

Study on the Long-Term Thermal-Oxidative Aging Behavior of Polyamide 6

Ying Shu, Lin Ye, Tao Yang

The State Key Laboratory of Polymer Materials Engineering, Polymer Research Institute of Sichuan University, Chengdu 610065, China

Received 5 March 2008; accepted 30 April 2008

DOI 10.1002/app.28647

Published online 10 July 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The long-term thermal-oxidative aging behavior of polyamide 6 (PA6) was studied by comparison with the stabilized sample in this work. The variation of mechanical properties of the pure and the stabilized samples of PA6 with aging time at 110°C, 130°C, and 150°C were investigated, respectively. The aging mechanism of PA6 under heat and oxygen was studied in terms of the reduced viscosity, crystallization behavior, dynamic mechanical behavior, and chemical composition through the methods of polarized light microscopy (PLM), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), X-ray photoelectron energy spectrum (XPS), and

so on. The results indicated that at the initial stage of aging, the molecular crosslinking reaction of PA6 dominated resulting in the increase of the mechanical strength, reduced viscosity, and the glass transition temperature of the sample. And the molecular degradation dominated in the subsequent aging process resulting in the decrease of the melting temperature, the increase of the crystallinity, and the formation of the oxides and peroxides products. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 945–957, 2008

Key words: polyamide; thermal-oxidative aging; structure; property

INTRODUCTION

Polyamide 6 (PA6) has a wide range of applications in industry because of its excellent mechanical properties. As one of the most common engineering plastics and fibers, the aging behavior and mechanism of PA6 have been concerned by people for a long time. Usually, the carbon–hydrogen bond on the methylene group adjacent to nitrogen is considered to be the weakest bond,¹ and people think that most oxidation reaction proceeds on this carbon² and the changes of PA6 in physical and mechanical properties are proportional to oxygen consumption during oxidation process.³ The oxidation reaction of PA6 is very complicated, and its products may contain unstable hydroxyl compounds which may produce aldehyde, carboxylic acid, carbonyl compounds, ketone, cycle compounds, and so on.^{4,5} Besides, the observed degradation products implied that all the methylene may be attacked at random by free radicals.⁶

Polyamide (PA) was usually studied on its degradation mechanism and kinetics of pyrolysis through the method of GC-MS, DTA, TGA, FTIR, NMR, SEM, and so on.^{7–16} In recent years, oxygen uptake and chemiluminescence (CL) were also applied to the study on the oxidation mechanism of PA and the function of stabilizers, which was useful though the relationship between the CL intensity and the rate of oxygen uptake had not been very clear.^{17–24} Dan Forsström considered that the CL intensity-time curves for both pure PA6 and stabilized PA6 showed an initial period at a high intensity level followed by a basically sigmoidal increase and a subsequent maximum. He figured that this maximum was found to occur at a time corresponding to a drop in strain at break, and it was unlikely that the rate of oxidation solely depended on the concentration of peroxides, since peroxides were accumulating throughout the oxidation process, whereas the rate of oxygen uptake was decreasing. At the same time, the CL intensity is not directly related to the rate of oxygen uptake. Instead, the CL intensity in oxygen seems to be related to the content of peroxides. Thermal-embrittlement and oxidative-embrittlement mechanism was usually applied in the analysis of the mechanical properties of polymers during aging. They would also influence each other. On one hand, thermal-embrittlement could promote oxidative embrittlement, which would primarily occur on the weak bond of the molecular chain of the amorphous

Correspondence to: L. Ye (yelinwh@126.com).

Contract grant sponsor: Key Natural Science Fund of China; contract grant number: 50533080.

Contract grant sponsor: Program for Changjiang Scholars and Innovative Research Team in University; contract grant number: IRT0449.

region. During thermal-oxidative aging process, the concentration of weakness would rise in amorphous region, which would accelerate the oxidation degradation in noncrystalline region without doubt. On the other hand, the low molecular-weight polymers and small molecules produced by oxidation reaction would be apt to form imperfect spherulite, which would promote thermal embrittlement.²⁵

In this work, the dumb-bell injected sample and granular sample of PA6 were used for the systematic study on the long-term thermal-oxidative aging behavior to provide valuable results for the industry applications of PA6. And this present study was also aimed at revealing the thermal oxidative aging mechanism of PA6 by the measurements of the reduced viscosity, end group concentration, crystallization behavior, dynamic mechanical behavior, and mechanical composition of PA6. The aging behavior and mechanism of PA6 stabilized with the commonly used stabilizers in industry were also studied for the purpose of the comparison with the pure sample.

EXPERIMENTAL

Materials

The pure polyamide 6 used in this work is a commercial grade granular product (YH800) without any additives and supplied by Yueyang Petrochemical Co. (Hunan, China), with relative viscosity of 2.85 ± 0.03 . The stabilizers with the analytical purity, including 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, were available from Ciba-Geigy Corporation. The composition of stabilizers applied in the sample of the stabilized PA6 was 0.2 wt % Irganox 1010/0.2 wt % Irgafos 168/0.3 wt % Tinuvin 770/0.3 wt % Tinuvin 234.

Preparation of the materials

The materials applied in our work were pure PA6 and stabilized PA6. The stabilized PA6 was prepared by mixing the pure PA6 in dry form with stabilizers (Irganox 1010/Irgafos 168/Tinuvin 770/Tinuvin 234) in the high-speed mixer, and then being extruded with the TSSJ-25/03 twin-screw extruder from Chengguang 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 purpose, pure PA6 was extruded, palletized, and dried by the same technique. Then the granules were injected into standard dumb-bell splines (length: 155 mm,

thickness: 4.2 mm) with K-TEC40 of Germany according to ISO 294-1.

Thermal oxidative aging

The dumb-bell injected sample and granular sample of PA6 were subjected to thermal oxidative aging in the ambient atmosphere at 110, 130, 150°C, respectively, in the oven. The samples were taken out at regular time intervals and used for mechanical and chemical characterization. The temperature fluctuation in the oven was $\pm 1^\circ\text{C}$.

Measurement

Mechanical property

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

The notched charpy impact strength of the samples was measured with the ZBC-4B impact testing machine from Xinsansi Co. (Shenzhen, China) according to ISO 179-1993 standards.

Reduced viscosity

The samples of about 0.5 g were dissolved in 100 mL of formic acid. The time of outflow of the solution was measured with 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.

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

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

Crystal morphology

The crystal morphology measurement of samples was performed with a Leitz Laborlux (Germany) polarized light microscopy (PLM). The samples were heated and melted on a hot plate at 250°C, pressed to a flake, and then crystallized at a given temperature of 180°C for 3 h.

Nonisothermal crystallization analysis

The nonisothermal crystallization was performed with a Netzsch 204 Phoenix DSC (Germany). The

