Research progress of high temperature resistant nylon 10T

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Abstract: Researches about synthesis and modification of nylon 10T (PA10T) in domestic universities and scientific research institutions are reviewed in this paper. The results show that, due to the different performance requirements, PA10T is studied from the co-polymerization, blending modification and filling modification of these three aspects. Meanwhile, the existing problems are analyzed and the development prospect of PA10T is predicted.

Key words: PA10T; high temperature resistant nylon; material modification

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0 Introduction

In recent years, with the requirements of polyamide plastic in the fields of automobile, electronic appliance, aerospace, war industry and chemical industry, the market demand for polyamide with typical excellent properties of nylon and high heat-resistant temperature is rapidly expanding[1]. In view of the current use of heat resistant polyamide, processing and production costs and other aspects, there are still many deficiencies. And production technology of nylon 6T (PA6T) and nylon 9T (PA9T) is only controlled by a few large foreign companies. Researches and development of polyamide with independent intellectual property rights, low cost, short synthesis route, long carbon chain, new type environmentally-friendly technology, low water absorption rate[2], high strength, high heat resistance and good processing properties, have very important significance and value in academic and industrial applications.

Compared with long carbon chain high temperature resistant nylon and all aromatic high temperature resistant nylon, semi-aromatic high temperature nylon[3] not only has low water absorption, but also has dimensional stability and heat resistance. PA10T is a homopolymer of 1, 4-phthalic acid and 1, 10-diaminodecane, the basic physical and chemical properties are comparable to PA9T, but the melting point is higher than the PA9T. Soldering temperature resistant of PA10T is 270 ℃, which is equivalent to PA9T and better than PA6T, so PA10T is very suitable for surface mount technology process. In addition, PA10T molecular chain contains benzene ring and long 1, 10-diaminodecane flexible chain, so the polymer molecules have moderate mobility. Besides, it has a high crystallization rate, crystallization degree and excellent injection molding performance. Finally, from the point of view of the raw materials of synthesis PA10T, 1, 10-diaminodecane is from castor, which has a wide range of sources with low prices and renewablility. And production process of 1, 10-diaminodecane is relatively simple and the production cost is relatively low, which greatly reduce the PA10T production costs.

However, the melting point of pure PA10T is 319 ℃ and close to its decomposition temperature (350 ℃), which makes PA10T easily decomposed during the processing. Therefore, the polyamide resin can be modified by chemical or physical way to broaden the processing window and improve the comprehensive performance of the polyamide, such as co-polymerization, blending modification, filling modification and so on[4]. This paper will elaborate on the relevant research of domestic universities and research institutions on the synthesis and

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modification of PA10T.

1 Co-polymerization

In 2008，Cao et al.[5] from Sun Yat-Sen University，used 1，4-phthalic acid and 1，10-diaminodecane through salt formation，prepolymerization and solid phase viscosity to synthesize PA10T with high intrinsic viscosity (1.43 dL/g). Then PA10T was modified with 1，6-hexanediamine and 1，6-adipic acid (PA10T/66)，1，10-diaminodecane and 1，10-sebacic acid (PA10T/1010)，1，10-diaminodecane and 1，3-phthalic acid (PA10T/10I). Results show that the melting point and the melting enthalpy of PA10T are obviously lower when PA10T is modified. When the mole fraction of PA10T in PA10T co-polymer is 85%，the melting point and crystallization temperature of PA10T/66 are the lowest. Due to the higher aromatic content，PA10T/10I melting point and crystallization temperature are higher. PA10T/1010 has higher heat of fusion，indicating that PA10T/1010 is easier to crystallize with a high crystallization degree.

Table 1 Thermal properties of PA10T co-polymers

Co-polymer	T_m(℃)	T_c(℃)	$\triangle H_m$(J/g)
PA10	319.1	286.4	72.2
PA10T/66(X(PA10T)=85%)	281.9	250.7	46.5
PA10T/1010(X(PA10T)=85%)	285.8	265.2	59.4
PA10T/10I(X(PA10T)=85%)	288.7	267.2	45.2

The experimental results show that the addition of co-monomer can significantly reduce the melting point，crystallization temperature and heat of fusion，thus improving the molding ability. At present，PA10T and its co-polymers are mostly synthesized by three-step synthesis that is salt formation，prepolymerization and solid-phase thickening at last. Although the product performance is pretty good by this synthesis process，there are many process steps，long polymerization cycle，high production costs，which is not conducive to continuous industrial production. And in the high temperature melting conditions，there are many problems in the synthesis process，such as the high viscosity，difficult to discharge，easy oxidation of air，agglomerate formation in reducing the temperature，insufficient reaction of prepolymer and so on.

