Samples of PA6 of about 0.1 g were dissolved in 50 mL of a mixed solution of sulfuric acid/methanol (0.4 mol/L). The ultraviolet absorption measurements for the solutions, for characterizing the structure during aging, were carried out with a U3010 spectrophotometer (Hitachi, Japan).

Scanning Electron Microscopy Analysis (SEM). Analysis of the surface morphology of samples was performed with a JEOL JSM-5900LV scanning electron microscopy (SEM) (Japan). The operating voltage was 20 KV.

Results and Discussion

Reduced Viscosity of PA6

Figure 1 shows the variation of the reduced viscosity of PA6 with acid aging time. The difference of the initial reduced viscosity between the pure sample and the stabilized sample of PA6 may result from the relatively high thermal oxidative stability of the stabilized sample during melt processing. Afterwards the reduced viscosity of the samples declined monotonically and dropped by about 70% at the end of the test.

Because the reduced viscosity characterizes the viscosity average molecular weight of polymers, the decline of the reduced viscosity of the samples indicated the rapid molecular degradation of PA6 during the acid rain aging, resulting from hydrolysis of the amido links. The reduced viscosity of the stabilized sample was very close to that of the pure sample during aging, indicating that the stabilizers didn't seem to have any effect of anti-acid rain degradation.

Mechanical Properties of PA6

The variation of mechanical properties of PA6 with aging time in acid rain is shown in Fig. 2. In the initial stage of the aging, lots of water penetrated the molecules of PA6, functioning as plasticizers[14] and resulting in a decrease of the tensile strength of PA6 by about 50% after 7 days' aging and a decrease of the bending strength of PA6 by about 50% after 3.5 days' aging. However, at the same time, moisture absorption also played the function of toughening and led to the increase of the elongation at break of PA6 by about 50% and the increase of the notched Charpy impact strength of pure PA6 by about 24 times the initial value after 3.5 days of aging. However, with the continuation of aging, the molecular weight of the sample decreased gradually, which finally resulted in the decline of mechanical properties of PA6. In addition, the experimental results also showed that the stabilizers of the stabilized sample did not play a remarkable positive function.

Chemical Structure of PA6

The variation of acid concentration of the sample of PA6 with aging time is shown in Fig. 3. Terminal amine groups were not detected during the whole aging process, which indicated
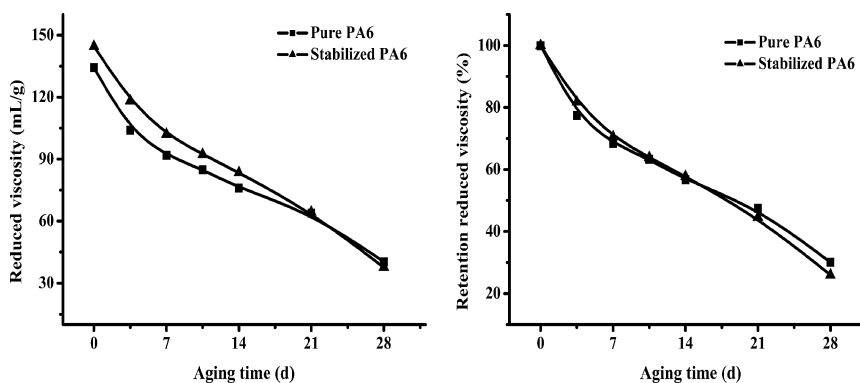

