

Modification of Melt, Light, and Heat Stability of Polyamide 6 by Hindered Piperidine Amine and Tertiary Amine

Xitao Guo,^{1,2} Yaoming Zhao,¹ Ping Ning,¹ Linkai Li²

¹Institute of Materials, South China University of Technology, Guangzhou, People's Republic of China

²Guangdong Rongtai Co., Ltd., Jieyang, People's Republic of China

Received 9 November 2005; accepted 18 March 2006

DOI 10.1002/app.24533

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

ABSTRACT: Hindered piperidine amine (HPA) and tertiary amine (TA) were introduced into hydrolytic polymerization of caprolactam, and polyamide 6 (PA 6) modified by additives [HPA/TA = 1 : 1 (w/w)] was obtained. The effects of additives on the melt, light, and heat stability of PA 6 were studied. The results showed that with an increase in additive content, the viscosity of PA 6 increased and the elastic response decreased. Thus, the drawing property of PA 6 fibers during melt spinning was improved. With the addition of 0.1%–0.2% additives, the degree of variation in amino end group content and relative viscosity decreased during the process going from resin to fiber, indicating the modified PA 6 had improved melt stability. During light and heat aging, the ratio of retained frac-

ture strength of PA 6 filament increased after modification by 0.1%–0.4% additives. Scanning electron microscopy showed that the surface morphology of the modified fiber remained almost the same, whereas that of the unmodified fiber was seriously destroyed when exposed to xenon light for 8 days or heated to 180°C in air for 1.5 h. The degree of variation of relative viscosity of the PA 6 fiber also decreased after modification by 0.1%–0.2% additives under oxidative degradation. All these results indicate PA 6 had better melt, light, and heat stability when modified by additives. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 538–544, 2007

Key words: PA 6; melt stability; light stability; heat stability

INTRODUCTION

Polyamide (PA) 6 is widely used in the plastic and textile industries, and it offers a desirable combination of qualities, such as high tensile strength, rebound elasticity, and wear. However, because of its large surface-to-volume ratio, PA 6 is readily susceptible to degradative attack during heat processing and application, causing a loss in molecular weight, a change in the end groups, and the development of color.¹ The negative effects of PA 6 oxidative degradation can be suppressed by the addition of small amounts of stabilizers such as hindered phenol, aromatic amine, metallic salt, and so on.

Forsstrom et al.² found that phenolic antioxidants Irgonax 1098 and Irgonax B1171 can improve the heat stability of PA 6 films (shown by the drop in strain at break). Lanska et al.^{3–6} studied the efficiency and mechanism of various antioxidants, such as phenol, hindered amine, and alkali metal salts, in improving the light and heat stability of PA 6. Malik et al.⁷ found that melt, light, and heat stability could be improved by incorporating an organic additive, *N,N'*-bis(2,2,6,6-

tetramethyl-4-piperidyl)-1,3-benzendicarboxamide. However, this method has a problem. The disperse uniformity and size of the additives in the PA 6 matrix will influence the spinning process of PA 6 resin.

Unlike these stabilizers, the complex amine additives hindered piperidine amine (HPA) and tertiary amine (TA) can react with the carboxylic end groups of PA 6.⁸ So HPA and TA were introduced during the hydrolytic polymerization of caprolactam, and PA 6 resin modified by amine modifiers was obtained. The aim of the present work was to investigate the effects and mechanisms of HPA/TA in improving the melt, light, and heat stability of PA 6.

EXPERIMENTAL

Materials

The polymeric materials used in this study were ϵ -caprolactam, supplied by Toray Industries, Inc. (Osaka, Japan); compound acid (isophthalic acid and benzoic acid), supplied by Shanghai Chemical Reagent Co. (Shanghai, China); and hindered piperidine amine stabilizer (HPA) and tertiary amine (TA), supplied by Beijing Be-Lin-Wei Chemical Technique Co. (Beijing, China). HPA is 4-amino-2,2,6,6-tetramethylpiperidine, and TA is 3-diethylamino-1-propylamine (Fig. 1).

