

# Thermal Stabilization Effect of Biphenol Monoacrylate on Polyamide 6

Tao Yang, Lin Ye, Ying Shu

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

Received 27 December 2007; accepted 11 April 2008

DOI 10.1002/app.28543

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

**ABSTRACT:** Biphenol monoacrylate (AL) was combined with a traditional hindered phenolic-based binary antioxidant system to form a ternary stabilization system for the purpose of further improving the thermal-oxidative stability of polyamide 6 (PA6). The thermal stabilization effect of the antioxidant AL on PA6 was studied in terms of the reduced viscosity, the chemical structure, the yellow index, and the mechanical properties. The results showed that the antioxi-

dant AL, with the proper chemical structure, could improve the thermal stability of PA6 effectively through a unique bifunctional stabilizing mechanism. The interaction of the molecules of PA6 with the antioxidant AL was investigated. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 856–863, 2008

**Key words:** additives; degradation; mechanical properties; polyamides; stabilization

## INTRODUCTION

Polyamide (PA), as one of the most common engineering plastics, has a wide range of applications in industry because of its excellent mechanical properties. Usually, the carbon-hydrogen bond on the methylene group adjacent to nitrogen is considered to be the weakest bond,<sup>1</sup> and the most complicated oxidation reaction proceeds on this carbon with exposure to heat, oxygen, light, and water. It leads to a reduction of the molecular weight, subsequent deterioration in the physical and mechanical properties, increasing yellowing, and eventually embrittlement.<sup>2–8</sup> Generally, PA ranks among the polymers that are less resistant to radical reactions, and the service life of most PA products is mostly controlled by their ability to resist oxidation.<sup>3–5</sup> Therefore, the development of stabilization technology for PA is substantially important for its industrial applications.

Binary systems composed of a hindered phenolic as the main antioxidant and a phosphorus-based melt processing stabilizer as the secondary antioxidant are often used as traditional thermal stabilizing systems for PAs.<sup>9–11</sup> They may react with peroxy or

alkoxy radicals, and the secondary antioxidants prevent the cleavage of hydroperoxide.<sup>8</sup> However, the disadvantages still remain: they do not immediately stop the autoxidation of the polymer in the early stage of the alkyl radical.<sup>12</sup> In this work, biphenol monoacrylate (AL), which can react with alkyl radicals through a unique bifunctional stabilizing mechanism, was combined with phenols and phosphites to form a ternary antioxidant system. It was expected to trap all radicals produced during the degradation of polyamide 6 (PA6) and interrupt the autoxidation cycle as soon as it started, and the thermal stability of PA6 was expected to be improved efficiently.

## EXPERIMENTAL

### Materials

The PA6 used in this work was a commercial-grade granular product (YH800) without any additives; it was supplied by Yueyang Petrochemical Co., Ltd. (Hunan, China), and had a relative viscosity of  $2.85 \pm 0.03$ . The antioxidants Irganox 1010 and Irgafos 168 were both bought from Ciba-Geigy Corp. (Basel, Switzerland). A series of ALs were available from the Chemical Engineering Institute of Shanxi Province (Shanxi, China).

### Preparation of the stabilized PA6

The stabilized PA6 was prepared through the mixing of pure PA6 in a dry form with various stabilizers in a high-speed mixer and then extrusion with a TSSJ-25/03 twin-screw extruder from Chenguang

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.

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. Then, some of the granules were used for the chemical analysis, and some of them were injected into a standard dumbbell specimen (155 mm long and 4.2 mm thick) with a K-TEC40 (Malterdingen, Germany) for the mechanical property measurements.

### Oven aging

The injected dumbbell samples and granular samples of PA6 were subjected to oven aging in the ambient atmosphere at 130°C. The samples were taken out at regular time intervals and used for mechanical and chemical characterization. The temperature fluctuation in the oven was  $\pm 1^\circ\text{C}$ .

### Measurements

#### Mechanical properties

The tensile performance of the samples was measured with a 4302 material testing machine from Instron Co. (Norwood, MA) according to ISO 527/1-1993 standards. The test speed was 50 mm/min, and the sample length between bench marks was  $50 \pm 0.5$  mm.

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

#### Reduced viscosity

A sample of about 0.5 g was dissolved in 100 mL of formic acid. The time of outflow of the solution was measured with an Ubbelohde viscometer in a water bath at 25°C according to ISO 307-1984. Then, the reduced viscosity ( $\eta$ ) was calculated with the following equation:

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

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 of PA6<sup>13</sup>

*Carboxylic acid.* A sample 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 by NaOH (ca. 0.02 mol/L), with phenolphthalein used as an indicator. The concentration of carboxylic acid ( $X$ ) was calculated with the following equation:

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

where  $a$  is the consumption volume of the NaOH solution for the sample of PA6 (mL),  $b$  is the consumption volume of the NaOH solution for the solvent (mL),  $n$  is the molar concentration of the NaOH solution (mol/L), and  $W$  is the weight of the sample (g).