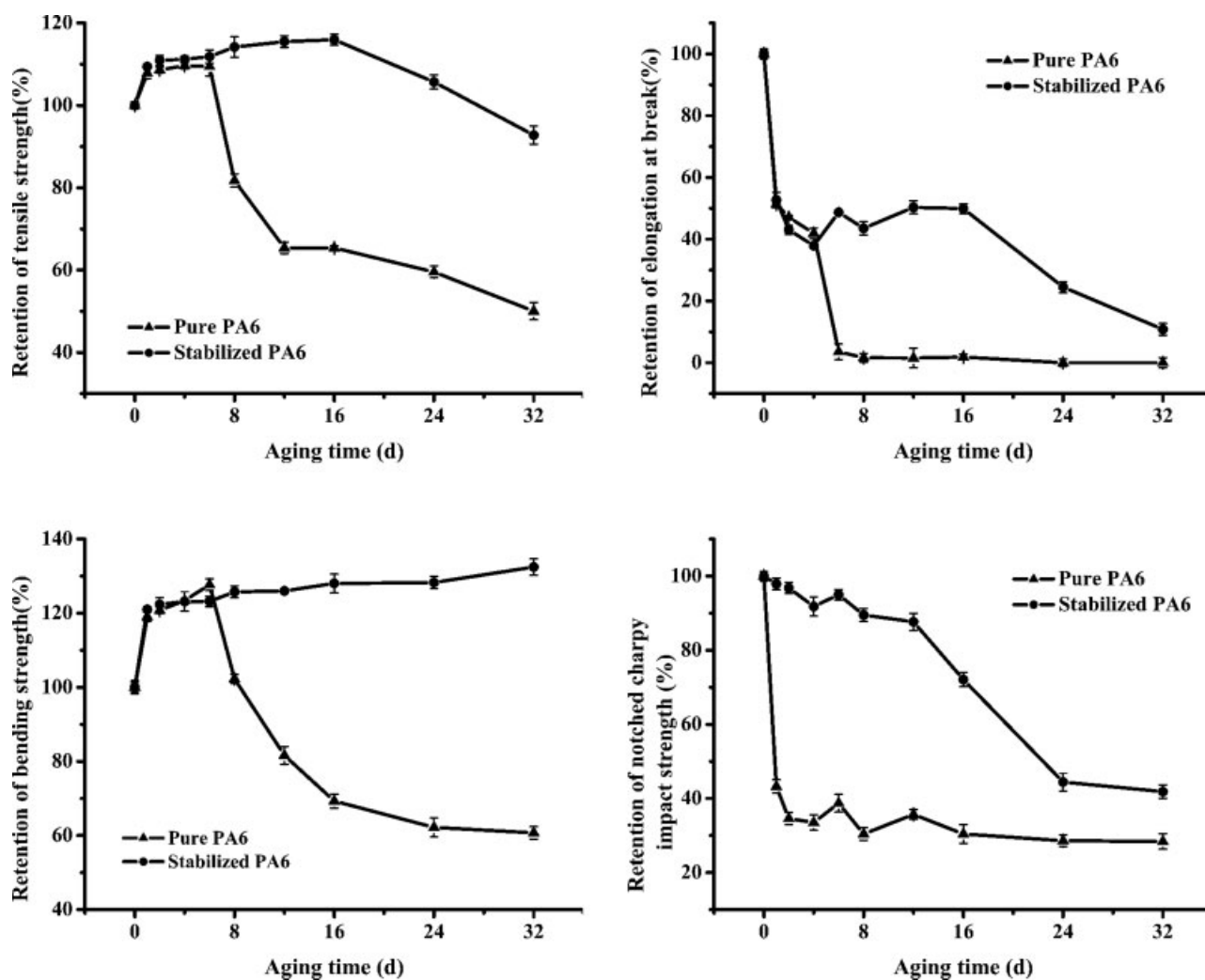


Figure 1 Retention of the mechanical properties of PA6 as a function of aging time at 110°C.

temperature scale of DSC was calibrated with indium. The granulated samples of about 10 mg were heated quickly from ambient temperature to 250°C under a nitrogen atmosphere. After waiting for 5 min to eliminate the effects of the previous thermal history, the samples were cooled to ambient temperature at a constant rate of 10 K/min, and then heated to 250°C at the same constant rate.

The quantity of heat absorbed during the melting of the polymer is substantively equivalent to that required to break down the crystal structure. The higher the crystallinity (X_c), the higher the melting heat. X_c can be calculated with the following formula.

$$X_c = \left(\frac{\Delta H_m}{\Delta H_0} \right) \times 100\% \quad (2)$$

where H_m is the melting enthalpy and H_0 is the balance melting enthalpy, that is, the melting enthalpy of 100% crystallizing PA6, which is 190 J/g.

Dynamic mechanical analysis

Dynamic mechanical experiment was performed at 3 Hz with the heating rate of 3°C/min from -100 to 150°C with Izod mode by using a TA Instruments Q800 apparatus (USA). Samples with size of 30 mm × 6 mm × 1.2 mm prepared by press molding (10 MPa, 250°C) were cooled quickly down to -100°C with liquid nitrogen and allowed to equilibrate at -100°C for 5 min before the measurements. The peak temperature of the $\tan \delta$ was regarded as the glass transition temperature (T_g) of the sample.

The end group analysis²⁶

The carboxylic acid. The sample of PA6 of about 0.3 g was dissolved in 20 mL of phenylcarbinol at 150°C. Then 3 mL of propyl alcohol was added, and the hot solution was titrated with NaOH (about 0.02 mol/L) by using phenolphthalein as the indicator.

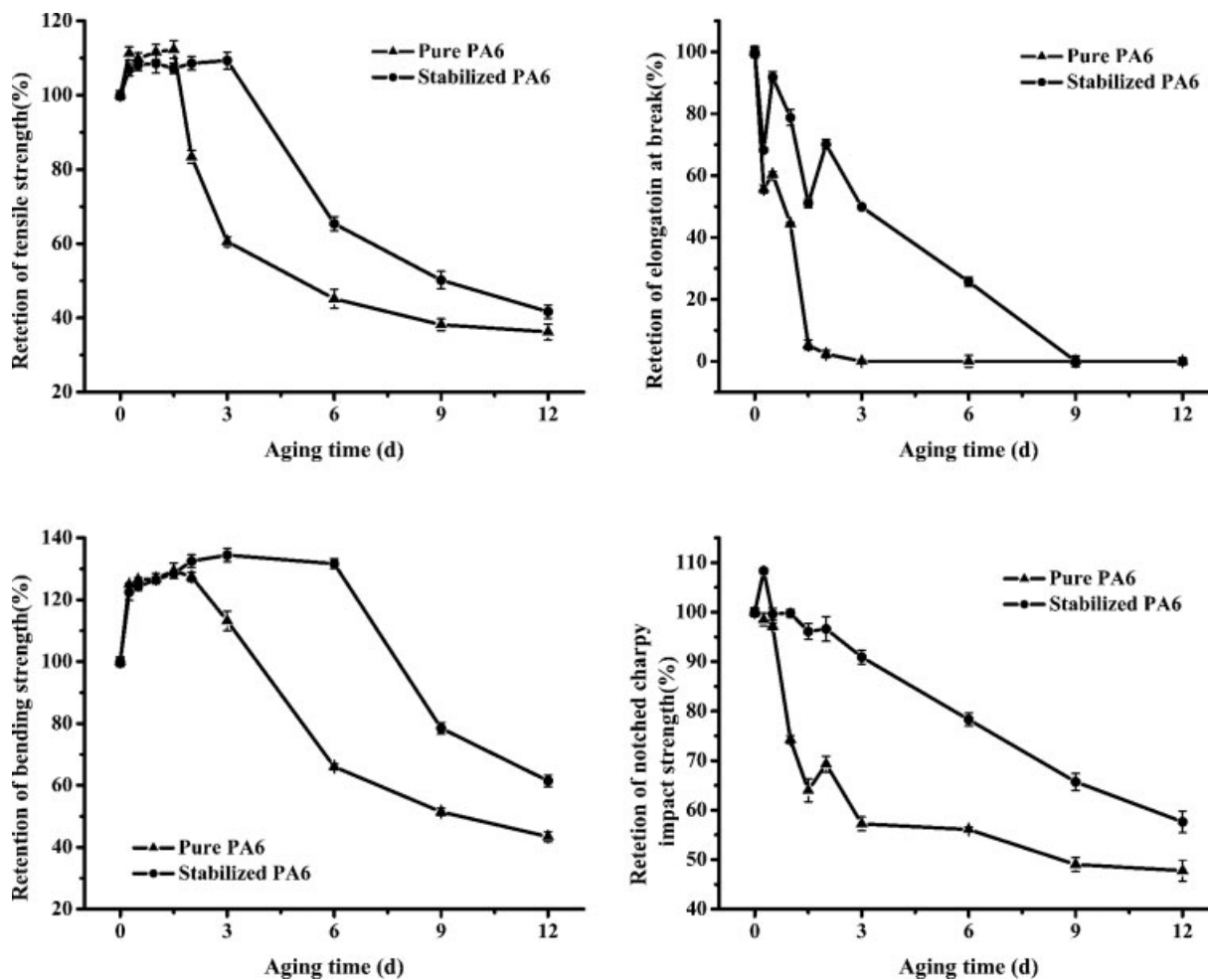


Figure 2 Retention of the mechanical properties of PA6 as a function of aging time at 130°C.

The content of the carboxylic acid can be calculated with the following formula.

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

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

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

$$Y = \frac{(A - B)n}{W} \times 10^{-3} \quad (4)$$

where A is the consumption volume of HCl solution of the sample (mL), B is the consumption volume of

HCl solution for the solvent (mL), n is the molar concentration of HCl solution (mol/L), and W is the weight of the sample (g).