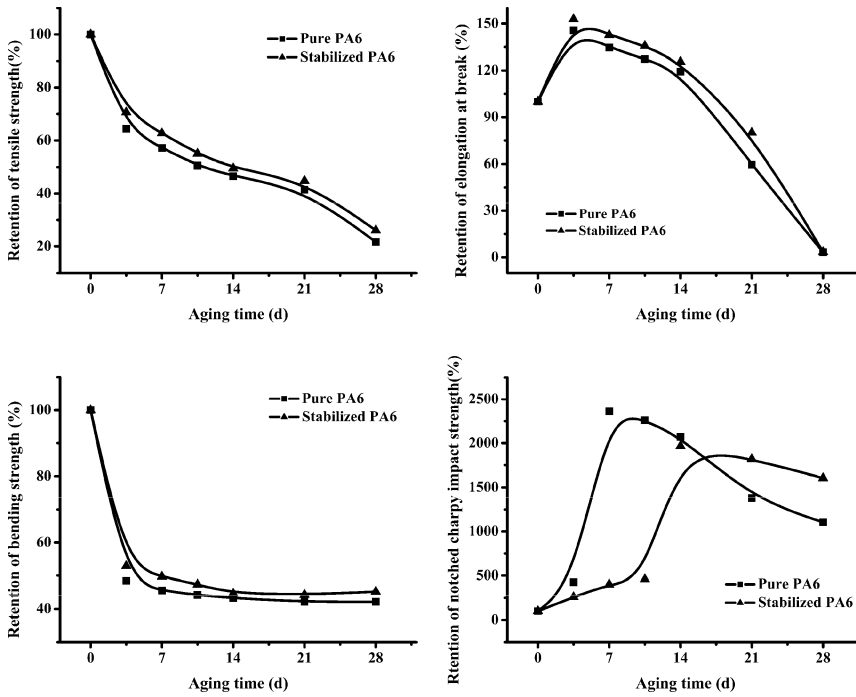**Figure 1.** Reduced viscosity of PA6 as a function of acid rain aging time.

Figure 2. Retention of the mechanical properties of PA6 as a function of acid rain aging time.

that such groups had been consumed and totally reacted with acid. The content of the carboxylic acid calculated from titration was not only the concentration of carboxylic acid end groups of the sample, but included the acid from the simulated acid rain immersion liquid.
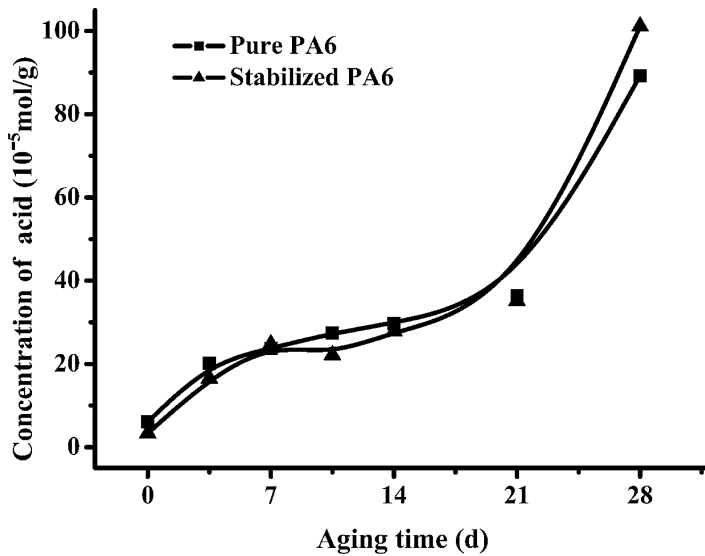

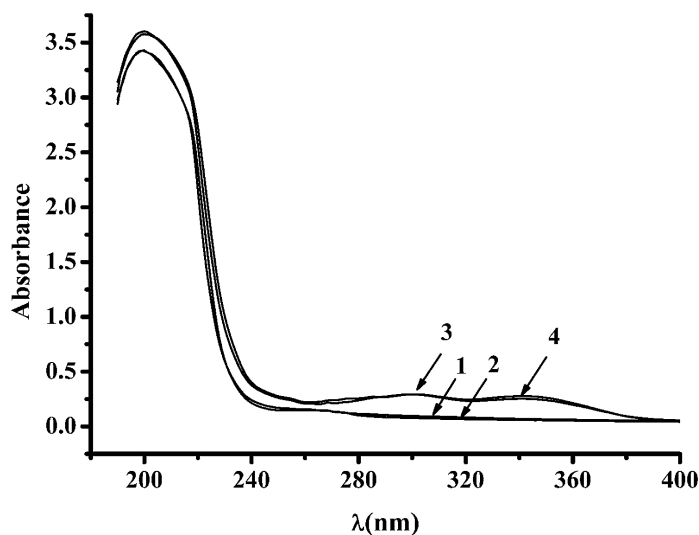**Figure 3.** Carboxylic concentration of PA6 as a function of acid rain aging time.