*Amine end group.* A sample of about 0.3 g was dissolved in 25 mL of a mixing solution of phenol and methyl alcohol (volume ratio = 1 : 1) at 55°C. Then, the solution was titrated with HCl (ca. 0.005 mol/L) with thymol blue as the indicator. The concentration of the end amine groups ( $Y$ ) was calculated with the following equation:

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

where  $A$  is the consumption volume of the HCl solution (mL) for the sample of PA6,  $B$  is the consumption volume of the HCl solution for the solvent (mL),  $n$  is the molar concentration of the HCl solution (mol/L), and  $W$  is the weight of the sample (g).

#### Yellow index (YI)

YI was measured with a DC-P3 fully automatic chromatic aberration meter from Xingguang Instrument Co. (Hangzhou, China). The samples were pressed into flakes with a thickness of 1.5 mm. In accordance with Standard GB 2409-80 of China, a few points on the flakes were selected, and the relevant stimulus values ( $X$ ,  $Y$ , and  $Z$ ) were measured. Then, YI was calculated with the following equation:

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

#### Ultraviolet-visible (UV-vis) spectrum

The UV-vis spectra of the samples were obtained with a UV-240 UV-vis spectrophotometer (Hitachi Ltd., Japan). The samples were prepared through the dissolution of PA in a 0.4 mol/L sulfuric acid/methanol mixture.

#### Fourier transform infrared (FTIR) spectrum

The FTIR analysis of the samples was conducted with a Nicolet-560 infrared spectrometer (Waltham, MA). The samples were prepared through the dissolution of PA in formic acid, which was cast onto a slide to form a film and dry.

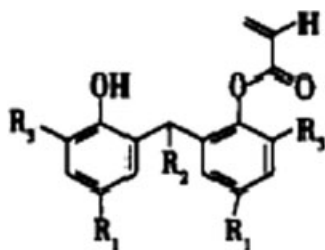
TABLE I  
Formula of the Antioxidant System

Antioxidant system	Irganox 1010 (wt %)	Irgafos 168 (wt %)	Antioxidant AL (wt %)
Binary system	0.2	0.2	0
Ternary system	0.2	0.2	0.2–0.3

## RESULTS AND DISCUSSION

The antioxidant system developed in this work was composed of Irganox 1010 as a hindered phenolic primary antioxidant, Irgafos 168 as a hydroperoxide decomposer, and AL as a scavenger of alkyl radicals. The traditional antioxidant system Irganox 1010/Irgafos 168 was also studied for comparison. The formula of the antioxidant system used in this study is summarized in Table I.

The structure of AL has a substantial effect on its functions as a thermal stabilizer. Its general formula with different substituents can be presented as follows:



where  $R_1$  is *tert*-butyl,  $R_2$  is a hydrogen atom, and  $R_3$  is *tert*-butyl for AL-1;  $R_1$  is *tert*-butyl,  $R_2$  is methyl, and  $R_3$  is *tert*-butyl for AL-2; and  $R_1$  is methyl,  $R_2$  is a hydrogen atom, and  $R_3$  is *tert*-butyl for AL-3.

### Effect of the antioxidant AL on the reduced viscosity of PA6

As shown in Figure 1, the variation of the reduced viscosity of PA6 with the aging time was investigated at 130°C. For PA6 with the traditional binary antioxidant system Irganox 1010/Irgafos 168, the reduced viscosity rose during the first 1 day, and then it leveled off gradually. After 6 days, it began to decline sharply. However, with the addition of the antioxidant AL, the reduced viscosity of PA6 kept rising during the first 4 days, and then it fell slowly and maintained a higher reduced viscosity than that of the binary system during the whole aging procedure. The various structures of the antioxidant AL showed different effects on the thermal stability of PA6, and the sample with Irganox 1010/Irgafos 168/AL-2 presented the highest reduced viscosity at the end of the aging. Moreover, the reduced viscosity of the sample increased with the content of AL-2.

