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Nylon 66/nano CaCO3 composites

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ABSTRACT

The nylon 66/nano-CaCO3 composites were prepared by melt blending on a twin-screw extruder. Scanning electron microscopy (SEM), polarized light microscopy (PLM), thermal loss (TGA) and differential scanning calorimetry (DSC) The effects of nanometer calcium carbonate on the polycrystalline behavior and thermal properties of nylon 66/nano CaCO3 composites were investigated. The results show that the nanometer calcium carbonate particles are dispersed in the nylon 66 matrix and exist in the form of aggregates. The nanometer calcium carbonate has the effect of heterogeneous nucleation, which can reduce the size of the spherules. The decomposition temperature of the nylon 66 is 400 °C, the addition of nano-CaCO3 to reduce the decomposition temperature. At the same time, DSC test showed that the β-crystalline form in the material reduced the melting temperature of the material. The addition of nano-CaCO3 in the nylon 66 matrix resulted in the decrease of the crystallization temperature and the increase of the half-height width of the endothermic peak. The lower the crystallization temperature, the wider the crystallization temperature range.

KEYWORDS: nanometer calcium carbonate; nylon 66; crystallization; cooling rate

1. Introduction

1.1. Nylon 66

Nylon 66 (PA-66) is the most important varieties of nylon, the output of about 70% of nylon engineering plastics [1]. Nylon 66 is made from hex methylene diamine and adipic acid, nylon is a semi-crystalline - crystalline material, PA66 PA series is the highest mechanical strength, the most widely used varieties, because of its high crystallinity, so its rigidity, heat resistance are higher. As the nylon 66 amorphous part of the amide is easy to combine with water molecules, nylon 66 at room temperature, the higher water absorption. Compared with the general plastic, nylon 66 toughness, excellent wear resistance, friction noise is small, in addition, nylon 66 on hydrocarbon solvents, especially gasoline and lubricants are more resistant. Nylon 66 has a low viscosity and is temperature sensitive and can therefore be used to process very thin components, but to strictly control the temperature. Due to the presence of the amide polar groups, the nylon 66 is extremely water-absorbent and must be dried before the product to take into account the impact of moisture absorption; nylon 66 molding process is good, can be used for extrusion, blow molding, injection molding, casting molding.

The structure of nylon 66 is shown in Figure 1-1:

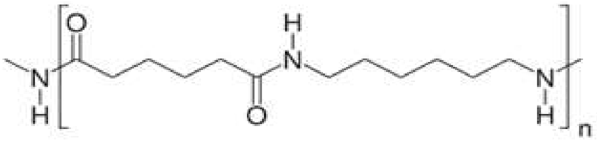

Figure 1-1 Structure of nylon 66

The nylon 66 is easily crystallized by hydrogen bonding between hydrogen and oxygen. The crystals of nylon 66 are shown in Figure 1-2 below:

Figure 1-2 Nylon 66 crystal structure

The modification of nylon can be divided into physical modification and chemical modification. The main methods of chemical modification are: graft copolymerization and functionalization of polymer. The main methods of physical modification are: blending, sex, etc. [2]. In the plastic processing process generally use physical modification. Nylon 66 can be reinforced in nylon 66 filled with fiber reinforced materials, to maintain its excellent performance on the basis of the heat resistance, chemical stability and mechanical properties improved [3]; nylon 66 by the capacity of toughening (MAH) grafted PP, PE, will increase the impact strength of the material, and grafted elastomer EPDM, POE due to its own impact performance, the impact of the impact of nylon 66 more and the toughening agent is also a non-polar polymer, the water absorption is small, and the polar group of the toughening agent after grafting is the same as that of the nylon 66 The reaction of the group results in a decrease in the water absorption of the composite.

1.2. Nanometer calcium carbonate

Nano-calcium carbonate is a new type of nanomaterials that are used in many fields and have been industrialized. Nano-calcium carbonate and other nano-materials compared to the raw materials easy to obtain, high performance, low cost, non-toxic and tasteless; compared with ordinary calcium carbonate, small particle size, large surface area, high whiteness, high activation rate, Structure and so on. At present, the application technology of nano-calcium carbonate is the most mature in the plastics industry. The nanometer calcium carbonate has four nano-effects (quantum size effect, small size effect, surface effect and macroscopic quantum tunneling effect), which can improve the mechanical properties and improve the thermal stability and reduce costs. China's plastics, rubber, coatings and other industries led to the rapid development of nano-calcium carbonate, the increasing demand for him, therefore, nano-calcium carbonate has a strong market competitiveness.