X-ray photoelectron energy spectrum

The surface structure composition of PA6 at the start and end of aging was measured with the X-ray photoelectron energy spectrum XSAM800 (Britain). The samples were prepared by press molding (10 MPa, 250°C) with size of 8 mm × 8 mm × 1.2 mm.

RESULTS AND DISCUSSION

Mechanical properties of PA6

The mechanical properties of PA6 aging at 110°C, 130°C, and 150°C were investigated, respectively. The variation of the mechanical properties of PA6 aging with time at 110°C was shown in Figure 1. The retention of the tensile strength and bending strength of the pure and the stabilized PA6 was found to increase during the first 6 days. However,

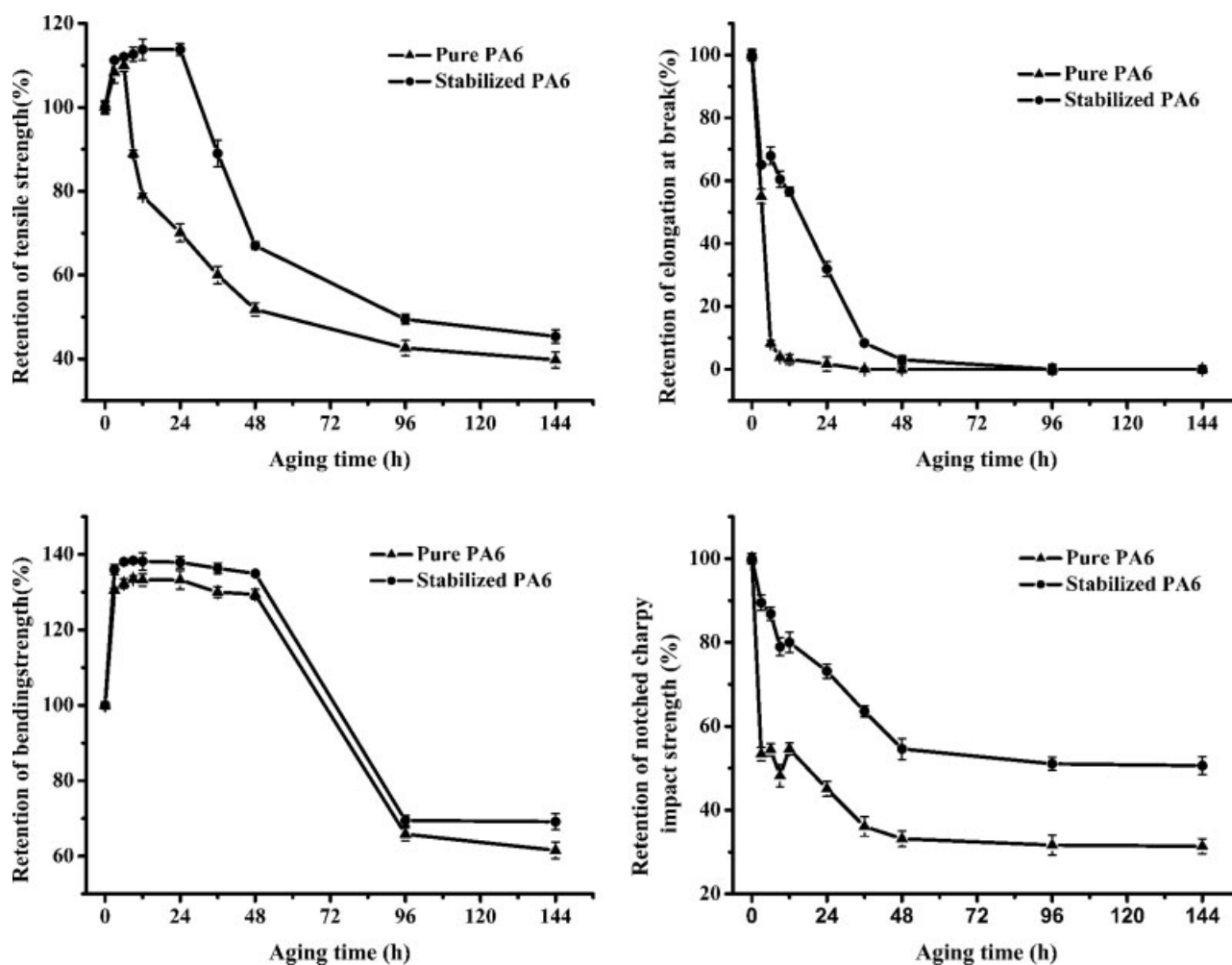


Figure 3 Retention of the mechanical properties of PA6 as a function of aging time at 150°C.

the subsequent variation of strength differed for these two kinds of PA6. For pure PA6, the retention of the tensile strength and bending strength was found to decrease afterward. On the other hand, the turning point of the retention of the tensile strength was postponed 10 days for the stabilized PA6, which ultimate value was much higher than that of the pure sample. In addition, the retention of the bending strength of the stabilized sample increased gradually up to the time when the test ended. The retention of elongation at break of the pure PA6 decreased rapidly with aging time, and after 6 days, its elasticity was almost completely lost. While for the stabilized sample of PA6, a relatively high retention of the property was remained stable up to the 16th day, and finally it dropped to 10% of the retention at the end of the test. The difference in the retention of the notched charpy impact strength of the two kinds of PA6 was more obvious. For pure PA6, the remarkable drop in the impact strength occurred on the first day, then it gradually dropped to 30% of the retention in the rest of time. However,

for the stabilized sample, it took 12 days to drop to about 90% of the retention, and then the value was lowered to 40% of the retention in the rest of time. In a word, compared with the pure sample, the retention of the mechanical properties of the stabilized PA6 decreased slowly with aging time, and showed high thermal stability in mechanical properties during long-term thermal oxidative aging.

As shown in Figures 2 and 3, when the test temperature rose to 130°C and 150°C, the whole variation tendency of mechanical properties of PA6 was similar to that of the sample aged at 110°C, except that the elongation at break of the sample decreased relatively sharply, and there is no persistent increase of the bending strength during whole aging process for the stabilized sample. The difference on mechanical properties between the two kinds of PA6 was reduced gradually when the test temperature rose from 110 to 150°C, especially their bending strength was very close to each other when aging at 150°C, indicating that the higher the aging temperature, the less remarkable the function of the stabilizers. The

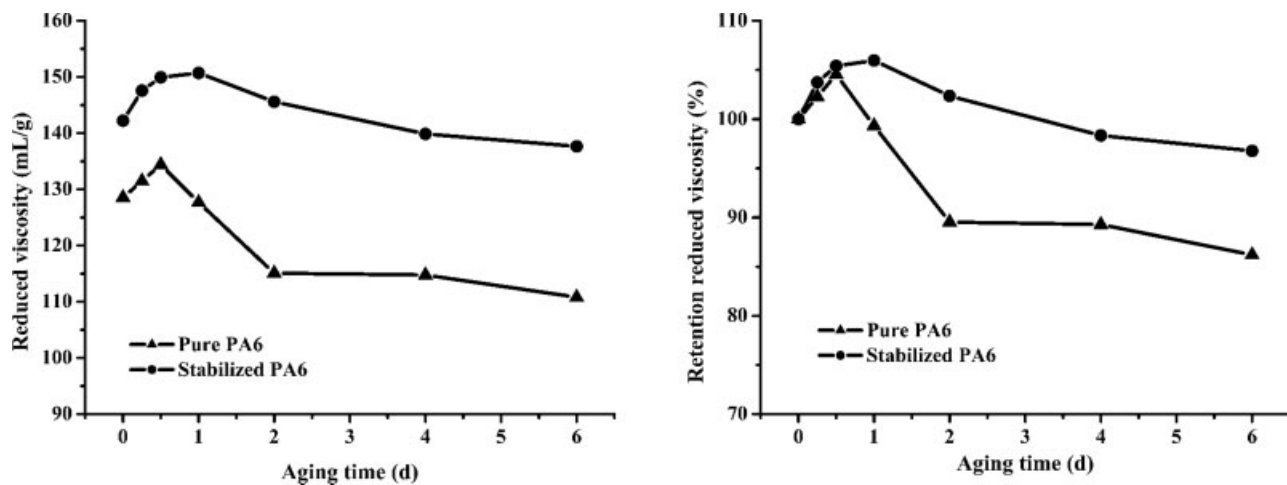


Figure 4 Reduced viscosity of PA6 as a function of aging time at 150°C.

evaporation of the small molecule stabilizers during aging at high temperature may be responsible for the reduction of the efficiency of the stabilizers.