The stabilizing mechanism of the antioxidant AL was confirmed to be a unique bifunctional mecha-

nism consisting of polymer radicals trapped by the acrylate group followed by fast hydrogen transfer through intramolecular hydrogen-bonded phenolic hydroxyl groups and carbonyl groups, resulting in stable phenoxyl radicals (see Scheme 1).<sup>12</sup> When the substituent  $R_2$  is a hydrogen atom (AL-1 and AL-3), the free rotation of the two benzyl rings leads to a change in the configuration of the molecule, weakening of the hydrogen bonding, and a reduction of the bifunctional stabilization effect of the antioxidant AL. For AL-2, the substituent  $R_2$  is methyl, the rotation of the benzene rings can be restricted because of the space hindrance, and the bifunctional stabilization effect can be promoted.<sup>12,14</sup> Therefore, AL-2 exhibited very effective stabilization for the thermal degradation of PA6.

It is well known that the reduced viscosity characterizes the viscosity-average molecular weight of a polymer, and the results indicated that during the

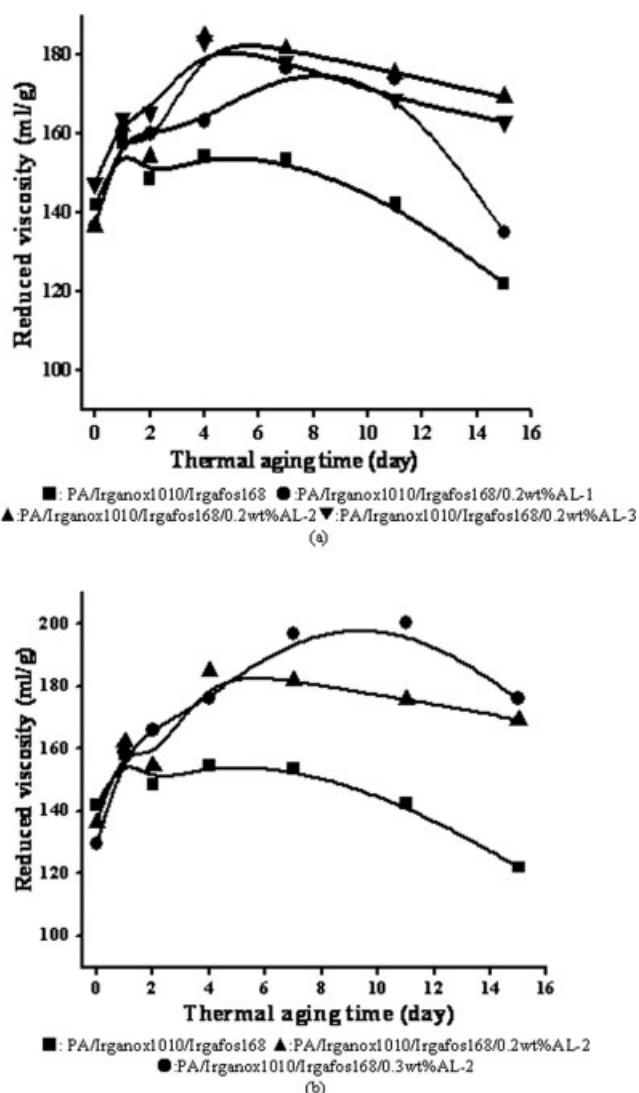
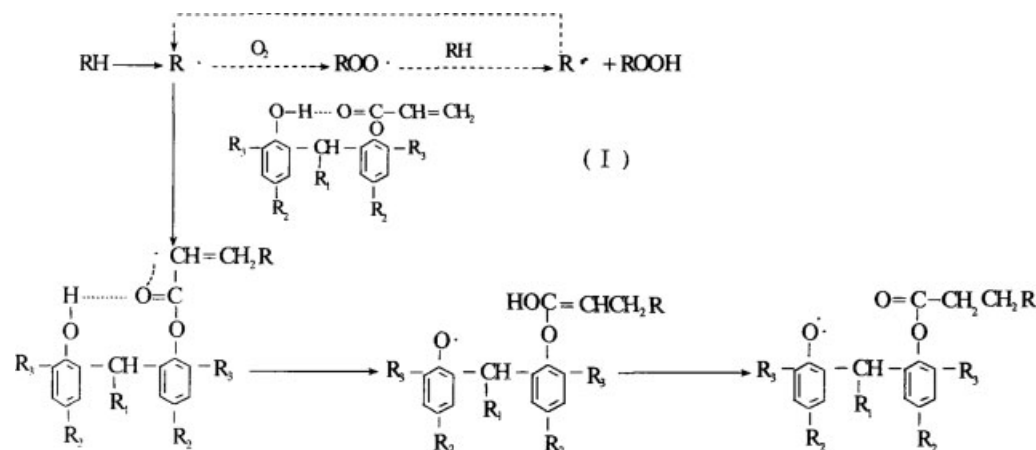


Figure 1 Effect of the antioxidant AL on the reduced viscosity of PA6 aging at 130°C.