In 2009，Wang et al.[6] from South China University of Technology，synthesized the high molecular weight PA10T (intrinsic viscosity $[\eta]=$ 1.73 dL/g) by salt formation，prepolymerization and solid phase polymerization，with 1，4-terephthalic acid and 1，10-diaminodecane as raw materials. The thermal degradation and thermal degradation kinetics of PA10T were studied by thermal gravity analysis and differential thermal gravity. The results show that the thermal decomposition of PA10T is one step degradation，the initial equilibrium degradation temperature is 435.3 ℃，and the equilibrium degradation temperature is 470.7 ℃. Under the maximum degradation rate，the equilibrium degradation temperature is 459.5 ℃. In the same year，Zhang et al.[7] from Zhuzhou New Materials Co.，Ltd. analyzed 31 kinds of cleavage products of PA10T by thermal cleavage gas chromatography and mass spectrometry，which mainly contains benzonitrile，terephthalonitrile，benzoic acid，N-alkyl benzoate olefins，diolefins，alkanes，alkyl nitriles and other derivatives of benzene. The main chain of the polymer containing benzene ring is not easy to break down，and chain break occurs mainly in the C-N bond and benzene ring and amide linked to the bond.

The above two experiments put forward the thermal cracking mechanism of PA10T by different methods，which provide a theoretical basis for better control of its forming conditions and application scope.

In 2012，Shi[8] from Southwest University of Science and Technology，used 1，4-terephthalic acid，1，3-isophthalic acid and 1，10-diaminodecane to synthesize low molecular weight PA10T prepolymer by suspension polymerization，and then solid phase thickening technique was used to prepare the high molecular weight PA10T and its co-polymer resin (PA10T/10I). The effects of polymerization conditions on the polymerization products were investigated，and the effects of water absorption and thermal stability on the mechanical properties were also researched. The results show that the amount of displacement has an effect on the degree of polymerization. The prepolymer is solidified，and its relative viscosity can reach 2.1—2.3 at 260 ℃；the relative viscosity can reach 2.1—2.7 at 270 ℃. Infrared spectroscopy found that the prepolymerized product contained characteristic absorption peaks of 10T salt and PA10T，indicating that the polymerization reaction is carried out step by step. Thermal analysis shows that PA10T in the annealing conditions can form an imperfect crystallization，and water absorption has not impact on the mechanical performance.

The suspension polymerization method used in this experiment has great limitations and is very unfavorable to continuous industrial production. However, it is undeniable that the contribution of the experiment to the research progress of PA10T. Through this experiment, it is understood that the effect of polymerization conditions on the polymerization products and the influence of the water absorption and thermal stability of the polymerization products on the mechanical properties.

In 2012, Liu et al.[9-11] from North University of China, synthesized PA10/11 co-polymerized nylon by high temperature melting poly-condensation with 1, 10-decanediamine, 1, 4-terephthalic acid and 11-aminoundecanoic acid as monomers and water as solvent. The results show that the high temperature performance of PA10T/11 co-polymerized nylon is excellent, the initial decomposition temperature of PA10T/11 co-polymer is 385. 2 ℃, and the thermal decomposition temperature is 439. 2 ℃ and the melting point is 281. 64 ℃ when the mass fraction of PA10T is 70%. In the following year, the optimum process conditions were determined by studying the effect of prepolymerization and melting thickening reaction on the intrinsic viscosity of the product. The heat resistance, mechanical properties and non-isothermal crystallization behavior of PA10T/11 copolyamides were tested and studied by some characterization methods, such as differential scanning calorimetry, thermal gravity analysis and dynamic mechanical testing.

The first thing to emphasize is that the measurement method used in this experiment, one-step melt polymerization, is the development and innovation of the previous three-step process of salt formation, prepolymerization and solid phase viscosity. Compared with other polymerization methods, the process steps are fewer, the polymerization cycle is shorter, the production efficiency is higher and the production cost is lower. Second, the performance of the product under the synthetic process conditions meets the application requirements. That is to say, it creates the conditions for continuous industrial production in the future.

In 2013, Ma et al.[12] from Zhengzhou University, used terephthaloyl chloride and 1, 10-diaminodecane through the interface polymerization method to synthesize PA10T, and studied the influence of interfacial polymerization conditions on the molecular weight of PA10T polymer. The molecular weight of PA10T polymerization product obtained by interfacial polymerization was further enhanced by solid phase polycondensation. So the relative viscosity of PA10T increased from 1. 32 to 1. 96. The relationship between the polymerization conditions and the melting point of PA10T was analyzed by differential scanning calorimetry analysis.