Correspondence to: Y. Zhao (psymzhao@scut.edu.cn).

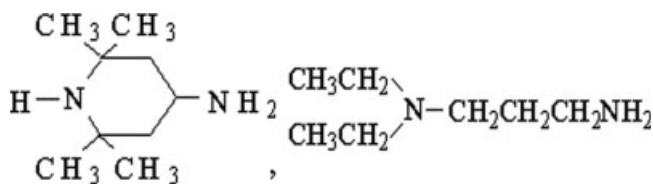


Figure 1 Formation of additives.

PA 6 synthesis, spinning

PA 6 resin was produced in a continuous hydrolytic-polymeric process in which caprolactam was polymerized at 246°C–258°C in the presence of water as initiator, isophthalic acid and benzoic acid as chain regulators, and special additives as modifier by polymerizing caprolactam in a polymeric kettle in the presence of 7.5 wt % water, 0.2 wt % isophthalic acid, 0.1 wt % benzoic acid, and from 0 to 0.4 wt % additives, all relative to caprolactam, at an ordinary pressure over the entire polymerization time of 11–12 h. The polymerization space was protected by N₂.

PA 6 fiber 24.9 dtex in size was prepared on a single-screw extruder with an L/D of 24 and a spinneret size of Φ 0.5 mm × 12. The spinning temperatures were 235°C–240°C, 250°C–255°C, 250°C, 248°C, and 245°C successively. The extruded multifilaments were cooled in air, rolled at a speed of 330 m/min, and drawn on a heat plate at 60°C with a ratio (DR) of 4.

Measurements

Dynamic viscoelastic properties of the PA 6 resin were determined by a Rheometric Dynamic Analyzer, RDA-III (Rheometric Scientific Inc., America) in the parallel plate mode (10-mm diameter plates with a distance of 0.2 mm). Angle frequency (ω) scans were

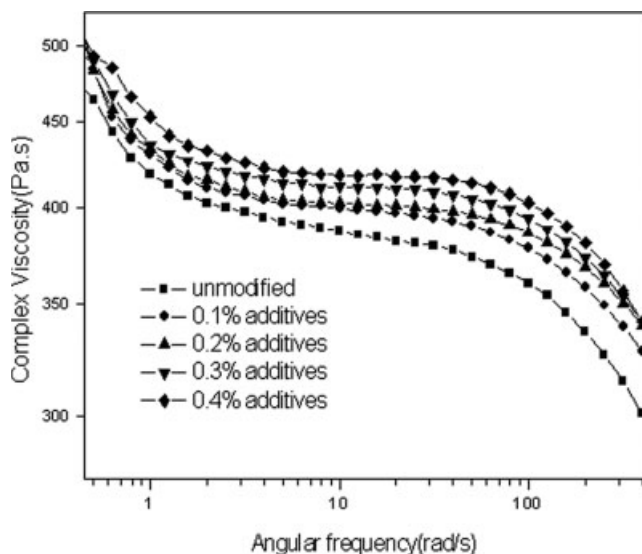


Figure 2 Complex viscosity versus frequency for PA 6.

made from 0.1 to 400 rad/s at a fixed temperature of 250°C and a strain of 10%.

The light fastness properties of PA 6 fiber were determined with a Ci400 Light Fastness Tester (ATLAS, America) according to GJB150 with a xenon lamp as a light source and Boro/Boro filters. PA 6 fibers were tested for 4, 8, and 12 days successively. A cycle was defined as 1 day, with each cycle divided into two stages. In the first stage, fibers were subjected to a Xenon arc light for 20 h with a blackboard temperature of 79°C, a housing temperature of 49°C, 50% relative humidity, and 0.55 W/m² and irradiance of 340 nm. In the second stage, the xenon lamp was turned off for 4 h with a housing temperature of 49°C and 50% relative humidity.