Scheme 1 Bifunctional stabilizing mechanism of the antioxidant AL.<sup>12</sup>

primary aging time, the molecular crosslinking reaction of PA6 predominated, resulting in an increase in the reduced viscosity; afterwards, the molecular

degradation of the polymer predominated, resulting in a reduction of the reduced viscosity. Therefore, the sample containing the antioxidant AL displayed a relatively high reduced viscosity, and this indicated that the antioxidant AL could inhibit the molecular degradation of PA6 effectively during long-term thermal oxidative aging.

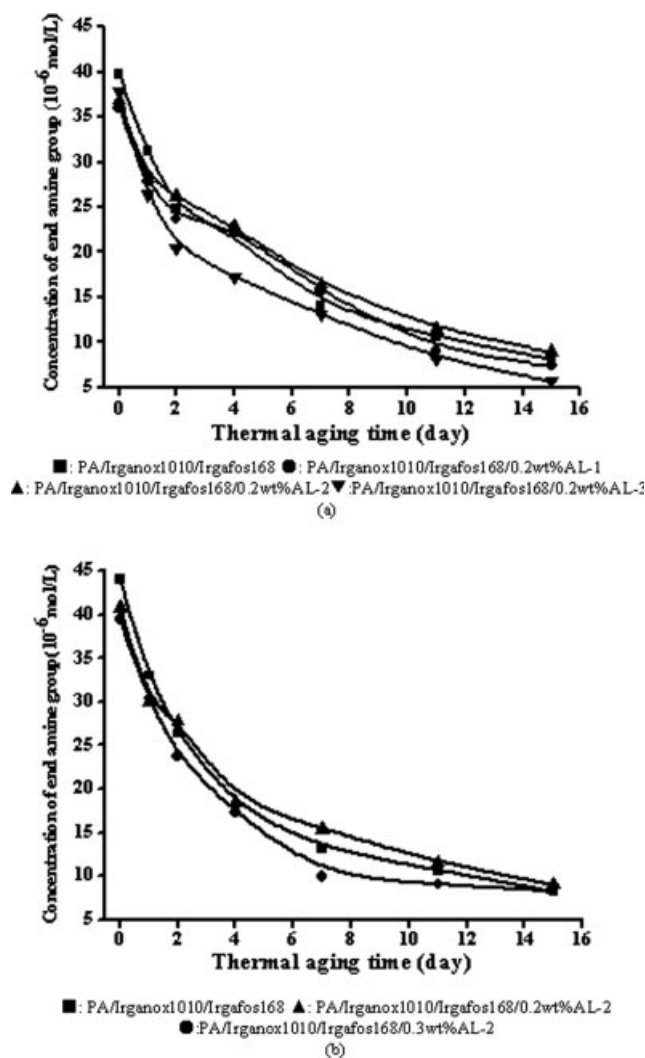


Figure 2 Effect of the antioxidant AL on the content of end amine groups on the molecules of PA6 aging at 130°C.

### Effect of the antioxidant AL on the chemical structure of PA6

The amido bond is considered to be the weakest bond in a molecule of PA. The rupture of the amido bond and the adjacent C—C bond results in the formation of carboxylic acid, carbonyl, and end amine groups, which may promote the further degradation of the polymer. During thermal oxidative aging, the higher the concentration is of the carboxylic acid, the more quickly the oxidation aging of the polymer will occur.<sup>7</sup> However, the end amine group has a thermal stabilization effect on PA. A high concentration of end amine groups in the molecules of PA6 is favorable to its thermal oxidative stability.<sup>8</sup> The chemical structure of PA6 during aging at 130°C is shown in Figures 2 and 3. With an increase in the aging time, the carboxylic acid concentration rose and the end amine group concentration dropped monotonously for PA6. The carboxylic acid concentration of PA6 in the presence of the antioxidant AL was lower than that of the sample of PA6 with the traditional binary antioxidant system Irganox 1010/Irgafos 168, except for the sample with AL-1, which had a higher carboxylic acid concentration before 4 days. In the initial stage of the aging, the sample with the traditional binary antioxidant system had a relatively high end amine group concentration because the antioxidant AL itself had carboxylic groups in its molecules. AL-2 also displayed the best stabilization effect on PA6 with the lowest carboxylic