The whole aging behavior of the mechanical properties of PA6 in absence or presence of the stabilizers was analogous at three different temperatures, which included so-called thermal-embrittlement and oxidative-embrittlement mechanism. When the aging temperature was in the range of $T_g \sim T_m$, there was an annealing process of PA6 at first. In this case, the internal stress of PA6 would be reduced, meanwhile, the spherulites of PA6 would grow bigger and its crystallinity would increase. Therefore, at the primary stage of the aging process, the tensile strength and bending strength would increase to some extent, the notched charpy impact strength would decrease and the brittleness of PA6 would rise. The damage mode of PA6 would also transform from yield defor-

mation to brittle fracture with increase of aging time when subjected to bending stress.

For the case when both hot air and oxygen exist, there would be thermal oxidation reaction, including the molecular chain degradation and crosslinking in PA6 matrix. At the initial stage of aging, the crosslinking reaction was dominating, which made the tensile strength and bending strength of PA6 increase to some extent. However, with increase of aging time, molecular degradation dominated, and the remarkable decline of the molecular weight would make the mechanical strength decrease greatly. During the whole oxidation process, the molecular-weight distribution would be widened, the regularity of molecular chain would become poor and the hydrogen bonding and Van der Waals force between the molecules would become weak, besides, the defects in the matrix would increase, which

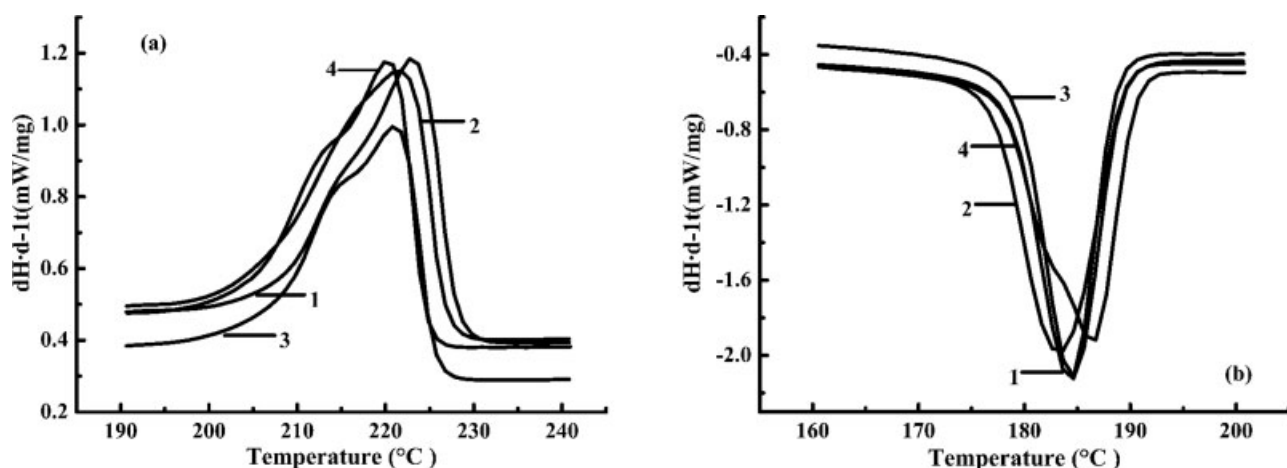


Figure 5 DSC curves of PA6 (1: Pure PA6/0 day. 2: Pure PA6/6 days. 3: Stabilized PA6/0 day. 4: Stabilized PA6/6 days).

TABLE I
Crystallization Parameters of PA6 at Different Aging Time at 150°C

No.	Sample	T_{onset} (°C)	T_c (°C)	T_m (°C)	ΔW (°C)	X_c (%)	ΔH (J/g)
1	Pure PA6/0 day	189.1	184.3	223.1	7.6	37.83	58.55
2	Pure PA6/6 days	189.4	183.2	221.7	9.0	39.50	61.72
3	Stabilized PA6/0 day	188.6	184.4	221.1	6.6	34.18	51.68
4	Stabilized PA6/6 days	190.4	186.3	220.4	9.3	37.47	56.99

resulted in the decline of the elongation at break and notched charpy impact strength of PA6.

Reduced viscosity of PA6

The variation of the reduced viscosity of PA6 with aging time was investigated at 150°C. The reduced viscosity of pure PA6 before processing was 142.54 mL/g, and the reduced viscosity of pure PA6 and the stabilized PA6 after melt extruding was 128.55

and 142.42 mL/g respectively, which demonstrated that stabilizers had already functioned during processing. The reduction of the reduced viscosity of the pure sample may be resulted from the molecular degradation led by the high processing temperature (250°C) and shear force of the twin-screw during melt extruding. As shown in Figure 4, at first, the reduced viscosity of the pure sample rose during the first half day, then it began to decline sharply, and after 2 days it leveled off gradually. However, the

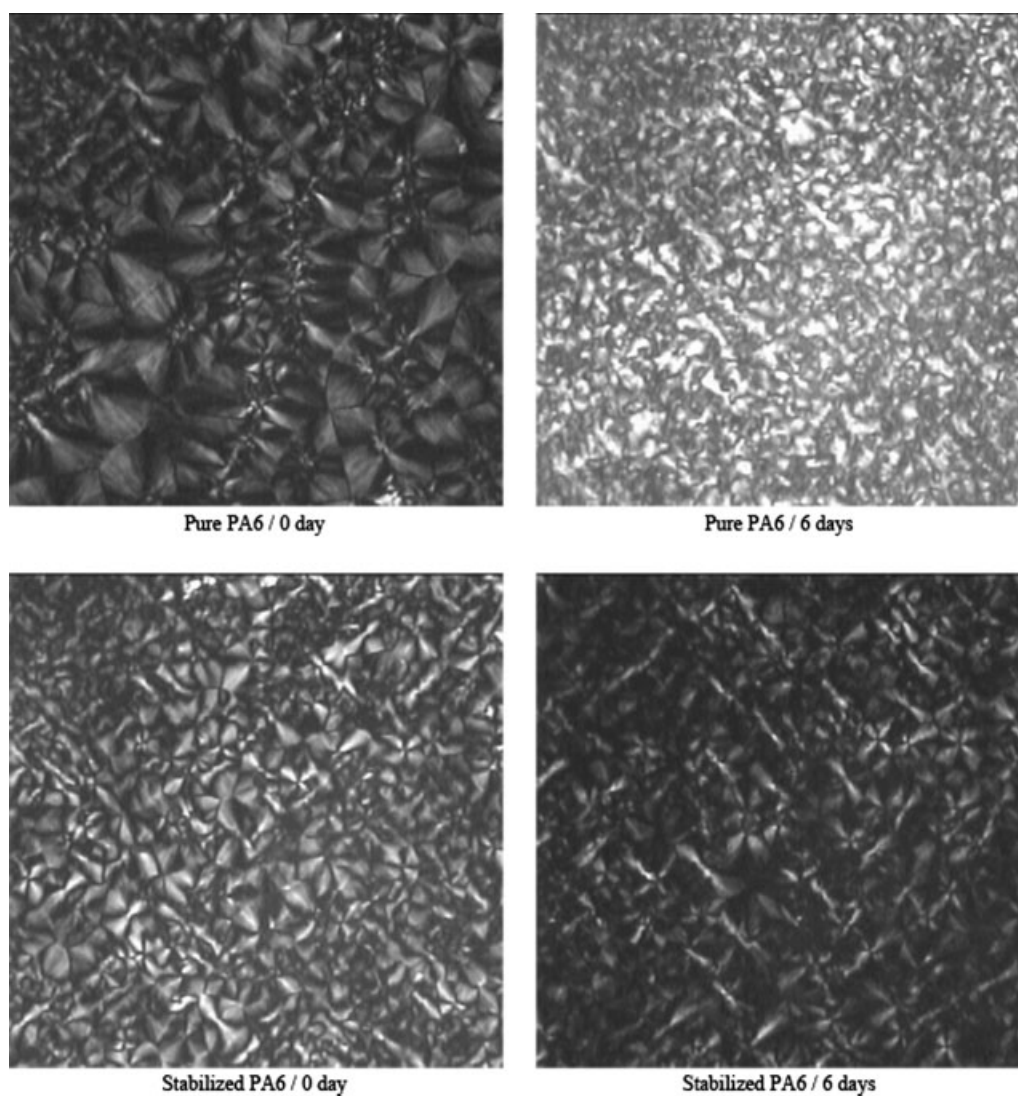


Figure 6 PLM images of PA6 at different aging time at 150°C.

