

Application of Hindered Piperidine Amine and/or Tertiary Amine in the Modification of Polyamide 6

Xitao Guo, Yaoming Zhao, Ping Ning, Xiying Ai

Institute of Materials, South China University of Technology, Guangzhou, China

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ABSTRACT: PA 6 resin was produced in a hydrolytic-polymeric process in which ϵ -caprolactam was polymerized in the presence of water as initiator, isophthalic acid and benzoic acid as chain regulators, by polymerizing caprolactam in the presence of 7.5% by weight of water, 0.2% by weight of isophthalic acid, 0.1% by weight of benzoic acid, each percentage being based on caprolactam. By adding hindered piperidine amine and/or tertiary amine to the polymeric system, the effects of additives on the polymer were studied. The results showed that: the addition of 0.1

~ 0.2% additives can improve the melt stability of polyamide 6; the addition of 0.2% additives can protect mechanical properties of polyamide 6 fibers after exposure to high temperature; and the addition of 0.05 ~ 0.25% additives can increase the amino end group content of polyamide 6 and thereby increase the dyeability of polyamide fibers. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 2489–2493, 2004

Key words: PA 6; hindered amine; tertiary amine; stability; dyeability

INTRODUCTION

Polyamide fiber is the earliest industrial synthetic fiber and one of the most important synthetic fibers. It offers a desirable combination of qualities, such as high intension, rebound elasticity, wear, and antifatigue property. As a result, polyamide fiber is widely used in clothing, decoration, and industry.^{1–5} However, it has some negative effects, such as poor light resistance, poor heat resistance, and dyeing behavior. To suit various purposes, study on modified polyamide fiber is needed. Furthermore, the spinning ability of polyamide resin is needed along with the development of high speed spinning technique.

To improve the spinning ability of polyamide, a dicarboxylic acid instead of acetic acid is used as chain regulator, for acetic acid has negative effects such as low boiling point, being susceptible to volatilization in high temperature, and fluctuant molecular of the end products. Chain regulators also have the function of setting the end group content of the polyamide, in particular the amino end group content, to a desired value.⁶

Degradation of polyamide fiber can be induced by sources such as sunlight, heat, oxygen, impurities, and additives resulting mainly in bond scission of the polymer chain. Due to its large surface-to-volume ratio, polyamide fiber is readily susceptible to degrading

attack. The principal effects of polyamide fiber degradation under thermo-oxidative conditions are a loss in molecular weight, increase of acid end groups, decrease of amine end groups, and color development.⁷ The negative effects of polyamide degradation can be suppressed by the addition of stabilizers.

Kaul et al.⁸ found that the dyeability of synthetic polyamides can be improved by incorporating a compound having at least one sterically hindered amino group. Breiner et al.⁹ found that a modified polyamide polymer having a high amino end group content, with more than 30% of the amino end groups being secondary or tertiary amine, dramatically improves the dye bleed performance. Matthies et al.⁶ considered a defined constant amino end group content as necessary for the production of polyamide fibers to ensure a defined uniform dyeability.

In this work, hindered piperidine amine and tertiary amine were added to the hydrolytic-polymeric system of caprolactam to improve some negatives of polyamide 6.

EXPERIMENTAL

Materials

Polymeric materials used in this study were ϵ -caprolactam supplied by Toray Industries, Inc. (Japan), compound acid (isophthalic acid and benzoic acid) supplied by Shanghai Chemical Reagent Co. (China), and hindered piperidine amine stabilizer and tertiary amine supplied by Beijing Be-lin-wei Chemical Technique Co. (China).

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

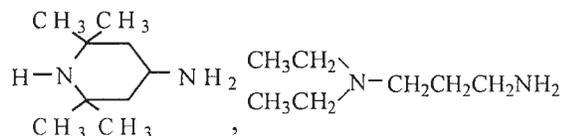


Figure 1 Formation of additives.

