In-situ Polymerization of Rare-Earth Luminous PA6

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Summary: Luminous polycaprolactam (PA6), synthesized through in-situ polymerization, is a composite of PA6 and uniformly dispersed luminous pigment. During the polymerization, it is found that as luminous pigment was added, the time of prepolycondensation was longer and the molecular weight increased by end-group analysis. It is also indicated that there was chemical coalescence between luminous pigment and PA6 through the end-group analysis and FTIR. From the results of DSC, it is shown that the luminous pigment had large effect on the crystal structure of the luminous PA6. The crystallinity of luminous PA6 varied with the content of the luminous pigment and the heat-treated conditions. From the crystallization kinetics analysis, it is shown that the crystallization rate of the composites increased as luminous pigment added.

Keywords: crystallization behavior; luminous material; polyamides; ring-opening polymerization; structure

Introduction

Research on luminous materials began from the beginning of the 20th century. They are mainly applied for lightening, safety mark and decoration. The development of luminous materials experienced three stages. At first stage, it is sulphide luminous materials including ZnS, CaS and so on, which can give out many different colors. However, the disadvantages of low luminance, short glow time and poor chemical stability make it be used in very small range. In order to increase the glow time, the sulphide luminous material is often contained radioactive element, which would do harm to people's health and environment. In the 1960's, came the second stage. That is the luminous material doped by rare-earth ions. The glow time, luminance and chemical stability are far better than sulphide luminous materials. The rare-earth doped luminous material is also environment-friendly, which brought it great prospect. In the 1990's, came the stage of the application for rare-earth doped luminous material. More practical luminous materials were developed such as luminous plastics, luminous coat and luminous fiber.[1]

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Combined with the addvantages of polymer materials, polymer-based luminous material is of interest to increase the application of luminous pigments. During the past research work, two ways to prepare luminous polymer products have been reported. First, luminous pigments were blended with the polymer melts or polymer solutions, which is a common and simple method to prepare polymer composites. Some luminous polymer products have been prepared such as luminous PVA, luminous PMMA and luminous viscose fiber.[2] However, there is such a fatal weakness of this method that it is difficult for the luminous pigments to disperse in the polymers, which results to the lower lumanance and poor mechanical properties of the final products. In our preceding work, we take the measure to improve the dispersibility of luminous pigments in polymer melts by surface treatment.[3] Second, luminous pigments were doped with the monomer before polymerization. The luminous pigments can disperse well in the low-viscosity monomers with the strong stir in the polymerization process, which is helpful to improve the processing and machanical properties. Nevertheless, the special chemical structure of the rare-earth element often leads to high reactivity of the luminous pigments, which has large effect on the polymerization.[4] For instance, when the rare earth doped luminous pigments were added in the process of polyester, it was found that the molecular weight of polyester was much lower than that of the common polyester.

Through our work, we find that it is an effective way to prepare luminous PA6 with satisfied molecular weight by adding luminous pigments ($SrAl_2O_4{\cdot}Eu^{2+},Dy^{3+}$) into the monomer before polymerization. However, the polymerization and the structure of the PA6 were influenced by the luminous pigments. Therefore, the polymerization, the molecular weight, the chemical structure, the crystallization behavior as well as the luminous properties of the PA6 composites were investigated in detail.

Experimental Part

Materials

The luminous pigment, $SrAl_2O_4{\cdot}Eu^{2+},Dy^{3+}$, used in this experiment is a laminated photoluminescence material with the particle size of 20μm supplied by Shanghai Yuelong New Materials Co., Ltd. Caprolactam, ω-aminolauric acid, adipic acid and distilled water were commercially available.

Polymerization

The luminous pigment, $SrAl_2O_4{\cdot}Eu^{2+},Dy^{3+}$, Caprolactam, ω-aminolauric acid, adipic acid and distilled water were mixed in a 500ml three-necked separable flask in N_2 atmosphere under normal presure. The mixture was heated and stirred at 140℃ for 30min, and then heated at 250℃ for more than 5 hours. After polymerization, the products were washed with water at 80℃ to remove monomers and then dried at 90 °C under vaccum.