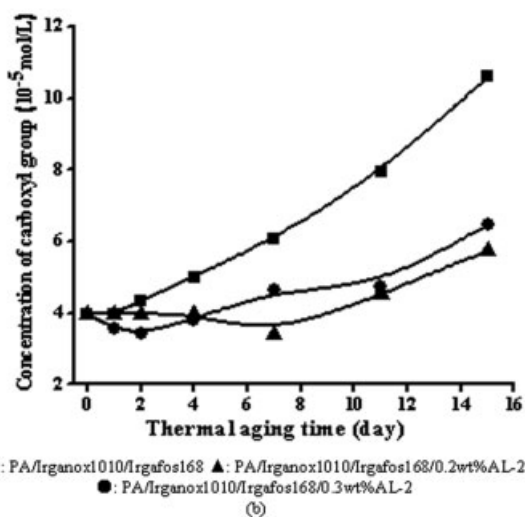
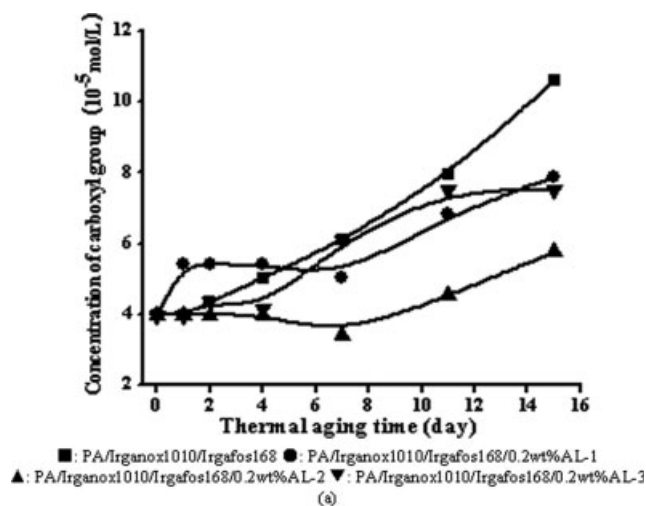


Figure 3 Effect of the antioxidant AL on the content of carboxyl groups on the molecules of PA6 aging at 130°C.

acid concentration and highest end amine group concentration of the sample.

However, with an increase in the content of the antioxidant AL-2, there was a slight increase in the carboxylic acid concentration and a drop in the end amine group concentration. The antioxidant AL-2 itself contained carboxylic groups, which may have made the carboxylic groups of the polymer system higher. The greater amount of double bonds of the acrylate group on the molecule of the antioxidant AL may have consumed more amine groups of PA6.

#### Effect of the antioxidant AL on YI of PA6

The variation of YI of PA6 with the aging time at 130°C is shown in Figure 4. During the whole aging procedure, the sample of PA6 stabilized with the ternary system in the presence of AL-2 had the lowest value of YI and showed the best resistance to discoloration. The sample in the presence of AL-3 had the

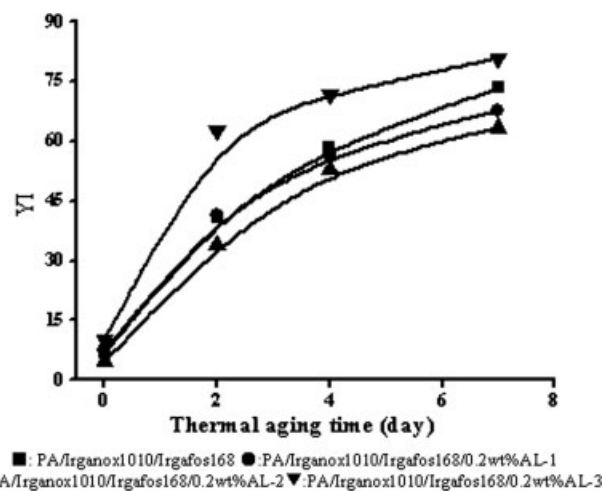


Figure 4 Effect of the antioxidant AL on the YI of PA6 aging at 130°C.

highest value of YI, and the extent of discoloration was even more serious than that of the sample of PA6 with the binary antioxidant system. For the