The relative viscosity ([η_r]) of PA 6 was determined with a Ubbelohde viscometer (Cannon-Ubbelohde State College, PA) with 98% vitriol as the solvent at

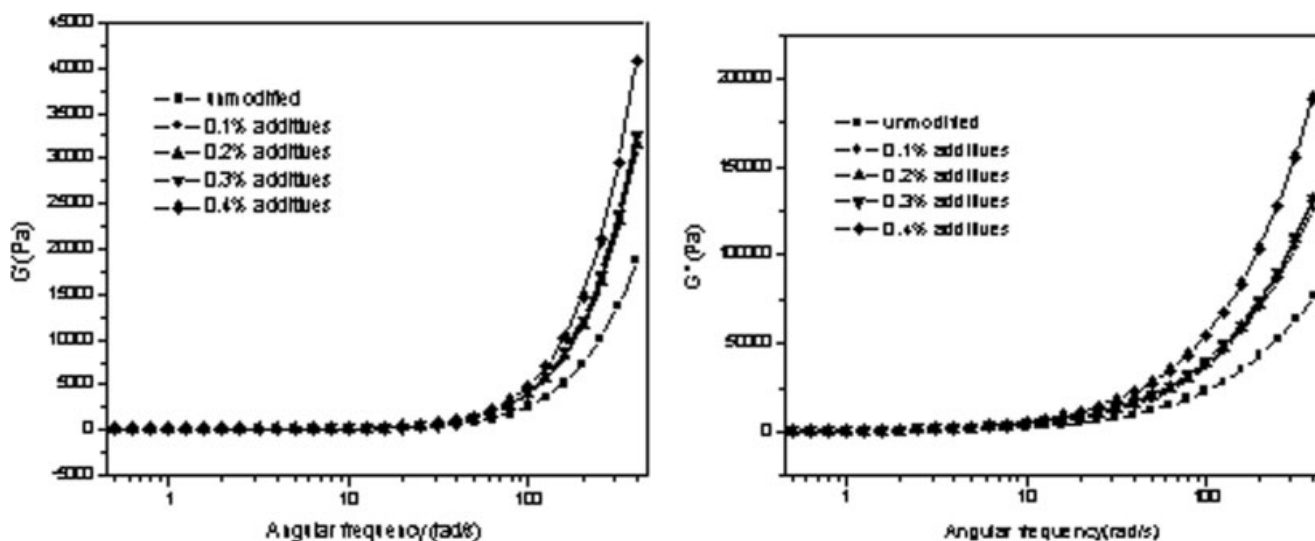


Figure 3 Dynamic loss modulus (G'') and dynamic storage modulus (G') versus frequency for PA 6.

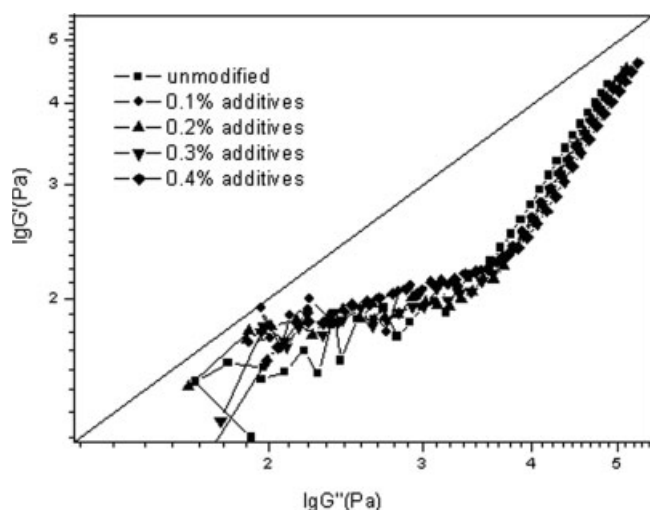


Figure 4 Log G' versus log G'' for PA 6 with different amine modifier contents.

20°C. Amino end group content was determined by acidimetric titration with perchloric acid in 70 : 30 (w/w) phenol/methanol as the solvent.

Tensile properties of a single fiber were measured at 20°C and 65% relative humidity using a YG001A Single-Fiber Tensile Tester (Chinese Tai-Chang Instrument Co.). All results are averages of at least 10 measurements.