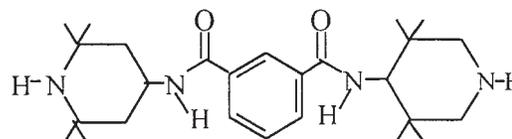


Figure 2 Formation of S-EED.

Polymer synthesis, spinning, and dyeing

Polyamide 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% by weight of water, 0.2% by weight of isophthalic acid, 0.1% by weight of benzoic acid, and from 0 to 0.25% by weight of additives, each percentage being based on caprolactam, at an ordinary pressure through the entire polymerization time for 11 to 12 h. The polymerization space was protected by N₂.

PA 6 fibers were prepared on a single-screw extruder with L/D of 24, and the spinneret size is ϕ 0.5mm \times 12. The spinning temperatures in heat zones were given as 235 ~ 240°C, 250 ~ 255°C, 250°C, 248°C, and 245°C, successively. The extruded multi-filaments were cooled by air, rolled at a speed of 330M/min, and drawn on a heat plate at 60°C with a ratio (DR) of 4.

Dyeing of PA 6 fibers involved heating the material in an aqueous bath containing 100 mL AGL acid dye (2.5g/L), 100 mL auxiliary retarding and leveling agents (0.1%), 50 mL HAc (0.1%), 50 mL NaAc (0.1%), and 700 mL H₂O. The rate of the initial temperature increased from 20 to 85°C in 45 min and was kept 30 min at 85°C. The bath pH controls the rate of dye uptake so that coloration was uniform. During the dyeing process, the aqueous bath was stirred slightly with a glass rod.

Measurements

The rheologic behavior of PA 6 resin was measured by a Rheometric Dynamic Analyzer RDA III (American Rheometric Scientific Inc) at 215°C. Tensile properties of a single fiber were measured at 20°C, 65% relative humidity by using a YG001A Single-fiber Tensile Tester (Chinese Tai-chang Instrument Co.). All the results were averages of at least 10 measurements. TGA behavior was performed using a TGA 2050 Thermal Analysis Instrument (American TA Instruments Co.) in an inert atmosphere. The amino end group content was determined by acidimetric titration with perchloric acid in 70 : 30 w/w phenol/methanol as solvent.

RESULTS AND DISCUSSION

Structure of additives

Hindered piperidine amine (HPA) is 4-Amino-2,2,6,6-tetramethylpiperidine and tertiary amine (TA) is 3-Diethylamino-1-propylamine (Fig. 1).

HPA can react with isophthalic acid and produce an organic additive N,N'-bis(2,2,6,6-tetra-methyl-4-piperidyl)-1,3-benzendicarboxamide (S-EED) (Fig. 2). This additive, which mimics the polyamide structure, significantly improves the polymer processability, long-term stability, and fiber dyeability.¹⁰

Rheologic behavior of PA 6 resin

The rheologic behavior of modified PA 6 resin and blank PA 6 resin were compared when heated up to 215°C (Fig. 3). The modified PA 6 resin was produced by putting 0.1% and 0.2% additives (PHA/HA = 1 : 1, by weight) into the polymerization reaction.

It was clearly shown that the apparent viscosity of PA 6 resin decreased with increasing shear rate, and the decreased extent became less with increasing content of additives. The molecular weight stability of the

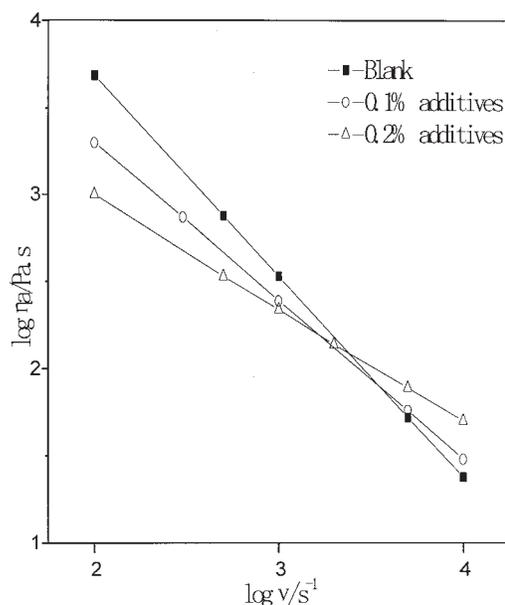


Figure 3 Shear rate versus apparent viscosity of PA 6 resins with various contents of additives.