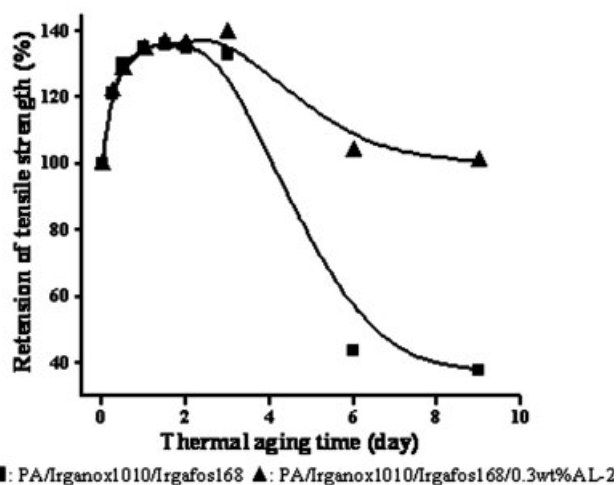
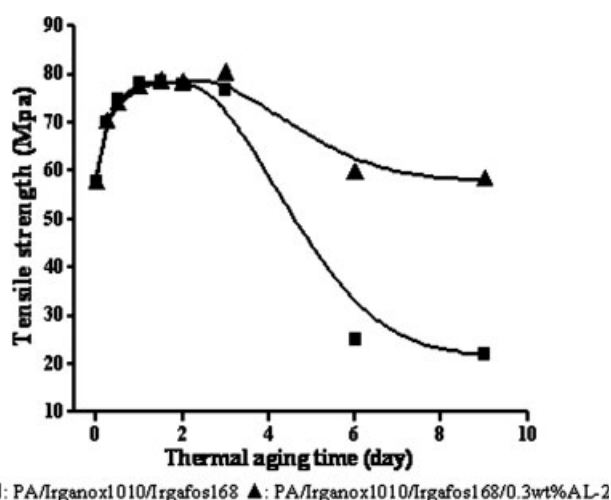


Figure 5 Effect of the antioxidant AL on the tensile strength of PA6 aging at 130°C.

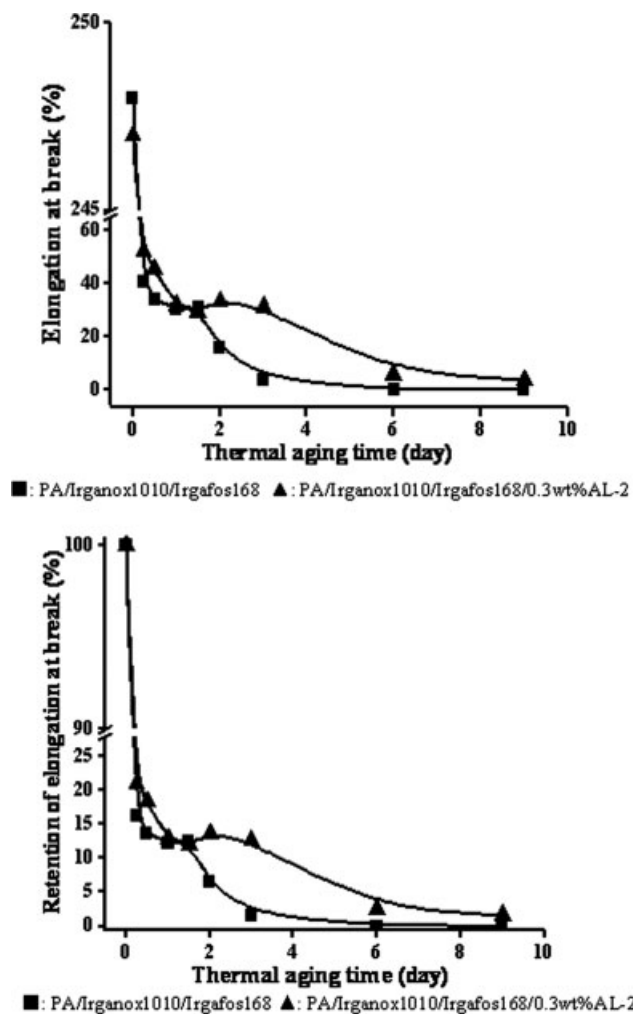


Figure 6 Effect of the antioxidant AL on the elongation at break of PA6 aging at 130°C.

molecular structure of AL-3,  $\alpha$ -H of methyl ( $R_1$ ) on the opposite site of the phenolic hydroxyl group led to the yellowing of the sample. However, as for AL-1 and AL-2, for which  $R_1$  was *tert*-butyl, the sample containing these two antioxidants proved to be more color-stable.<sup>14–16</sup>

#### Effect of the antioxidant AL on the mechanical properties of PA6

The mechanical properties of stabilized PA6 aged at 130°C were investigated. As shown in Figure 5, the tensile strength of PA6 increased during the first 2 days. However, the subsequent variation of the strength differed for various samples of PA6. For PA6 with the binary antioxidant system, the tensile strength decreased dramatically after 4 days and reached 38% in 9 days. On the other hand, the tensile strength of PA with the AL-based ternary system declined much more slowly, and the value was still 101% at the end of the aging. The retention of

the tensile strength presented a similar trend with the aging time.

As shown in Figure 6, the elongation at break of the sample with the binary antioxidant system decreased rapidly with the aging time, and it decreased to 16% after 1 day, 6% in 3 days, and 0% in 6 days because of the brittle rupture. For the sample stabilized with the AL-based ternary system, the value of the elongation at break decreased to 21% in 1 day and 13% in 3 days and kept a certain value of the elongation at break in 6 days.