The morphology of PA 6 fibers was observed with a S-500 Scanning Electron Microscope (Hitachi, Japan) that was coated previously by sputtering with gold in order to achieve a conducting and protecting layer.

RESULTS AND DISCUSSION

Dynamic viscoelastic properties of PA 6

The melt stability of PA 6 was closely associated with the viscoelastic properties of the bulk polymer. The dynamic rheological properties of the unmodified PA 6 resin and the PA 6 resin modified by 0.1%–0.4% additives [HPA/TA = 1 : 1 (w/w)] were studied with a rheological dynamic analyzer.

Complex viscosity (Eta^*) is an important index of the flow ability of a polymer melt, and its value reflects the

moving speed of a polymer molecule chain under stress. Figure 2 shows the complex viscosities of unmodified and modified PA 6 at different angular frequencies (ω). For the sterically resistant action of hindered piperidine stabilizer (HPA), the unfolding of a modified PA 6 chain under stress became difficult, and the Eta^* of the PA 6 melt increased with an increasing content of additives. So the additional content of HPA could not be too high. In this work, TA, which is less sterically resistant, and HPA were used as complex additives.

Figure 3 shows the variation in the storage modulus (G') and loss modulus (G'') of unmodified and modified PA 6 at different frequencies (ω). With an increase in frequency, the storage modulus and loss modulus increased. For the sterical resistance of the additives, the G'' and G' of the modified PA 6 increased according to the content of additives.

The viscoelastic properties of the polymer melt could be evaluated by the Cole–Cole curve, suggested by Harrell.⁹ The relative contribution of the elastic response, G' , and the viscous response, G'' , on the polymer melt can be seen in the log $G' \sim \log G''$ plots. When log $G' \sim \log G''$ was plotted to the right of the diagonal line, the viscous response led.

Figure 4 shows the log $G' \sim \log G''$ relation of unmodified PA 6 to modified PA 6. The log $G' \sim \log G''$ plots showed that both unmodified and modified PA 6 were characterized by a viscous response. With an increase in the additive content, the viscous response increased and the elastic response decreased for the log $G' \sim \log G''$ plots that departed from the diagonal line to the right and below. The increase in the viscous response was beneficial to the drawing of PA 6 during melt spinning.

Variation in relative viscosity and amino end group content of PA 6

It is well known that the relative viscosity and amino end group content of PA 6 during melt processing result from the condensation reaction of amino end groups and carboxylic end groups. The melt stability of PA 6 can be measured by the degree of variation.

The increase in the relative viscosity and the decrease in the number of amino end groups during the processing of melt spinning are shown in Table I. With the

TABLE I
Relative Viscosity and Amino End Group Content of PA 6

	Unmodified	0.1% Additives	0.2% Additives
Relative viscosity			
Resin	2.35	2.36	2.34
Fiber	2.44	2.43	2.41
Difference	0.09 (3.8%)	0.07 (3.0%)	0.07 (3.0%)
Amino end group content (mmol/kg)			
Resin	28	41	45
Fiber	24	36	40
Difference	-4 (-14.3%)	-5 (-12.2%)	-5 (-11.1%)

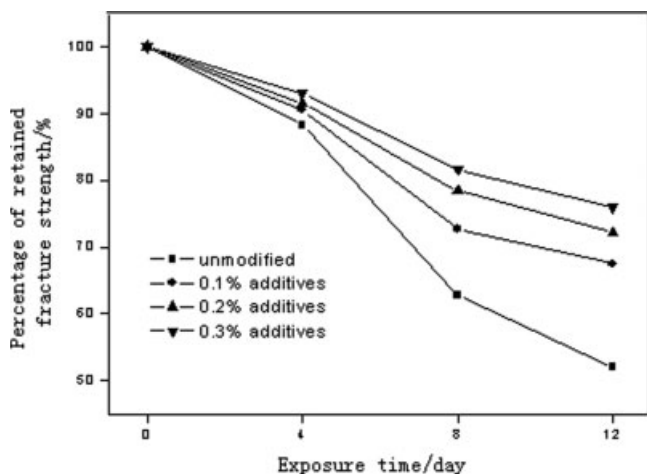


Figure 5 Ratio of retained fracture strength for PA6 filament after light aging.