1.3. Preparation of polymer/nano CaCO3 composites

Polymer nanocomposites are prepared by a variety of methods, including intercalation, blending, in situ polymerization, sol-gel, and blending in this experiment.

1.3.1 Interlayer insertion method

Interlayer insertion method is an important method to prepare polymer nanocomposites, which is the hotspot of current research. Interlayer insertion method is the use of inorganic nano-particles layered structure, the organic polymer dispersed into the inorganic layer, the inorganic material was stripped into a nano-scale layered structure, evenly dispersed in the nylon matrix and made nylon inorganic nano composites. The method can be divided into four kinds: melt intercalation polymerization, solution intercalation polymerization, polymer melting intercalation, polymer solution intercalation. The melting intercalation polymerization method is the most widely used. The intercalation method is rich in raw materials, low price, and the nanoparticles are ordered in the material. Therefore, the obtained materials have anisotropy, high interfacial strength, good barrier property and good dispersibility, but have some claim. This method also has drawbacks, such as the uneven dispersion of the catalyst between the layers, nano-minerals will reduce the catalyst activity, which will have an impact on the performance of composite materials.

1.3.2 Blending method

Blending is the easiest way to prepare polymer nanocomposites, similar to polymer blending. Blending can be divided into four methods: solution blending, emulsion blending, melt blending, mechanical blending, wherein the melt blending is a method in which the polymer is blended with the nanoparticles in a molten state to produce a composite material, the application is more extensive. Melt blending less energy consumption; no use of organic solvents, no harm to the environment and reduce waste; can be used conventional processing technology for production, simple process, easy to industrial; cannot be used in situ polymerization of the polymer can be used blending the however, the melt blending has some limitations. If the decomposition temperature of the polymer is lower than the melting point, this method cannot be used and the particles are easy to agglomerate during heating. Therefore, attention should be paid to the surface treatment with the coupling agent and the dispersant.

1.3.3 In situ polymerization method

In situ polymerization [16] is a method in which inorganic nanoparticles are uniformly dispersed in a polymer monomer and a suitable catalyst is initiated to initiate monomer polymerization. This method is suitable for the preparation of most polymer nanocomposites and maintains excellent properties of the material. Compared with other preparation methods, the reaction conditions of the method are mild and there is no hot working, so that the nano-particles in the material are dispersed uniformly and the performance is not damaged. In situ polymerization can be used to prepare reinforced polymer nanocomposites, but the use of certain limitations.

1.3.4 Sol-gel method

Sol-gel method is the most commonly used and mature method for preparing nylon inorganic nanocomposites. The principle of this method is colloidal chemical method, that is, the precursor is dispersed in a certain organic solvent to form a homogeneous solution, by adding acid, alkali, or neutral salt catalyzed hydrolysis of the formation of sol, and then by heating or solvent evaporation the sol is converted to a gel. The preparation method is simple and easy to operate, and the surface of the material can be controlled by controlling the process of hydrolysis of the precursor to make the material excellent. However, in the process of drying the gel, the small molecules in the material are easily volatilized, resulting in the generation of shrinkage stress, so that the performance of the composite material.

The purpose and significance of this research

With the development of china's automobile, electronics, aviation and other industries, the requirements of the material performance are getting higher and higher, the development of high-performance PA66 new varieties become the focus of research. The research on nylon nanocomposites has achieved great success, especially in the case of nylon 6/clay nanocomposites. On the use of nano-SiO2, nano-montmorillonite PA66 reported a lot, but for the use of nano-CaCO3 modified PA66 reported very little. Nano-CaCO3 with other nano-materials and ordinary calcium carbonate does not have excellent performance, if the successful preparation of nylon 66/nano CaCO3 composite material, will save a lot of cost, application prospects. In this study, nano-CaCO3 modified PA66, nano-CaCO3 as a nucleating agent [18-20] with heterogeneous nucleation, can change the crystallinity of the polymer and crystalline morphology, thereby affecting the performance of composite materials.

2. Experimental part

2.1. Experimental principle

2.1.1 Effect of nano-CaCO3 nucleating agent on PA66

The effect of nano-CaCO3 nucleating agent on PA66 is mainly through the following two aspects:

1) Nano CaCO3 on the crystallization behavior of PA66. Nylon 66 in the general case only α crystal form, and nylon nanocomposites in addition to α crystal form, as well as β crystal form, nano-CaCO3 is through heterogeneous nucleation to make nanocomposite polymorphic, and thus affect its performance. Nano-CaCO3 as a nucleating agent will make the polymer to form a small spherule, and the crystal structure is uniform. The addition of nano-CaCO3 will limit the movement of nylon 66 molecular chain, induced β crystal form, the crystallization rate and crystallinity increased, the crystallization temperature decreased.