TABLE I
Data of TGA of PA 6 Resin

	Original decompose temperature (°C)	Semi-decompose temperature (°C)	Peak value of TGA (°C)
Blank	363.87	420.60	451.76
0.2% additives (PHA/HA = 1 : 1, by weight)	367.04	421.09	450.54

polymer can be shown approximately by the variation of viscosity; the less viscosity variation of PA 6 melt clearly confirmed that the addition of 0.1–0.2% additives can improve the PA 6 melt stability. The melt stability was increased by adding a sterically hindered piperidine amine stabilizer (HPA) to the polymer. The role of the aromatic amide part in the polymer produced by reaction of HPA and isophthalic acid is to provide a high thermal stability that is necessary to withstand the severe conditions. It is well known that the relative viscosity increase of PA 6 during melt extrusion results from the condensation reaction of amino end groups and carboxylic end groups.¹¹ The role of the sterically hindered piperidine group is not only to provide for long-term stabilization properties, but also to reduce the number of end groups available for reaction and thus improve the melt stability of the PA 6 resin during the melt processing operation.

Heat resistance of PA 6 resin

TG analysis

Data TGA of PA 6 resin is documented in Table I. From TGA it was found that the additivated PA 6 resin is more stable, for the original decompose temperature has increased nearly 3°C.¹² At the same time, the semidecompose temperature and peak value of TGA almost remain the same. Due to the inherent stability of the polymer, not only melt stability was improved, but also the heat stability of the PA 6 resin.

Mechanical properties of PA 6 fibers

Again, the additivated PA 6 filament was compared with the blank one when heated up to high temperature in air for 1 h (Table II).

This treatment should simulate different kinds of downstream yarn treatments, such as heat setting.

TABLE II
Fraction Strength of PA6 Filament (CN/dtex)

	Blank	0.2% additives (PHA/HA = 1 : 1, by weight)
Original	4.55	4.60
180°C, 1 hour	1.91	3.91
190°C, 1 hour	0.91	3.68

Under this treatment, the fraction strength of additivated PA 6 filament only drops about 15 ~ 20% and the fraction strength of blank one drops to half (Table III). It is clearly confirmed that the additives can protect the mechanical properties of PA 6 fibers. It is possible to attribute the improved heat resistance of PA 6 fibers to the stabilization activity of the hindered piperidine groups and the aromatic amide part. For the role of the aromatic amide part of the molecule, it provides a high thermal stability that is necessary to withstand the severe conditions. The hindered piperidine functionality is a well-known light-stabilizing moiety, and when such piperidine groups are attached to a high molecular-weight skeleton, long-term heat resistant properties appear.¹⁰

Dyeing behavior of PA 6 fibers

The amino end group content of PA 6 resin

A defined constant amino end group content is necessary for the production of polyamide fibers to ensure a defined uniform dyeability. To study the effect of additives on the amino end group content of PA 6 resin and furthermore to affect the dyeability of PA 6 fibers, various contents of additives are added to the caprolactam hydrolytic-polymeric process.

Proportion of HPA and TA on the amino end group content of PA 6 resin

The effect of additives (various proportions of HPA and TA) on the amino end group content of PA 6 resin is shown in Table IV. The total content of additives is 0.1% by weight.