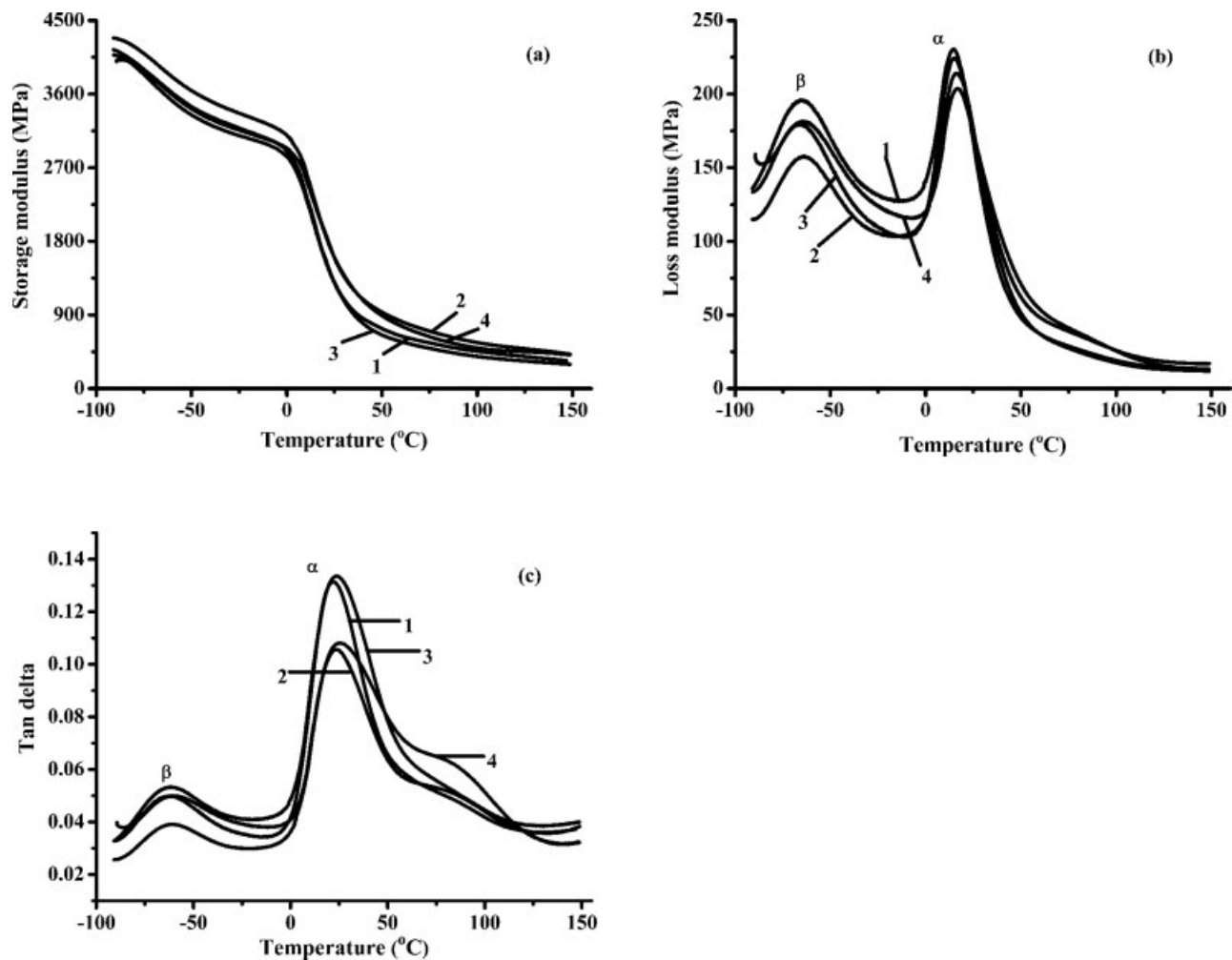


Figure 7 DMA spectra of PA6 at different aging time at 150°C (1: Pure PA6/0 day. 2: Pure PA6/6 days. 3: Stabilized PA6/0 day. 4: Stabilized PA6/6 days).

reduced viscosity of the stabilized sample kept rising during the first 1 day, then it fell slowly and reached a stable value. It is well known that the reduced viscosity characterizes the viscosity average molecular weight of polymers.²⁷ Therefore, the results showed that during the primary aging time, the molecular crosslinking reaction of PA6 predominated, resulting in the increase of the reduced viscosity, and afterward the molecular degradation of the polymer predominated resulting in the decrease of the reduced viscosity, which was in consistency with the whole variation of the mechanical strength of PA6 with aging time.

Moreover, the stabilized PA6 had higher reduced viscosity than that of the pure sample as a consequence of keeping higher molecular weight during aging, and the fluctuation of the molecular weight was relatively small, which implied that the stabilizers can hinder the molecular degradation of PA6 effectively during long-term thermal oxidative aging.

Crystallization and melting behavior of PA6

The nonisothermal DSC curves of the pure and stabilized samples of PA6 under different aging time with a heating and cooling rate of 10 K/min were shown in Figure 5, from which the onset crystallization temperature (T_{onset}), the crystallization peak temperature (T_c), the melting temperature (T_m), the melting enthalpy (ΔH_m), the crystallinity (X_c), and the crystalline half-peak width (ΔW) can be obtained, as listed in Table I.

It can be seen that the measurement of the crystalline fraction showed an increase in crystallinity for the aged sample, indicating the fact that post crystallization occurred as a result of the aging process, which can yield mobile chains in the amorphous region suitable to join the polymeric crystallites. However, the small molecules and polymers with low molecular weight produced by degradation may also contribute to a rise in the crystallinity. On the other hand, the thermal oxidative aging would

TABLE II
 T_{α} (T_g) and $\tan \delta_{\max}$ of PA6 at Different
 Aging Time at 150°C

No.	Sample	T_{β} (°C)	T_{α} (T_g) (°C)	$\tan \delta_{\max}$
1	Pure PA6/0 day	-62.2	20.0	0.13
2	Pure PA6/6 days	-61.2	23.5	0.11
3	Stabilized PA6/0 day	-62.3	24.2	0.13
4	Stabilized PA6/6 days	-60.8	25.4	0.11

primarily occur on the weak bond of the molecular chain in the amorphous region of the polymer. And the molecular degradation in this region resulted in the increase of the concentration of the crystalline region of PA6.

Meanwhile, some of low molecular weight products have nucleation effect on PA6, making it crystallize at comparatively high temperature. The low regularity of the molecular chains of the sample with branch chains of oxides and peroxides produced by oxidation would lead to the decrease of crystalline growth rate, presenting an increase of ΔW . In addition, the decrease of T_m mainly resulted from the decline of the molecular weight of PA6 during aging, which was in coincidence with the measurement results of the reduced viscosity mentioned earlier.

The PLM images of PA6 at the start and end of aging time at 150°C were shown in Figure 6. Before aging, the spherulites size of the stabilized PA6 was smaller than that of pure one perhaps due to the slight nucleation effect of the stabilizers in the system. After aging for 6 days, there were almost no spherulites to be observed in the sample of pure PA6, and the spherulites of the stabilized one became sparse. The possible reasons were that the crystallinity of PA6 was low itself generally, the samples were prepared by flaking at the melting point (250°C) and the crystalline morphology of some small molecules suffered damage during this process.