addition of 0.1%–0.2% additives, the modified PA 6 showed a viscosity buildup of 3.0%, whereas the unmodified fiber showed a viscosity buildup of 3.8%. Likewise, there was less of a decrease in amino end group content during the processing of melt spinning. These results indicate modified PA 6 had better melt stability and the potential to provide more stable spinning production.

Light stability of PA 6 fiber

The mechanical properties, relative viscosity, and surface morphology of PA 6 fiber modified by 0.1%–0.3% additives [HPA/TA = 1 : 1 (w/w)] were compared with those of the unmodified PA 6 fiber when exposed to xenon light for 4, 8, and 12 days.

Mechanical properties of PA 6 fiber

When exposed to xenon light for 4, 8, and 12 days separately, the ratios of retained fracture strength for PA 6 filaments were compared (Fig. 5).

Figure 5 shows that the ratios of retained fracture strength of modified PA 6 filament almost remained above 70%, whereas the unmodified PA 6 filament was 50% under the same condition of light aging. As a result of this excellent light stability of modified PA 6 fiber, no extra light stabilizers needed to be added.

Surface morphology of PA 6 fiber

Figure 6(a–c) shows the surface morphology of unmodified PA 6 fiber, PA 6 modified by 0.1% additives, and PA 6 modified by 0.2% additives, respectively, and Figure 6(a'–c') shows the surface of morphology of the same fibers after exposure to xenon light for 8 days.