Table IV shows that the amino end group content of PA 6 resin greatly increased by adding additives

TABLE III
The Ratio of Retained Fraction Strength for PA 6 Filament (%)*

	Blank	0.2% additives (PHA/HA = 1 : 1, by weight)
180°C, 1 hour	42	85
190°C, 1 hour	20	80

* Ratio of retained fraction strength (%), = Residual fraction strength/Original fraction strength × 100%

TABLE IV
Influence of the Proportion of HPA and TA on the
Amino End Group Content of PA 6 Resin

HPA/TA(w/w)	Amino end group content (meq/kg)
Blank	26
Pure HPA	45
3 : 1	44
2 : 1	40
1 : 1	47
1 : 2	39
1 : 3	37
Pure TA	32

(HPA and/or TA) to the polymeric reaction, and the amino end group content reduced with the increasing of TA in HPA/TA except when HPA/TA was 1 : 1. This means additive HPA can have a better effect on increasing the amino end group content of the polymer than additive TA. The addition of additives increases the number of amino end groups available for reaction with the carboxylic end groups and thus increases the amino end group content of PA 6 resin. When HPA/TA was 1 : 1, the amino end group content presents the maximum value. It may for the existence of a small quantity of tertiary amine be able to have a positive effect on increasing the amino end group content of PA 6 resin.⁹

Content of additives (HPA/TA = 1 : 1, w/w) on the amino end group content of PA 6 resin

The content of additives on the amino end group content of PA 6 resin under the optimal proportion (HPA/TA = 1 : 1, W/W) are shown in Figure 4.

It was found that the amino end group content of PA 6 resin was increased sharply at first and changed steadily when the content of additive exceeded 0.1%. This means that superabundant additives have no apparent effect on increasing the amino end group content of PA 6 resin. In the polymeric system, the role of the free amino groups in additives is to react with carboxylic groups in the polymer and thereby to increase the amino end group content of PA 6 resin. So the amino end group content of polymers greatly increased with the addition of additives originally. With increasing additives, the number of polyatomic amine in the polymeric system also increased. The increase of polyatomic amine was not only to protect escaping hindered amine to keep the ability of trapping radical and decomposing hydroperoxides, but also to increase the density of the functional group so that it could greatly improve the heat resistance. The protecting of thermal oxidative degradation and the following decreasing of bond scission of the polymer chain can restrain the increase of the amine end group con-

tent.^{13,14} In the effect of two factors, the amine end group content changed steadily.

Dyeing property of PA 6 fibers

Additives impart deep dyeability to PA 6 fibers with acid dye, which is documented in Figure 5.

Figure 5 shows the dye uptake content of PA 6 fibers increased with increasing content of additives (HPA/TA = 1 : 1, W/W). This also means that PA 6 fibers show deeper and stronger shades with increasing of the amino end group content.

X Radical Diffraction of PA 6 fibers is shown in Figure 6. The crystallinities of 0.2% additives (HPA/TA = 1 : 1, W/W) PA 6 fibers and the blank one are 47.18% and 46.97%, respectively. This means the crystallinity of PA 6 fibers almost remains the same after modification. So it can't explain the improvement of dyeability by the crystal variation of PA 6 fibers. Malik et al.¹⁰ thought that the presence of free amine groups in additives has a positive effect on polyamide fiber dyeability. Kaul et al.⁸ also found that a sterically hindered amino group can improve the dyeability of synthetic polyamides. Bruce et al.¹⁵ considered the absorption of acid dye by PA 6 fibers could be described as in eq. (1).

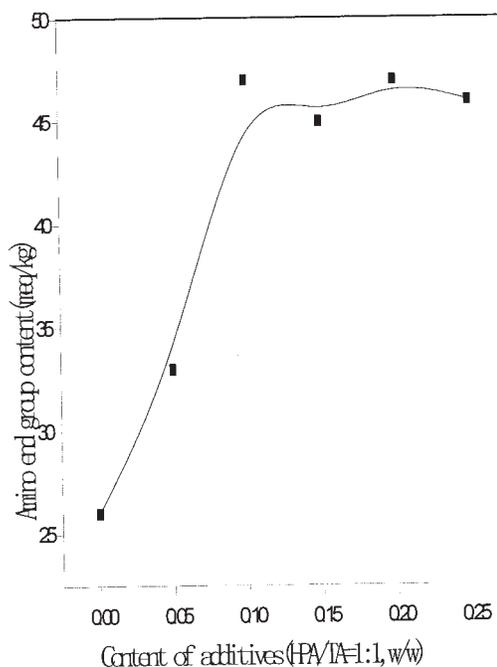
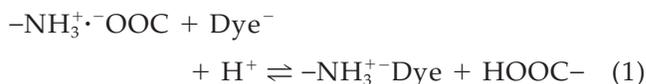


Figure 4 Relationship of the amino end group content versus the content of additives.