Figure 4. UV spectrum of PA6 for different acid aging time (in 0.4 mol/L sulfuric acid/methanol) (1: Pure PA6/0 day, 2: Pure PA6/28 days, 3: Stabilized PA6/0 day, 4: Stabilized PA6/28 days).

In the initial stage of aging, alot of acid rain infiltrated into the PA6 matrix to induce the rise of acid concentration. During the middle stage of aging, the acid concentration of the sample increased slowly to reach the diffusion balance of the acid rain. During the last stage of aging, severe hydrolysis occurred and lots of carboxylic acid was produced. The former diffusion balance was also broken, which resulted in the sharp rise of the PA6 acid concentration.

The UV spectrum of PA6 for different acid aging time is shown in Fig. 4. The maximum in the ultraviolet absorption at about 205 nm resulted from the n→π* electron transition
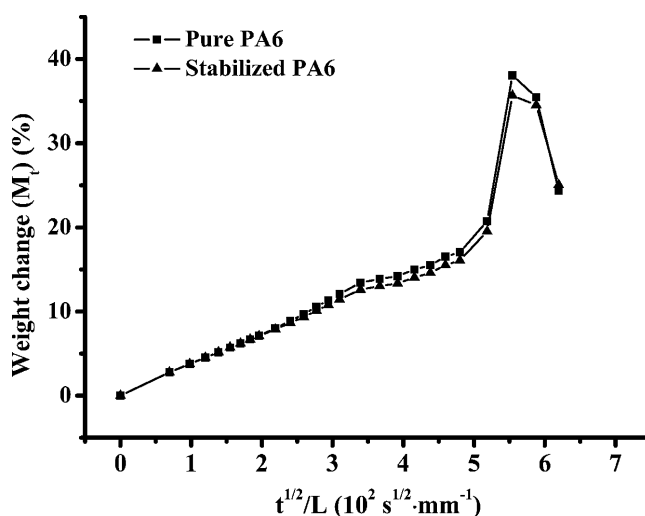

Figure 5. Water absorption of PA6 (L = 3 mm) at 40°C and pH = 1.

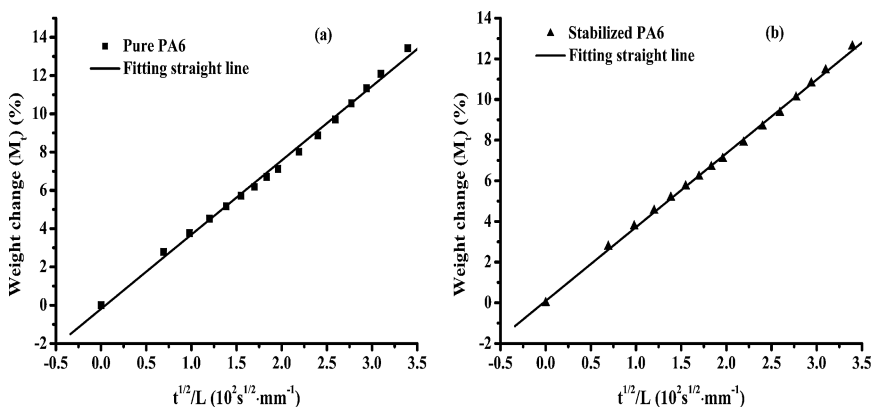**Figure 6.** The fitting straight line for the diffusion of acid rain in the pure and stabilized samples of PA6 (L = 3 mm, pH = 1, 40°C).