Dynamic mechanical behavior of PA6

As shown in Figure 7(a), the magnitude of storage modulus of all samples of PA6 decreased linearly with temperature in a glass transition region and its values of the aging samples were a bit higher than that of the samples before aging. As shown in Figure 7(b,c), there were two transition peaks for the loss modulus and $\tan \delta$ curves, corresponding to α relaxation arising from the chain segmental motion of the molecules, and β relaxation arising from the motion of units which are smaller than chain segments. The α relaxation temperature was usually regarded as the glass transition temperature (T_g) of polymers.

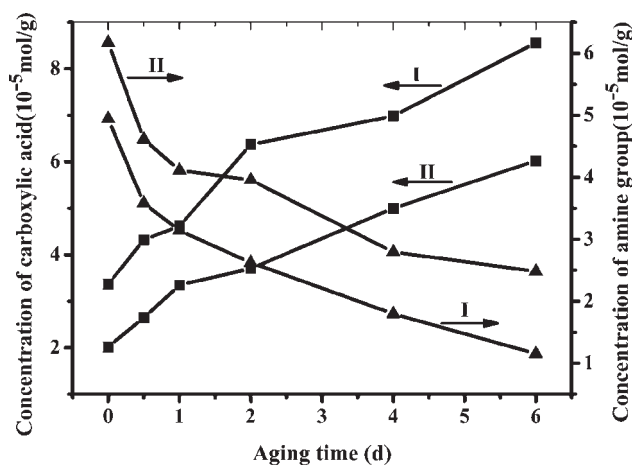


Figure 8 Concentration of carboxylic acid and end amine group of PA6 as a function of aging time at 150°C (I: pure PA6, II: PA6/stabilizers).

The samples of PA6 aging at 150°C for 6 days showed a $\tan \delta$ curve shifting slightly to higher temperatures compared with the samples before aging, resulting in a slight increase of T_g , which was led by the molecular crosslinking reaction during the primary aging stage though the molecular degradation predominated during the later stage of aging. The corresponding parameters of DMA analysis were listed in Table II.

All restrictions on mobility of the main chain of the polymer are expected to decrease the peak area of the loss modulus, which would also be reflected in the intensity of the $\tan \delta$ peak. Therefore, the intensity of the $\tan \delta$ peak at α relaxation temperature ($\tan \delta_{\max}$) is considered to reflect the extent of the mobility of the macromolecular chain segments at this temperature.²⁸ It can be seen that both the peak area of loss modulus and peak intensity of $\tan \delta_{\max}$

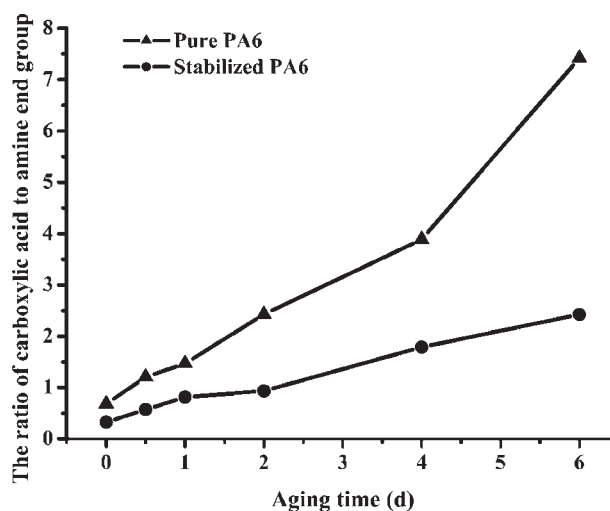


Figure 9 Ratio of carboxylic acid to end amine group of PA6 as a function of aging time at 150°C.

TABLE III
Percentage of Atomic Composition of PA6 at Different Aging Time at 150°C

Sample	Aging time (day)	C (%)	N (%)	O (%)
Pure PA6	0	82.71	5.42	11.87
	6	76.64	2.9	20.46
Stabilized PA6	0	80.24	2.48	17.28
	6	79.11	2.57	18.32

of the aged samples were lower than that of the samples before aging, which implied that the mobility of the molecules and the damping properties of PA6 were reduced during aging. Obviously, the crosslinking of molecules, thermal-embrittlement and oxidative-embrittlement would all make the chain relaxation much difficult.

The chemical structure of PA6

The variation of the chemical structure (the carboxylic acid and the amine end group) of PA6 with

aging time at 150°C was shown in Figure 8. With increase of aging time, the carboxylic acid concentration rose and the end amine group concentration dropped monotonically for PA6. The amido-bond is considered to be the weakest bond in the molecule of polyamide. The rupture of the amido-bond and the adjacent C—C bond resulted in the formation of the carboxylic acid, carbonyl, and the end amine group. The decline of the concentration of the end amine group of PA6 perhaps resulted from the reaction between end amine groups and carboxylic acids, or producing the compounds such as tertiary amine, or producing the compounds escaped from the matrix by aging degradation. During the thermal oxidative aging of PA6, the higher the concentration of the carboxylic acid, the more quickly the oxidation aging of the sample, and the further degradation of the polymers maybe promoted. However, the end amine group had thermal stabilization effect on polyamide.²⁹

As shown in Figures 8 and 9, the carboxylic acid concentration of the stabilized PA6 was lower than that of the pure sample, and its end amine group concentration was relatively higher during the whole

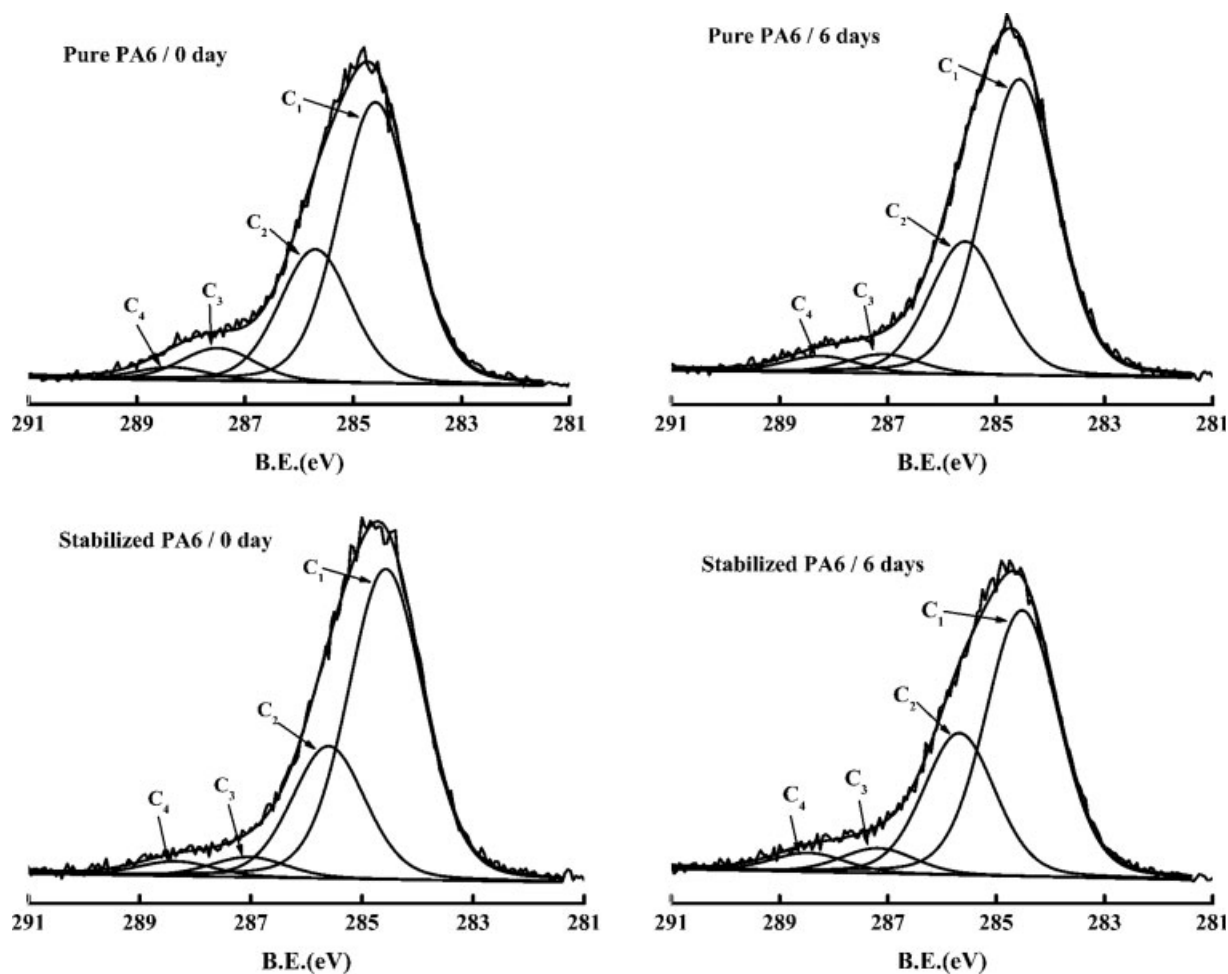


Figure 10 XPS C_{1s} spectra of PA6 at different aging time at 150°C.