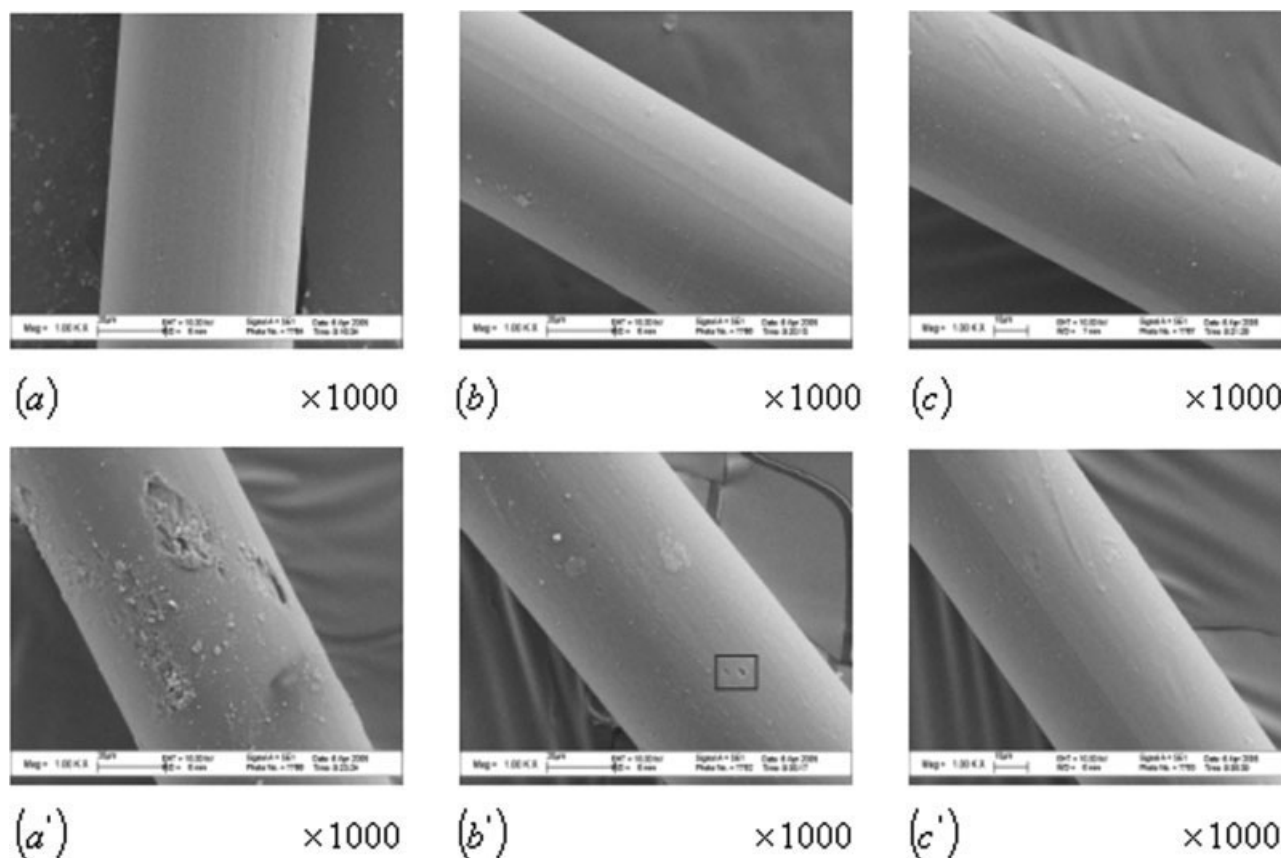


Figure 6 Scanning electron microscopy of the surface morphology of PA 6 fibers after light aging.

TABLE II
Relative Viscosity of PA 6 Fiber

Sample	Relative viscosity		
	Original	Light 8 days	Retained ratio
Unmodified	2.44	2.02	83%
0.1% Additives	2.43	2.09	86%
0.2% Additives	2.41	2.12	88%

Figure 6 shows that there were apparent holes and cracks on the surface of the unmodified fiber, although the surfaces of PA 6 modified by 0.1% or 0.2% additives were still in good condition. This showed that the light stability of PA 6 fibers was improved by modification with additives.

Ratio of retained relative viscosity of PA 6 fiber

The decreases in the relative viscosity ($\eta_{I,r}$) of PA 6 fiber when exposed to xenon light for 8 days are shown in Table II.

Degradation of PA 6 fiber could be induced by xenon light, resulting mainly in bond scission of the polymer chain. And bond scission resulted in the relative decrease in the viscosity of PA 6 fiber. The degree of variation in the relative viscosity of PA 6 fiber decreased under the same light-aging condition, which indicates the improved light stability of the modified PA 6 fiber.

Heat stability of PA 6 fiber

Again, the mechanical properties, relative viscosity, and surface morphology of modified PA 6 fibers were compared with those of the unmodified PA 6 fiber when heated to 180°C in air for 1.5 h.

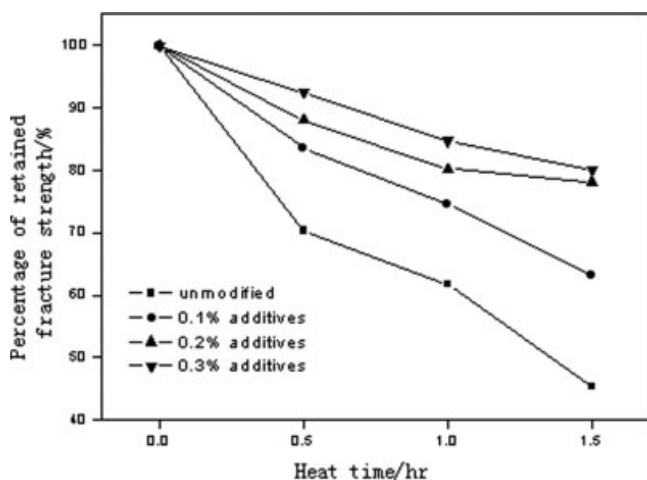


Figure 7 Ratio of retained fracture strength for PA 6 filament after heat aging.