of carbonyl in the amido links. The ultraviolet absorption of the isolated carbonyl is at 280 nm.[15] However, the auxochrome group (-NH-) in the vicinity of carbonyl led to the n-π conjugation effect and the increase of the energy of bonding orbitals and anti-bonding orbitals, which finally resulted in the blue shift of the corresponding ultraviolet absorption. In addition, because of many benzene rings in the stabilizers, the ultraviolet absorption of the stabilized sample was higher than that of the pure sample in the region of 205~300 nm, corresponding to the E_2 band and B band of benzene rings. In addition, the ultraviolet absorption in the region of 340 nm should result from the benzotriazol ultraviolet absorbent.

There was little change in the UV spectrum of the pure and the stabilized samples after 28 days' aging, which indicated that no matter whether the pure sample or the stabilized sample of PA6, the carboxylic acids produced from the hydrolysis of amido links also had
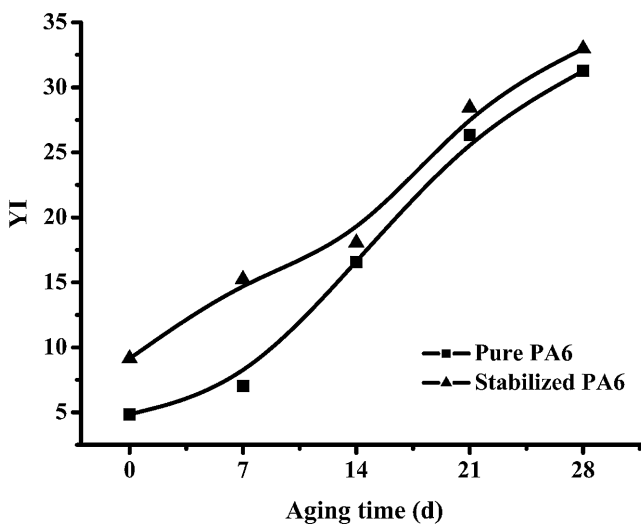

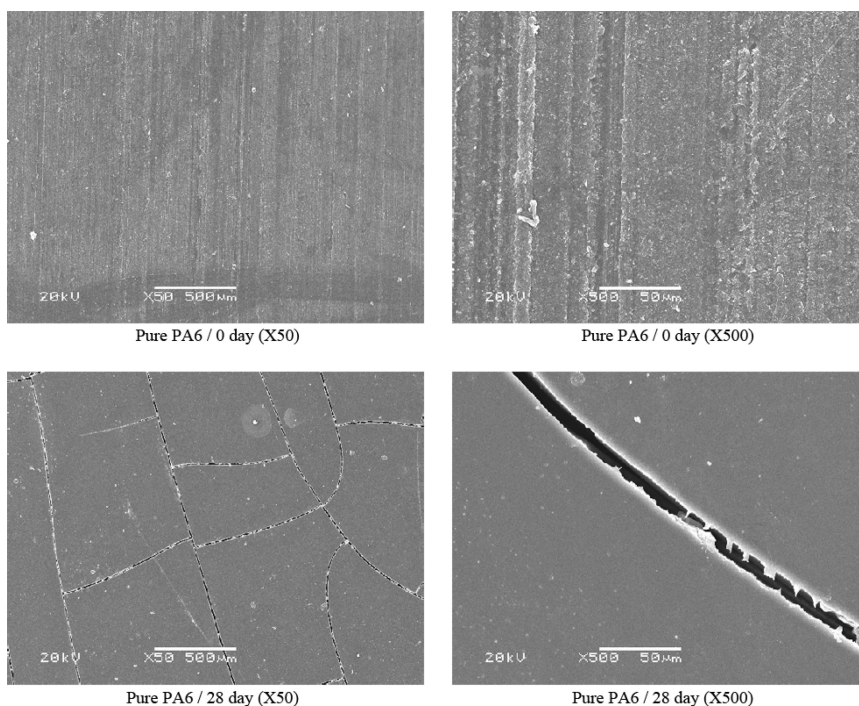**Figure 7.** YI of PA6 as a function of acid rain aging time.