The difference in the notched Charpy impact strengths of various samples of PA6 was more obvious (Fig. 7). The remarkable drop in the impact strength occurred on the first half-day, and for PA6 with the binary antioxidant system, it first dropped to 75%, then decreased slowly, and reached 25% in 6 days. However, for the sample stabilized with the AL-based ternary system, it first dropped to 72%, then kept this value at 3 days, and decreased to 42% in 6 days. In other words, compared with PA6

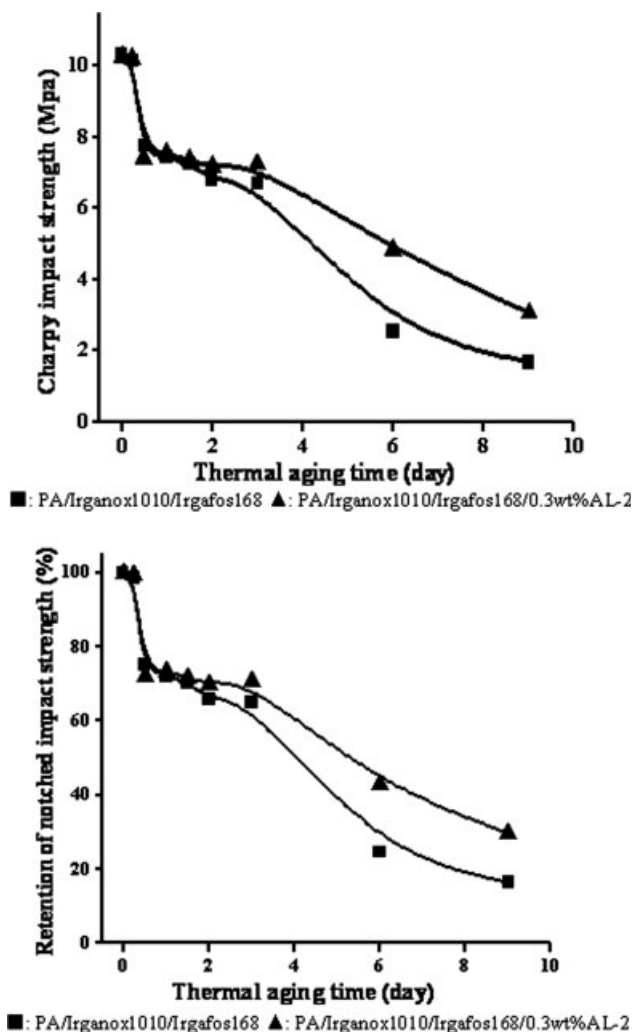


Figure 7 Effect of the antioxidant AL on the impact strength of PA6 aging at 130°C.

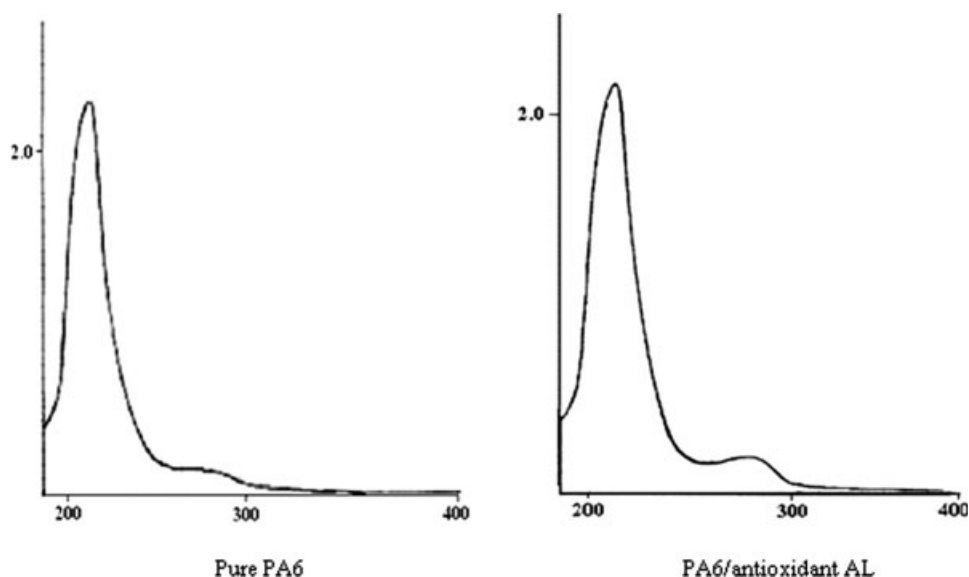


Figure 8 UV spectra of PA6 with and without the antioxidant AL.

stabilized with the binary antioxidant system, the sample of PA6 stabilized with the ternary antioxidant system exhibited relatively high thermal stability for its mechanical properties during long-term thermooxidative aging.