The main process of polyamide synthesis can be divided into the melt polycondensation, solid phase polycondensation, solution polycondensation, interfacial polycondensation and polyester polycondensation. The melt polycondensation method can be used alone, and the other four methods need to be used in combination to get high viscosity products.

2 Blending modification

In 2014, Yi et al.[13-14] from South China University of Technology, prepared the PA10T/PA6T/66 alloy by using a twin-screw extruder. And the change of the melting crystallization behavior and the fluidity of the alloy in different proportions were characterized by differential scanning calorimetry, infrared spectrum analysis and capillary rheometer. The results show that the PA6T/66 destroy the regularity of the PA10T molecular chain due to the amide exchange reaction, which leads to the melting point and the crystallization temperature decrease. With the increase of PA6T/66, the shear viscosity decreases. In the following year, the effects of different screw combinations and feeding methods on the dispersibility of spherical alumina in PA10T filled materials were investigated. The results show that after adding alumina to the extruder, reinforcing the screw shear does not have much help with the dispersion of alumina, the distribution of multiple concentrated shear blocks is properly dispersed, and the transmission speed of alumina is increased after feeding the extruder, which reduces the melt pressure and is more favorable for the dispersion of alumina. The study also finds that the addition of alumina and PA10T prepolymer powder to the screw also contributes to the dispersion of alumina. And the better the dispersion of alumina, the better the mechanical properties of the material, the higher the melt viscosity.

In 2016, Song et al.[15-16] from Guizhou University, prepared long glass fiber reinforced nylon 10T (LGF/PA10T) composites by melt blending method. The effects of different thermal aging ages on the static and dynamic mechanical properties of LGF/PA10T composites were investigated by differential scanning calorimetry, dynamic mechanical analysis, scanning electron microscope and mechanical properties. The results show that in the early stage of aging, the microcracking occurs between the PA10T molecular chains, and the rigidity of the materials increases slightly, but the molecular chain ruptures and the decrease of the molecular weight plays a leading role during the whole aging process. With the increase of aging time, the interfacial bonding between glass fiber and PA10T matrix is weakened, the glass transition temperature and damping performance decrease, and the tensile strength, bending strength and notched impact strength of the composites decrease obviously. The calculation results of activation energy show that the thermal oxygen aging can change the activity capacity of the PA10T molecular chain and reduce the thermal stability of the LGF/PA10T composite.

PA10T blending modification process is simple. The blending materials are of low cost, good performance and other advantages, which could satisfy people's requirements for the materials with diversification, high performance and functionalization. It is the fastest growing in all engineering plastics alloy.

3 Filling modification

In 2011, Mai et al.[17] from Blonde technology Co. Ltd, prepared the graphite/PA10T and the graphene/PA10T thermal conductive composites by the twin-screw extruder, and the effects of graphite and graphene on the mechanical properties and thermal conductivity of the composites were studied. It is found that the tensile strength and the notched impact strength of the cantilever beam of the thermal conductive composite increase first and then decrease with the increase of the thermal filler content, while the flexural modulus and the thermal conductivity increase with the increase of the thermal filler content. Compared with graphite, adding a smaller amount of graphene can significantly improve the mechanical properties and thermal conductivity of composite materials.

Yi et al.[18-20] used a phosphinic acid metal salt flame retardant (FRP) for PA10T flame retardant modification. The flame retardant of the system under different flame retardants was investigated by vertical combustion method. The limit oxygen index of the system under different flame retardants was tested by the limit oxygen index instrument, and scanning electron microscopy analysis of the residual carbon was carried out. The results show that with the increase of the amount of FRP, the amount of residual carbon increases after combustion, the carbon layer becomes denser and easier to pass the UL94 Flame Retardancy Test. In the following year, the influence of flame retardant content on the mechanical properties of modified PA10T was studied, and the thermal degradation behavior of PA10T with different flame retardants content was analyzed. The results show that the tensile strength of flame retardant PA10T material increases first and then decreases with the increase of flame retardant content.

Although the comprehensive performance of PA10T is excellent, taking the actual application into account, there may be a lot of shortcomings such as thermal conductivity and flame resistance. Kingfa Technology Co., Ltd. has done an in-depth study of these two kinds of properties and solved the problem by the filling modification. Filling modification not only reduces costs, but also simplifies the process. The Blonde Technology Co., Ltd. chose high thermal conductivity of graphite and graphene. And halogen-free flame retardant is chosed, which is a new type of flame retardant and can be the future development trend. It can be seen that the Blonde Technology Co., Ltd. is far sighted in the filling modification.