Figure 8. SEM images of the surface of pure PA6 for different acid rain aging times.

strong ultraviolet absorption in the region of 205 nm, and the hydrolysis of amido links was the primary reaction during the acid rain aging.

Long Term Water Absorption of PA6

Samples (3 mm thickness) of PA6 were dried under vacuum and weighed before their isothermal immersion in acid rain (pH = 1, 40°C). The weight (W_t) of the samples was determined at various immersion times t and the relative weight gain $M_t = 100[(W_t - W_0)/W_0]$ (W_0 is the original weight of the sample) was calculated. M_t is plotted vs $t^{1/2}/L$ (L being the sample thickness) in Fig. 5.

Theoretically, for the boundary condition, when the concentration of the solution on the surface of sample is constant and no chemical reaction occurs during the process of immersion, water absorption should be a Fickian process, which can be characterized by a constant coefficient of diffusion (D) and an equilibrium saturation weight (M_∞), and obeying the following relationship:[16]

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)} \exp\left[-\frac{(2n+1)^2 \pi^2 D}{L^2} t\right] \qquad (5)$$

In the initial process of immersion, the curve should have a good linear relationship as per the following formula:

$$\frac{M_t}{M_\infty} = \frac{4}{\sqrt{\pi}} \sqrt{\frac{Dt}{L^2}} \qquad (6)$$
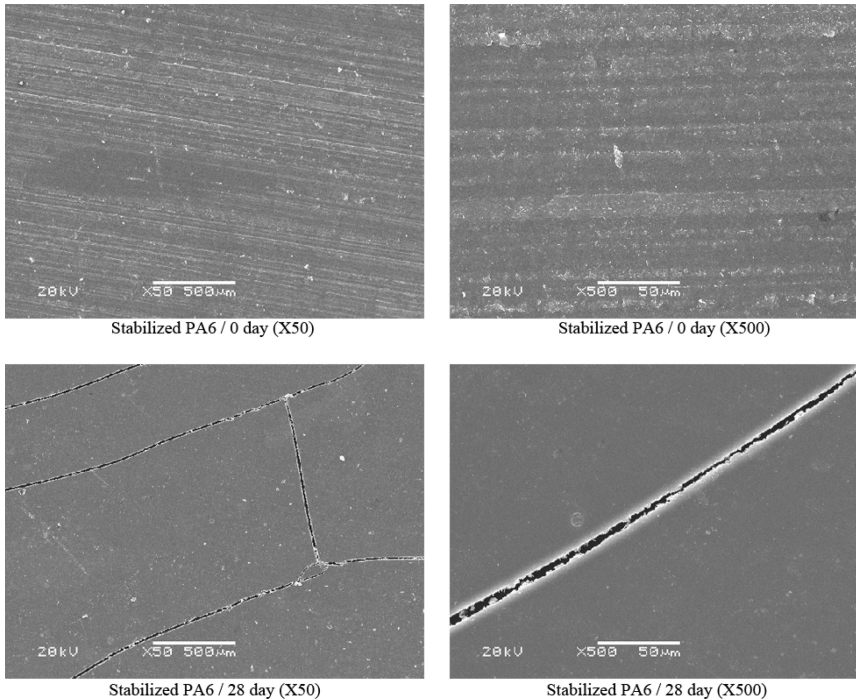
Figure 9. SEM images of the surface of stabilized PA6 for different acid rain aging times.

Then, according to the slope of line (K), D can be calculated when M_∞ is determined.