Measurements

The molecular weight of luminous PA6 was determined by end-group analysis[5], in which both amino end groups (NH_2) and carboxyl end groups(COOH) of PA6 were analyzed through a ZDJ-4A chemical electric displacement titrimeter from Shanghai Precise Instruments, Ltd.

FTIR curves were obtained using Nicolet NEXUS-670 spectrometer with the distinguishing rate of 2 cm^{-1}.

The DSC curves were recorded with a DSC822 instrument from Mettler Toledo Company. The samples were heated at the rate of 10℃/min from room temperature to 250℃, and then cooled and heated again at the same rate.[6,7]

The DLI (depolarized light intensity) data were obtained from a GIY-III instrument to analysis the crystallization kinetics of luminous PA6. The samples were melted at 250℃ and then tested at the temperature from 100~180℃.

Result and Discussion

Polymerization

In the bulk polymerization of PA6, the monomers were slowly heated from 140℃ to 250℃and one hour later it is found that the melts became viscous. However, this phenomenon can not be found until it was kept the temperature at 250℃ for two hours or so when luminous pigment was added. And the contents of luminous pigments larger, the time longer. The relationship of luminous pigment content and the molecular weight is shown in Table 1. An increasing trend can be found as the content of luminous pigment increased.

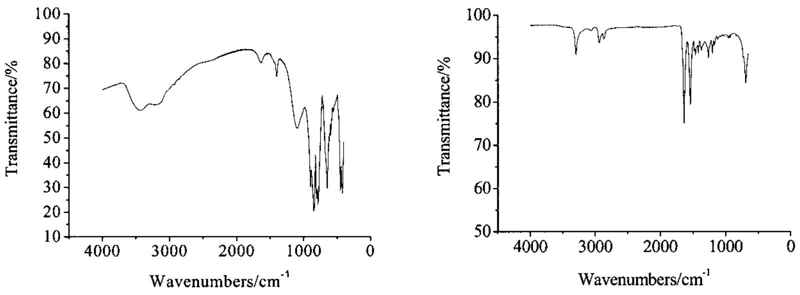
Table 1. Molecular Weight of PA6 and luminous PA6 from end-group analysis.

Samples	Content of $SrAl_2O_4{\cdot}Eu^{2+},Dy^{3+}$ %	C_{NH2} 10^{-5} mol/g	C_{COOH} 10^{-5}mol/g	Mn
PA6	0	5.010	27.62	7642.3
PA6/G-5	5	4.139	21.00	9253.20
PA6/G-10	10	4.537	19.46	11870.2
PA6/G-20	20	4.922	17.78	12995.4

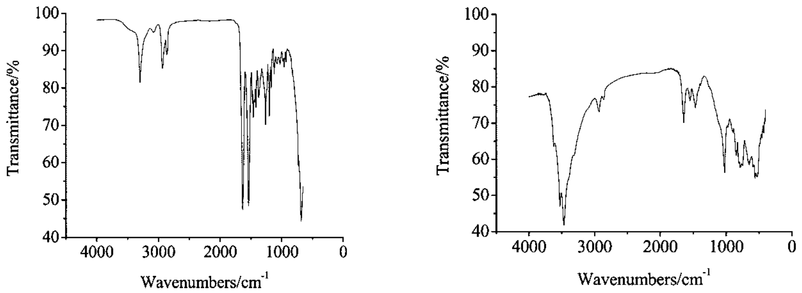
From Table1, it is also found that the end group COOH in luminous PA6 decreased relatively compared with NH_2. It can be deduced that some end groups COOH had chemical interaction with the luminous pigments. It can be verified further from the FTIR spectra. In Figure1(c), it displays stronger peaks in 3400 cm^{-1}, 2940 cm^{-1}, 2880 cm^{-1}, 1650cm^{-1} and 1570 cm^{-1} with the luminous pigment added. To learn whether there is interaction between PA6 and luminous pigments, luminous PA6 were solved in methyl acid and then extracted. From the Figure1(d) of extracted luminous pigment, peaks like –NH- (1570cm^{-1}), C=O(1650cm^{-1}), -CH-(2880 cm^{-1}) and -CH_2- (2940 cm^{-1}) can be easily found, while these were not seen from pure luminous pigment in Figure 1(a). It suggests that there is chemical coalescence between luminous pigment and PA6.