TABLE IV
XPS C_{1s} Data of PA6 at Different Aging Time at 150°C

Sample	Aging time (day)	C _{1s}							
		C ₁		C ₂		C ₃		C ₄	
		B.E.	%	B.E.	%	B.E.	%	B.E.	%
Pure PA6	0	284.59	61.75	285.7	28.29	287.5	7.16	288.35	2.80
	6	284.57	64.34	285.57	28.00	287.08	4.12	288.24	3.54
Stabilized PA6	0	284.57	65.59	285.6	27.08	287.03	4.24	288.35	3.09
	6	284.52	59.46	285.68	30.72	287.18	5.60	288.47	4.20

aging process. In addition, the ratio of carboxylic acid to end amine group of the stabilized PA6 was always remarkably lower than that of the pure sample, and the difference of the ratio between the two samples became greater with aging time. It indicated again that stabilizers inhibited the oxidation reaction of PA6 effectively. The high concentration of amine group in the sample was favorable to its thermal oxidative stability.²⁹ Therefore, the stabilized PA6 displayed better thermal oxidative stability than the pure one.

The surface composition of PA6

The surface composition of PA6 at the start and end of aging time at 150°C was investigated. As shown in Table III, the primary content of the element is different for the pure and stabilized sample of PA6. After aging for 6 days, the concentration of carbon and nitrogen atom of the pure sample decreased and the concentration of oxygen atom increased, as a result of the formation of oxides and peroxides on its surface. And the small molecule gas formed by

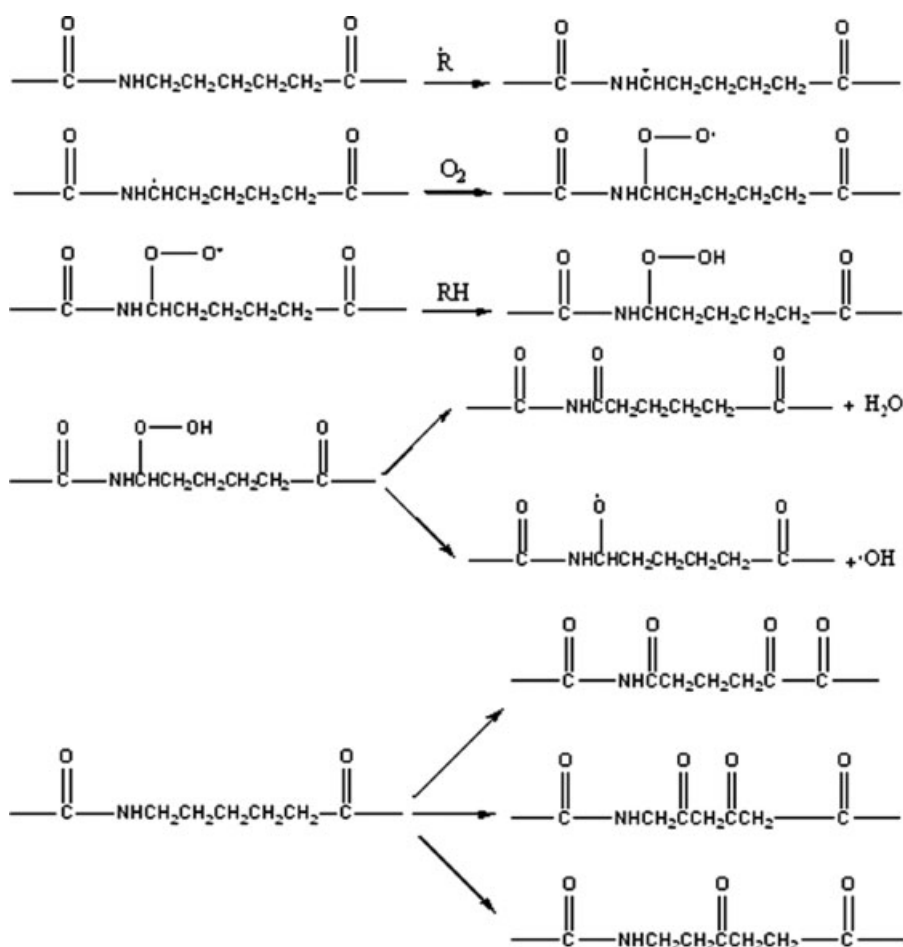


Figure 11 Formation of carbonyl groups in the chain of PA6 at random.

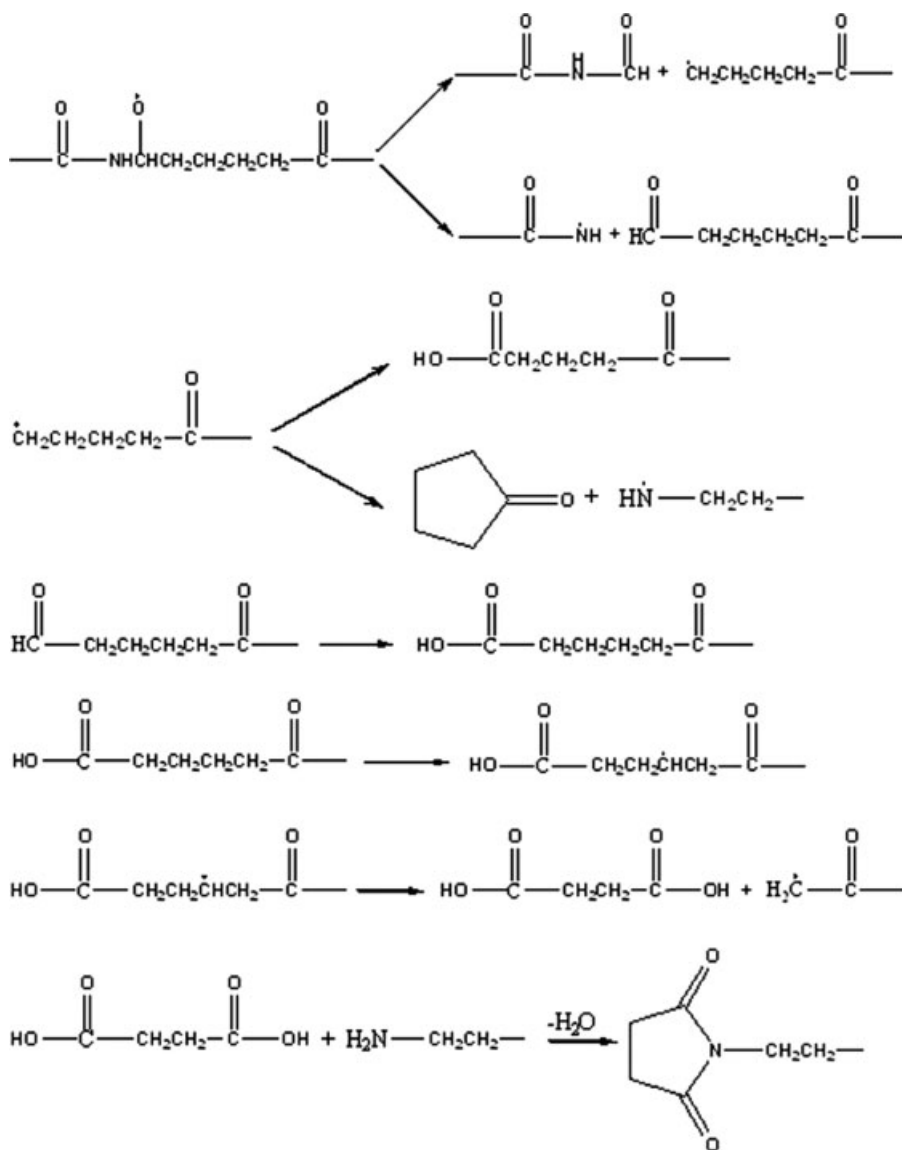


Figure 12 Formation of compounds like tertiary amine and compounds with more than one carbonyl or carboxyl group.

the molecular degradation can also lead to the decrease of the concentration of carbon and nitrogen atom. With respect to the stabilized PA6, there was relatively small variation of the concentration of these three elements, implying that the stabilizers could inhibit the oxidation reaction effectively. Besides, the slight increase of the nitrogen atom concentration of the stabilized sample perhaps resulted from the stabilizer's accumulation on the surface. In a word, oxygen was the main contaminant on the surface of the sample. Thus, it was very important to make further analysis of C_{1s} to understand the oxidation reaction mechanism of PA6.