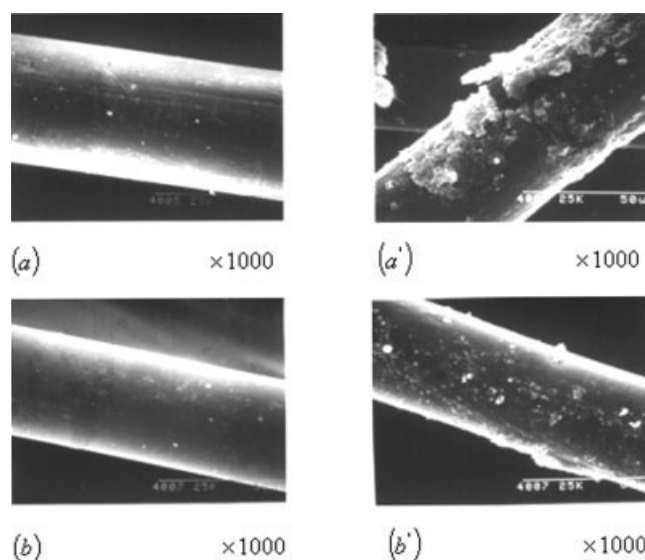


Figure 8 SEM surface morphology of PA 6 fiber after heat aging.

Mechanical properties of PA 6 fiber

The ratios of retained fracture strength for PA 6 filaments were compared when heated to 180°C in air for 1.5 h (Fig. 7).

Under treatment (180°C, 1.5 h), the ratios of retained fracture strength of PA 6 filaments modified by 0.2%–0.3% additives remained almost above 80%, whereas that of the unmodified fiber was below 50%. This clearly confirmed that the additives can protect the mechanical properties of PA 6 fiber and thereby improve the heat stability of modified PA 6 fiber.

Surface morphology of PA 6 fiber

Figure 8(a,b) shows the surface morphology of unmodified PA 6 fiber and PA 6 modified by 0.1% additives, respectively, and Figure 8(a',b') shows the surface morphology of the same fibers after being heated to 180°C in air for 1.5 h.

Figure 8 shows that the surface morphology of unmodified PA 6 fiber after heat aging for 1.5 h at 180°C in air was destroyed. There were apparent holes and chips on the surface of the fiber, although the surface of the modified fiber was still in good condition.

TABLE III
Relative Viscosity of PA 6 Fiber

Sample	Relative viscosity		
	Original	180°C, 1.5 h	Retained ratio
Unmodified	2.44	1.90	78%
0.1% Additives	2.43	2.06	85%
0.2% Additives	2.41	2.14	89%

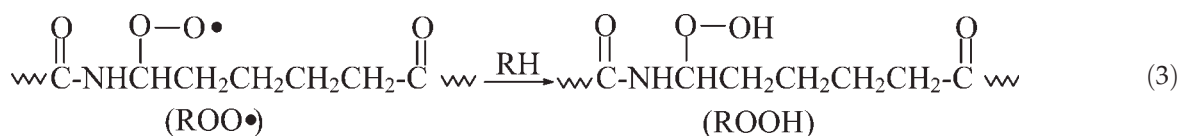
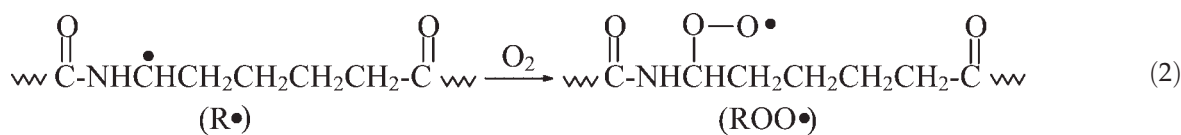
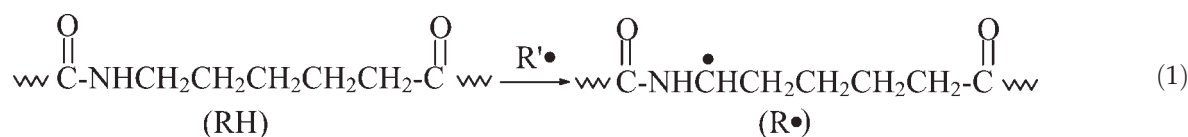
Ratio of retained relative viscosity of PA 6 fiber

The decreases in relative viscosity (η_r) of PA 6 fiber when heated to 180°C in air for 1.5 h are shown in Table III.