Eq. (1) shows that the acid dye molecule combined with the PA matrix by reacting with the amino end group. So the improvement of dyeability of PA 6 fibers with acid dyes is due to the increase of the amino end group content. The amino end group content of PA 6 resin increased from 26meq/kg to 47meq/kg after adding 0.2% additives to the polymeric system and the amino end group content of PA 6 fibers increased accordingly. So the dyeability of additivated PA 6 fibers greatly improved.

CONCLUSION

HPA and TA were multifunctional additives for PA. When they are applied to PA, they can have the following effects: first, they can improve the melt stability of PA 6 resin and provide a stable spinning production; second, they can improve the heat stability of the spun PA 6 fibers, such as the protection of mechanical properties of PA 6 fibers; third, they can enhance the dyeability of PA 6 fibers, producing such things as deeper and stronger shades.

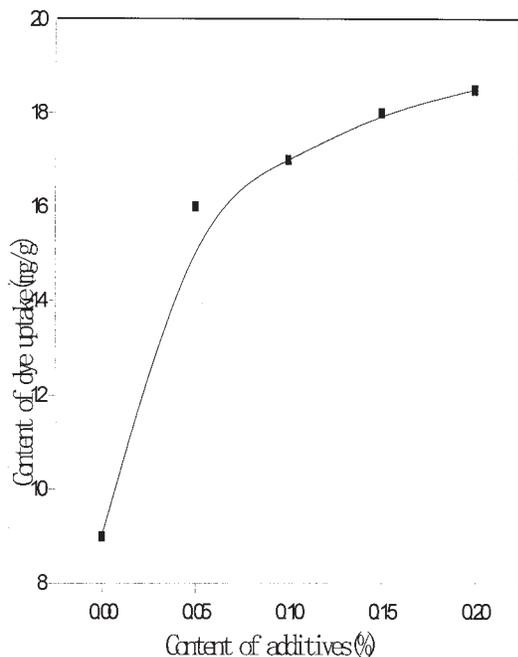


Figure 5 Influence of the content of additives on the dye uptake content of PA 6 fibers.

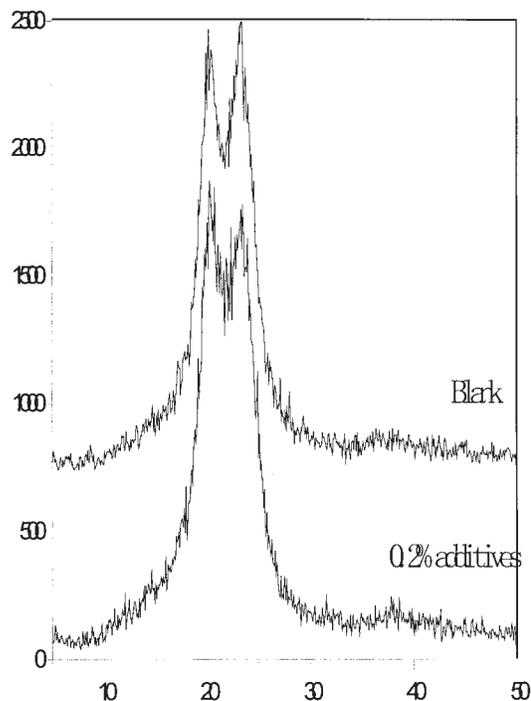


Figure 6 X Radial Diffraction of PA 6 fibers.

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