Crystal structure

Polyamide is a semi-crystal polymer with various crystal forms at different conditions. For PA6, α crystal is the typical and stable crystal form. In addition, γ crystal appears under the special conditions and it is not so stable as α crystal. At the same polymerization conditions, the luminous pigments have large effect on the crystal structure and crystallinity of PA6. In Figure2(a), two melting peaks can be found in luminous PA6. It suggested the appearance of γ crystal (at lower temperature) besides α crystal (at higher temperature) with the luminous pigments added in PA6. It indicates that luminous pigment has heterogeneous nucleation to PA6 in the polymerization process. However, in cooling and reheating process, these phenomena can not be found. The γ crystal disappeared due to the slowly cooling and reheating.



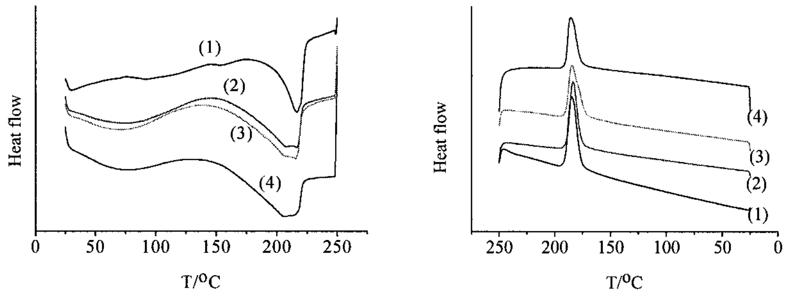
(a) Luminous pigment (b) PA6



(c) PA6/G-5 (d) Extracted luminous pigment

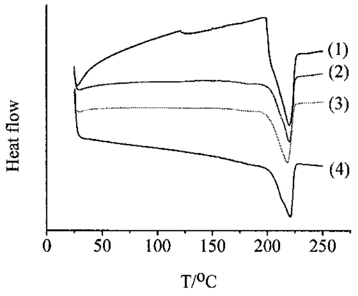
Figure 1. FTIR spectra of luminous PA6 and luminous pigments.

The crystallinity of luminous PA6 was calculated according to the heat flow from DSC. From Table 2, it is show that the crystallinity of was larger than that of pure PA6 when the samples were heated at the rate of 10℃/min. However, when the heated samples were cooled and heated again, the crystallinity decreased with increasing the content of luminous pigments. The variation of the crystallinity is also caused by the change of crystal form. Actually, there was much more γ crystal in the luminous PA6, which leaded to the increase of crystallinity in the 1st heating process. Meanwhile, the decrease of crystallinity resulted from the disappearance of γ crystal in the cooling and 2nd the heating process.



(a) 1st heating

(b) Cooling



(c) 2nd heating

Figure 2. DSC curves of luminou PA6: (1) PA6; (2) PA6/G-5; (3) PA6/G-10; (4) PA6/G-20.

Table 2. Cystallinity of luminous PA6 from DSC.