4 Other performance studies

In 2009, Luo[21] from Blonde Technology Co., Ltd., studied the rheological behavior of PA10T by Haake high pressure capillary rheometer. They obtained the rheological curves of melt apparent viscosity and temperature, shear stress, shear rate as well as the relationship between shear stress and shear rate. The results show that PA10T is a non-Newtonian pseudo-plastic fluid, and the relationship between apparent viscosity and temperature is in accordance with the Arrhenius equation. With the increase of temperature, the non-Newtonian index becomes larger. When the shear rate is 199.8—

3 000 s^{-1}, the temperature has a greater influence on the viscosity. That is to say to reduce viscosity, raising the temperature is much more obvious than increasing the shear stress.

The experiment, on the one hand, studied the processing performance of PA10, on the other hand, provided a theoretical basis for ensuring its reasonable processing technology and product quality.

In 2012, Long et al.[22] from Blonde Technology Co., Ltd., used dynamic head-space sampling—gas chromatography and mass spectrometry method to analyze PA10T. The results show that there are 15 kinds of volatile components in PA10T resin at the processing temperature of 320 ℃, which mainly contains of aldehydes, hydrocarbons, nitriles, aromatic ring substances and a small amount of nitrogen-containing ring material.

This method is simpler, faster, solvent free than other extraction techniques[23], and has good selectivity and high sensitivity to target detectors. It can be used as auxiliary testing for resin production quality monitoring.

In 2014, Wen et al.[24] from the Northeastern University, studied kinetics of isothermal and non-isothermal crystallization of PA10T in detail by differential scanning calorimetry. The isothermal crystallization kinetics of PA10T is described by Avrami equation. It is found that the growth pattern of PA10T is two-dimensional growth under the selected crystallization conditions. The nucleation mode is homogeneous nucleation and the Avrami index is 2, and the crystallization activation energy is 302.32 kJ/mol. After studying the non-isothermal crystallization kinetics of PA10T, it is found that with the increase of the cooling rate, the crystallization peak temperature decreases, the crystallization degree and the crystallization enthalpy increase and the crystallization rate increases significantly. The non-isothermal crystallization kinetics were described by the Mo equation. The cooling rate value ($F(T)$) increases with the increase of the relative crystallization degree, the α value is kept at 1.6, and the non-isothermal crystallization activation energy is 338.56 kJ/mol.

In general, the crystalline structure and morphology of the semi-crystalline polymer produced by the melt-cooling process ultimately affect the macroscopic properties of the polymer, so it is very important to study the crystallization kinetics of the polymer, both from the theoretical and the practical point of view.

5 Conclusion

At present, China's high temperature nylon engineering plastics rely heavily on imports, which greatly restricts China's continuous development of automobile, electronic appliances, defense industry and other industries. While the domestic relevant research for PA10T has been carried out more than ten years, it has been unable to have industrial results, which is maybe for the lack of a continuous synthetic methods for industrial production.

Domestic research on PA10T is more than ten years, from the production process to product synthesis, and then to product quality testing, the technology has been quite mature. The main question now is how to migrate PA10T from the laboratory to the factory in order to achieve mass and continuous industrial production. And, one-step melting method proposed by North University of China has great potential, for its less synthetic steps, short cycle, high efficiency and low cost. Considering that the processing window of PA10T is too narrow, the processing temperature range of the material will be expanded by adding the co-monomer. In addition, due to cost and environmental reasons, the choice of co-monomer mainly contains 1,3-isophthalic acid, 11-aminoundecanoic acid, the final product are PA10T/11 and PA10T/10I. The molecular structure of 1,3-isophthalic acid is asymmetric, so it is nor easy to crystallize, which makes the nylon toughness increase and the melting point reduce. And low melting point is easier to process. 11-aminoundecanoic acid and 1, 10-diaminodecane are also abstracted from castor bean.

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耐高温尼龙 10T 的研究进展

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摘　要： 本文按时间顺序综述了国内有关高校及科研机构对聚对苯二甲酸癸二胺(PA10T)的合成及改性研究情况。结果表明：出于对某种特定性能的需求，研究主要从共聚改性、共混改性及填充改性三个方面着手。分析了研究存在的问题，并对 PA10T 的发展前景进行了分析和展望。

关键词： PA10T；耐高温尼龙；材料改性

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