Figure 10 presented the XPS original spectrum and peak fraction of carbon C_{1s} of PA6 with aging time, and the corresponding data were listed in Table IV. It can be seen that each spectrum can be

divided into four peaks presenting four kinds of carbons (C_1 , C_2 , C_3 , and C_4 in different chemical environment respectively). As literatures^{30–32} described, C_1 , C_3 , C_4 should be $-\text{CH}_2-$ (binding energy: 284.5 eV), $\text{C}=\text{O}$ (binding energy: 287.1 eV), and $\text{O}-\text{C}=\text{O}$ (binding energy: 288.3 eV), respectively, and C_2 may be the carbons adjacent to C_3 or C_4 .

Comparing the samples before and after aging, the variation of C_{1s} concentration of the stabilized sample was easy to be understood. Some methylenes in the stabilized PA6 were oxidized to carbonyl groups during the long-term thermal oxidation aging and some molecular chains ruptured on the carbon atoms adjacent to the carbonyl groups. Therefore, the C_3 and C_4 concentration increased and the C_1 concentration decreased. But with respect to pure PA6, the phenomenon that the

relative concentration of C_3 decreased and the relative concentration of C_1 and C_4 increased to some extent with aging time was very complicated and interesting. The possible reasons were that during melt processing of PA6, many carbonyl groups were just formed in the chains (Fig. 11). In comparison, there were few new carbonyl groups formed during aging, and a lot of molecular chains may rupture to produce many volatile compounds like tertiary amine and small molecules which contain more than one carbonyl or carboxyl groups, as shown in Figure 12.³³ Obviously, as a result of the stabilization effect of the stabilizers, there was less content of such kind of volatile oxidized products in the stabilized sample.

CONCLUSION

The pure sample as well as the stabilized sample of PA6 were subjected to long-term oven aging at temperatures in the range of 110–150°C. At the initial stage of aging, the mechanical strength and the reduced viscosity of the samples increased because of the molecular crosslinking reaction and then dropped when the molecular degradation dominated. The existence of the stabilizers would endow PA6 with better retention of the mechanical properties, but the higher the aging temperature, the less remarkable the function of the stabilizers.

The crystallinity of PA6 increased, the crystallization growth rate and T_m decreased with aging time. The anneal process at high temperature and the small molecular products may be responsible for it. The thermal oxidative aging would primarily occur in the amorphous region of the polymer, and the molecular degradation in this region resulted in the increase of the concentration of the crystalline region of PA6. The rise of T_g and the reduction of the mobility of the molecules of the sample after aging were led by the molecular crosslinking reaction.

During aging, lots of carbon bonds of the samples were broken to form carboxylic acid, carbonyl, and the end amine group, and many amine groups may also be consumed by carboxylic acids, resulting in the increase of the carboxylic acid concentration and decrease of the end amine group concentration. The stabilized PA6 had relatively low content of carboxyl groups and high content of amine groups, indicating of better thermal oxidative stability. The surface composition analysis showed that the concentration of carbon and nitrogen atom of the sample decreased and the concentration of oxygen atom increased as a result of the formation of oxides

and peroxides on its surface. There was relatively small variation of the concentration of these three elements for the stabilized PA6, implying that the stabilizers could inhibit the oxidation reaction effectively.

References

- Hagler, A. T.; Lapicciarella, A. *Biopolymers* 1976, 15, 1167.
- Sargar, B. F. *J Chem Soc* 1967, B248, 1047.
- Šebenda, J.; Lánská, B. *J Macromol Sci* 1993, A30, 669.
- Lánská, B. *Eur Polym J* 1994, 30, 197.
- Gröning, M.; Hakkarainen, M. *J Chromatogr A* 2001, 932, 1.
- Du, Y.; Gong, J. X. *Zhan Jie* 2005, 26, 1.
- Michael, R. K.; Kishore, U.; John, C. M. *Macromolecules* 1997, 30, 4695.
- Dipasquale, G.; Larosa, A. D.; Recca, A.; Dicarolo, S.; Bassani, M. R.; Facchetti, S. *J Mater Sci* 1997, 32, 3021.
- Siat, C.; Bourbigot, S.; Bras, M. L. *Polym Degrad Stab* 1997, 58, 303.
- Chaupt, N.; Serpe, G.; Verdu, J. *Polymer* 1998, 39, 1375.
- Soto-Valdez, H.; Gramshaw, J. W. *J Mater Sci* 2000, 19, 823.
- Dabrowski, F.; Bourbigot, S.; Delobel, R.; Bras, M. L. *Eur Polym J* 2000, 36, 273.
- Lehrle, R. S.; Parsons, I. W.; Rollinson, M. *Polym Degrad Stab* 2000, 67, 21.
- Jain, A.; Vijayan, K. *J Mater Sci* 2002, 37, 2623.
- Pramoda, K. P.; Liu, T.; Liu, Z.; He, C. B.; Sue, H. J. *Polym Degrad Stab* 2003, 81, 47.
- Meng, L. H.; Zhang, Y.; Huang, Y. D.; Shibata, M.; Yosomiya, R. *Polym Degrad Stab* 2004, 83, 389.
- Lánská, B. *Polym Degrad Stab* 1996, 53, 89.
- Lánská, B. *Polym Degrad Stab* 1996, 53, 99.
- Lánská, B.; Matisová-Rychlá, L.; Rychly, J. *Polym Degrad Stab* 1998, 61, 119.
- Lánská, B.; Matisová-Rychlá, L.; Brožek, J.; Rychly, J. *Polym Degrad Stab* 1999, 66, 433.
- Lánská, B.; Matisová-Rychlá, L.; Rychly, J. *Polym Degrad Stab* 2001, 72, 249.
- Forsström, D.; Terselius, B. *Polym Degrad Stab* 2000, 67, 69.
- Forsström, D.; Reiberger, T.; Terselius, B. *Polym Degrad Stab* 2000, 67, 255.
- Cerruti, P.; Carfagna, C.; Rychly, J.; Matisová-Rychlá, L. *Polym Degrad Stab* 2003, 82, 477.
- Sanshuo, W. *The Aging of Plastic*; Defense Industry Press: Beijing, China, 1977.
- Chen, S. J.; Wang, Y. Z.; Huang, X. Y.; Yu, D. S. *Appl Eng Plastics* 1999, 27, 12.
- Manjun, H. *Polymer Physics*; Fudan Industry Press: Shanghai, China, 2002.
- Perera, M. C. S.; Ishiaku, U. S.; Ishak, Z. A. M. *NMR Polym Degrad Stab* 2000, 68, 393.
- Lánská, B.; Šebenda, J. *Eur Polym J* 1986, 22, 199.
- Massey, S.; Adnot, A.; Roy, D. *J Appl Polym Sci* 2004, 92, 3830.
- Bhat, N. V.; Upadhyay, D. J.; Deshmukh, R. R.; Gupta, S. K. *J Phys Chem B* 2003, 107, 4550.
- Rjeb, A.; Letarte, S.; Tajoute, L.; Chafik El Idrissi, M.; Adnot, A.; Roy, D.; Claire, Y.; Kaloustian, J. *J Electron Spectrosc* 2000, 107, 221.
- Li, R. F.; Hu, X. Z. *Acta Polym Sin* 2000, 2, 136.