Samples	Xc/%		
	1st heating	Cooling	2nd heating
PA6	33.84	32.50	37.33
PA6/G-5	40.47	27.85	21.29
PA6/G-10	46.23	24.43	19.06
PA6/G-20	39.48	22.90	16.67

Crystallization Kinetics

The crystallization kinetics of luminous PA6 were studied through DLI (depolarized light intensity). It is found in Figure 3 that the crystallinity rate ($1/t_{1/2}$) decreased as the content of luminous pigments was lower while the crystallinity rate ($1/t_{1/2}$) increased as the content of luminous pigments was higher than 10%. The luminous pigments have special reactivity and special light properties, so the effect of luminous pigments on the DLI data is complex and we will discuss it in other papers.

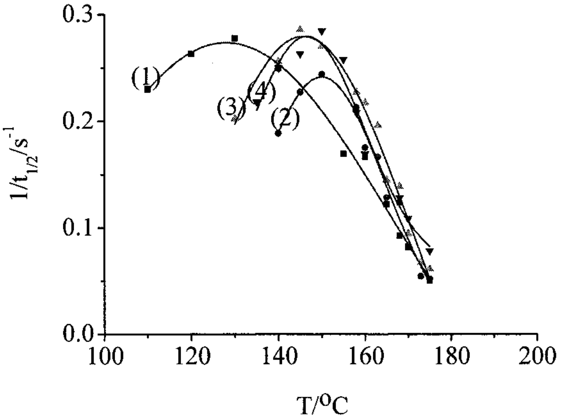


Figure 3. Crystallization Kinetics curves of luminous PA6: (1) PA6; (2) PA6/G-5; (3) PA6/G-10; (4) PA6/G-20.

Luminance

From Figure 4, it is obvious that luminance become largerer as increasing the content of luminous pigment. Especially, the glow time is longer than 1 hour and the luminance is larger than 1.0 mcd/m^2. Therefore, the luminous PA6 is a satisfied material for application.

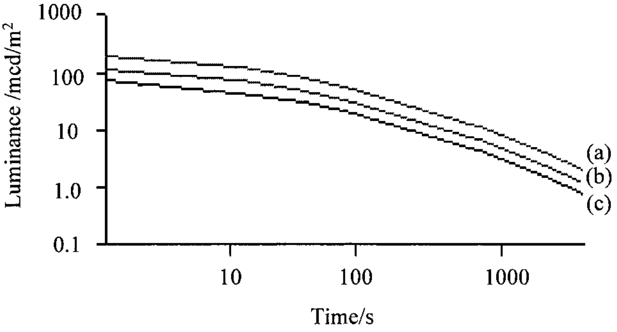


Figure 4. Luminance of luminous PA6.

Conclusion

It is an effective way to prepare luminous PA6 by in-situ polymerization, while the pre-condensation time of luminous PA6 became longer and the molecular weight higher. From the end-group analysis and FTIR spectra, it is duced that there is chemical coalescence between luminous pigment and PA6, which is helpful to the disperse of luminous pigments in PA6 matrix. Under the same conditions, it is easy to form γ crystal in luminous PA6, while it is not found in pure PA6. Luminous pigments play the role of nucleating agent in the crystallization of PA6. Besides, crystallinity of luminous PA6 increased as heated, and decreased while cooling and reheating from DSC. The synthesized luminous PA6 is a satisfied material for application and with the increase of luminous pigments, the luminance of luminous PA6 increased.

Acknowledgements

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[1] C. Li , J. Su, J. Qiu, *Chinese Journal of Luninescence* **2003**, *24*, 19.
[2] X. Ma, *Chinese Journal of Rare Metals* **2000**, *24*, 305.
[3] J. Wang, Y. Zhang, H. Wang, *Chinese Material Review* **2003**, *6*, 28.
[4] M. Tang, *OME Information* **2003**, *2*, 8.
[5] A. Usuki, Y. Kojima, *J. Mater. Res.* **1993**, *8*, 1179.
[6] Y. Kojima, A. Usuki, *Journal of Polymer Science, Part A, Polymer Chemical* **1993**, *31*, 1755.
[7] Q.Li, Z. Zhao, Y. Ou, Z. Qi, F.Wang, *Gao Fenzi Xuebao* **1997**, *2*, 188.