As shown in Fig. 5, during the initial stage of immersion (including 1∼16 points, time 0∼288 h), although almost no hydrolysis reaction of amido links occurs, the curve still had very good linear relationship and the 16th point could be considered as M_∞, indicating that the physical water absorption process dominated while the chemical degradation was insignificant. Fitting to these 16 points, the straight lines of the pure sample and the stabilized sample of PA6 obtained are shown in Fig. 6.

For the pure sample of PA6, the fitting line equation was:

$$y = 3.8786x - 0.1908 \tag{7}$$

and for the stabilized sample of PA6, the fitting line equation was:

$$y = 3.6292x - 0.0920 \tag{8}$$

Then, the coefficient of diffusion (D) could be calculated according to the following formula:

$$D = (K^2 \pi)/(4 \times 10^2 \, M_\infty)^2 \tag{9}$$

where K is the slope of the fitting straight line. Finally, the coefficient of diffusion of acid rain in the pure sample and the stabilized sample of PA6 were calculated to be $1.637 \times 10^{-6} \, (\text{mm}^2 \text{s}^{-1})$ and $1.625 \times 10^{-6} \, (\text{mm}^2 \text{s}^{-1})$, respectively, which also implied that the stabilizers had little influence on the diffusion process of acid rain in the matrix of PA6.

During the middle stage of the immersion [$3.6661 \leq t^{1/2}/L \leq 5.5426$ ($10^2 s^{1/2} \cdot mm^{-1}$)], the hydrolysis reaction of amido link gradually predominated. At first the weight of samples increased slowly, which can be considered as the induction period of the hydrolysis reaction. Afterwards, it rose quickly because the hydrolysis reaction led to the high consumption and absorption of water. In the last stage of the immersion ($t^{1/2}/L > 5.6(10^2 s^{1/2} \cdot mm^{-1})$), M_t began to drop sharply, which indicated that lots of low molecular weight compounds were extracted from the matrix and dissolved in the acid rain. The times for the various stages were essentially the same as for Figs. 1–3.

Appearance Properties of PA6

The variation of the yellow index (YI) of PA6 versus aging time is shown in Fig. 7. YI increased with aging time because some yellow substances were produced during acid rain aging. The initial value of YI of the stabilized sample was a little higher than that of the pure sample due to the light yellow color of the stabilizers. With the increase of aging time, the difference between the pure sample and the stabilized sample of PA6 was reduced.

As shown in Figs. 8 and 9, there were some striae on the surface of the sample of PA6, which came from the compression molding. During aging, some cracks were formed on the surface of the samples. The density and the width of cracks for the pure sample were obviously higher than that of the stabilized sample. In addition, it is possible that the low molecular weight compound on the surface of the sample of PA6 produced by degradation was dissolved in the acid rain, and the surface of the sample became much smoother after aging.

Conclusion

Both pure and stabilized samples of PA6 were subjected to long–term acid rain aging simulated by an aqueous solution with pH = 1 at 40°C. The aging behavior of PA6 under acid rain was studied in terms of changing in the mechanical property, reduced viscosity, chemical structure, appearance properties and long term water absorption behavior. The results indicated that the first stage of the aging was a Fickian process and corresponded to the physical absorption of water until equilibrium while the chemical degradation could be neglected, resulting in a decrease of the mechanical strength and increases of the elongation at break and impact strength of the sample of PA6. The hydrolysis reaction of the amido links of PA6 predominated during the middle stage of aging, and lots of low molecular weight compound were extracted from the matrix and dissolved in the acid rain during the last stage of aging, resulting in the decline of all the mechanical properties. The reduced viscosity of PA6 decreased monotonically during the whole aging process, resulting from the hydrolysis of amido links, indicating the molecular degradation of PA6 during the acid rain aging. Terminal amine groups could not be detected due to their reaction with acid. Carboxylic acid groups not only came from the carboxylic acid end groups produced by the degradation of the sample, but also from the acid rain. There was little change in the UV spectrum of the pure and the stabilized sample after 28 days of aging. The stabilizers didn't seem to have any effect of anti-acid rain degradation of PA6.

Acknowledgments

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