Table III shows that the bond scission for polymer degradation under heat and oxygen resulted in a relative decrease in the viscosity of PA 6 fiber. The ratio of retained relative viscosity of PA 6 fiber increased from 78% to 85% (or 89%) separately after modified by 0.1% (or 0.2%) additives, indicating the improved heat stability of the modified PA 6 fiber.

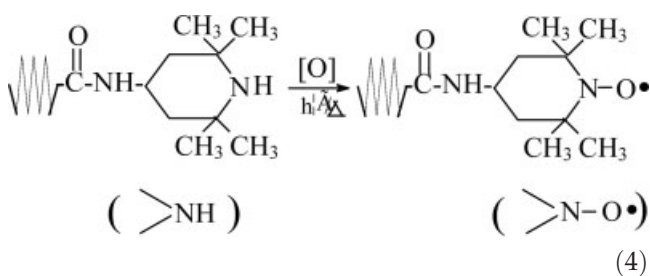
Mechanism by which additives improve light and heat stability of PA 6

Free radicals (R^\bullet) were formed during the preliminary oxidative degradation of PA 6, and these free radicals reacted with the hydrogen in the methylene adjacent to the N atom to form macromolecular radicals [R^\bullet ; Eq. (1)]. Then peroxy radicals (ROO^\bullet) and hydroperoxides ($ROOH$) were generated via chain transfer reaction [eqs. (2) and (3)]:¹⁰

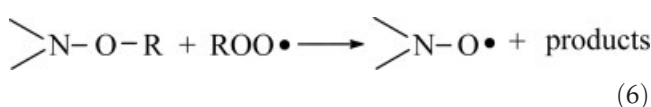


When they absorbed light energy or heat quantity, ROO^\bullet and $ROOH$ were decomposed to form aldehyde, carboxylic acid, and so on. And degradation of PA 6 was rapidly accompanied by these reactions.

HPA is a hindered piperidine amine modifier. It cannot absorb a beam whose wavelength is above 260 nm and cannot quench an excited-state chromophore. But it can absorb light energy or heat quantity under oxygen to form nitroxyl radicals [Eq. (4)]:¹¹⁻¹⁴



Generally, it is now assumed that these nitroxyl radicals appear in the oxidation chain reaction to form *N*-alkoxyamines [Eq. (5)], from which nitroxyl radicals are regenerated by some reaction with peroxy radicals [Eq. (6)]:



Additives (HPA/TA) were effective stabilizers for PA 6. The present work introduced the effects and mechanisms of additives [HPA/TA = 1 : 1 (w/w)] on the improvement of the melt, light, and heat stability of PA 6. The effect of additives on the dyeability of PA 6 fiber will be discussed in the next article.

CONCLUSIONS

Hindered amine additives (HPA/TA) were introduced during the hydrolytic polymerization of caprolactam, and amine-additive-modified PA 6 resin with improved melt, light, and heat stability was obtained. First, the viscous response of modified PA 6 melt increased and the elastic response decreased. Thus, the drawing property of the modified PA 6 fiber was improved during melt spinning. Second, the degree of variation in amino end group content and relative viscosity decreased during the process of resin to fiber, indicating the improved melt stability of the modified PA 6. Third, during light and heat aging, the ratio of retained

fracture strength of modified PA 6 filament increased. Scanning electron microscopy showed that the surface morphology of the modified fiber remained almost the same, whereas that of the unmodified fiber was seriously destroyed when exposed to xenon light for 8 days or heated to 180°C in air for 1.5 h. The degree of variation in the relative viscosity of PA 6 fiber also decreased after modification by 0.1–0.2% additives under oxidative degradation. All these results show that PA 6 had better melt, light, and heat stability when modified by amine additives.

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