For the case in which both hot air and oxygen existed, there was a thermooxidation reaction, including molecular chain degradation and crosslinking in the PA6 matrix. In the initial stage of aging, the crosslinking reaction dominated, and this made the tensile strength of PA6 increase to some extent. However, with an increase in the aging time, molecular degradation played a leading role gradually, and the remarkable decline of the molecular weight made the mechanical properties decrease sharply. During the whole oxidation procedure, the molecular weight distribution was widened, the regularity of the molecular chain became poor, and the hydrogen bonding and Van der Waals force between the molecules were weakened. Besides, the defects in the matrix increased, and this resulted in a reduction of the impact toughness of PA6.

#### Interaction of PA6 with the antioxidant AL

The interaction of the molecules of PA6 with the antioxidant AL was investigated. The stabilized sample was prepared through the mixing of pure PA6 with the antioxidant AL, then extrusion and pelletization, and finally purification to remove the residue of the antioxidant AL in the sample. As shown in Figure 8, the strong peak at  $\lambda = 220$  nm could be attributed to the  $p$ - $\pi$  conjugation of the amido bond of PA6. In comparison with the pure sample, a new peak at  $\lambda = 280$  nm for the stabilized sample could

be attributed to the benzyl group on the molecule of the antioxidant AL, and it demonstrated that the active amido group on the molecules of PA6 perhaps reacted with the double bond of the acrylate group of the antioxidant AL and that the molecule of the antioxidant AL could be grafted onto the molecule of PA6.

As shown in Figure 9, for pure PA6, the absorbance peaks at 3300, 3064, and 1545  $\text{cm}^{-1}$  were attributed to the stretching vibration and bending vibration of N—H in the amido bond. The peaks at 2938 and 2867  $\text{cm}^{-1}$  were attributed to the stretching vibration of C—H. The peaks at 1641  $\text{cm}^{-1}$  were

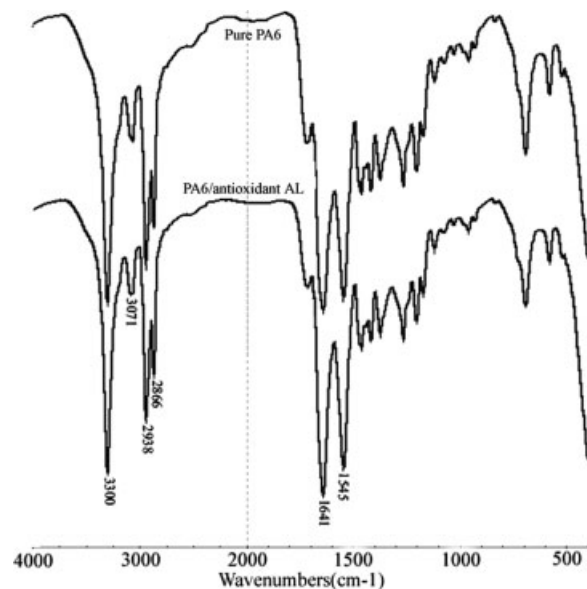


Figure 9 FTIR spectra of PA6 with and without the antioxidant AL.

attributed to the stretching vibration of the amido group. With the addition of the antioxidant AL, there was no obvious difference in the characteristic absorbance peaks of PA6, except that the peak at  $1641\text{ cm}^{-1}$  was enhanced slightly, and this was supposed to be attributable to the absorbance of the benzene group on the molecule of the antioxidant AL.

### CONCLUSIONS

AL, which can react with alkyl radicals through a unique bifunctional stabilizing mechanism, was combined with phenols and phosphites to form a ternary antioxidant system to further improve the thermal stability of PA6. During oven aging at  $130^{\circ}\text{C}$ , the antioxidant AL inhibited the reduction of the reduced viscosity and the molecular degradation of PA6 effectively, inhibited the formation and increase in the content of end carboxyl groups on the molecular chain and the decrease in the content of the end amine groups, and improved the resistance to discoloration of PA6. It also delayed the decrease in the mechanical properties of PA6, and higher retention could be achieved. Various structures of the antioxidant AL showed different behaviors for the stabilization of PA6, and the antioxidant AL-2 with *tert*-butyl as  $R_1$  and methyl as  $R_2$  presented the best thermal stabilizing effect on PA6. The UV spectrum and

FTIR analysis of PA6 indicated that a strong interaction and chemical bonding could form between the molecules of PA6 and the antioxidant AL.

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