2) Effect of nano CaCO3 on the interface of PA66. Nano-particles in nano-particles with a large contact area of the polymer, and nano-particles with four nano-effect, his surface area, high surface activity, and polymer affinity, strong physical and chemical effects, this effect will affect the performance of the material.

2.1.2 Principles of Test Instruments

A) Scanning electron microscopy (SEM) test

Scanning electron microscopy is a new type of electronic optics developed in the 1960s to evaluate the interaction of the interface. He combines the advantages of optical microscopy and transmission electron microscopy, which can directly observe large chunks of samples like optical microscopes, as well as high resolution and magnification as transmitted microscopes, and his sample preparation is simple and observes the Depth, image three-dimensional, so he is widely used to study the nylon 66/nano CaCO3 composite morphology characteristics.

B) Polarizing microscopy (PLM) test

Optical microscopic analysis technology is to use visible light to observe the material, the use of the nature of light to analyze the microstructure and crystal phase composition. Polarizing microscopy is the most effective tool for optical microscopy. Nowadays, due to the rapid development of science, polarizing microscope observation technology can not only qualitative analysis, but also quantitative analysis.

C) Thermogravimetric analysis (TGA)

Thermogravimetric analysis is a technique for measuring the relationship between material temperature and mass at programmed temperature. Substances in the heating or cooling process will sublimation, vaporization, decomposition of the gas or loss of crystal water and the quality of change, by analyzing the quality of different temperature changes, you can study the nature of the material changes in the crystal and some physical and chemical phenomena. Thermogravimetric analysis is highly deterministic and widely used in various fields related to chemistry.

D) Differential scanning calorimetry (DSC)

Differential scanning calorimetry is an important method of thermal analysis and is a technique for measuring the relationship between the power difference between the input sample and the reference and the temperature at the programmed temperature. Because differential thermal analysis technology can only be semi-quantitative or qualitative analysis work and many factors, so the development of differential scanning calorimetry, he not only differential thermal analysis of the general function, can be quantitative analysis, but also to obtain the process of change Sample temperature and various thermodynamics, kinetic parameters.

2.2. Experimental drugs and equipment

2.2.1 Experimental drugs

See Table 2-1 for experimental drugs

Table 2-1 Experimental drugs

Drug name	Level	Production business
Nylon 66	1300S3J1	ASAHI KASEI CHEMICALS
Nano CaCO3	industrial grade	Shanxi ruicheng huaxin nano materials co., Ltd. manufacturing
Liquid paraffin	industrial grade	Commercial

2.2.2 Test equipment

The experimental instruments are shown in Table 2-2

Table 2-2 Major laboratory equipment

Model	Name	Manufacturer
GH-10	High speed mixer	beijing yingte plastic machinery plant
CET35	Mixing with twin screw extruder	Kobelongkuoya (nanjing) machinery co., Ltd
DGF30022B	Electric blast oven	China chongqing galaxy test instrument co., Ltd
TK-C921EC	Polarized light microscope (PLM)	Victor company of japan limited
Q200	Differential scanning calorimetry (DSC)	TA
S-4800-1	Scanning electron microscope (SEM)	Japan HITACHI
STARe system	Thermogravimetric analysis (TGA)	MRTTLER TOLEDO

2.3. Preparation of composite materials

2.3.1 Preparation of pellets

1000 g of nylon 66 was dried in an electro thermal blast oven at a set temperature of 102 ° C for 6 hours and then mixed with nano-CaCO3 in a high-speed mixer, and an appropriate amount of liquid paraffin was added and mixed at room temperature for three minutes. Mixed with a good material into the twin-screw extruder extrusion, and finally with a cold pelletizer for pelletizing. The process parameters of the twin-screw extruder are shown in Table 2-3, where the mass fraction of nano-CaCO3 is 1%, 2%, 3% and 5%. The composite samples are designated PNC-01, PNC-02, PNC -03, PNC-04, pure nylon 66 is designated as PNC-05.

Table 2-3 Process parameters of twin-screw extruder

Process parameters	parameter value/℃	Process parameters	parameter value/℃
A district temperature control	180	district temperature control	260
Two district temperature control	240	eight district temperature control	260
Three district temperature control	250	nine temperature control	260
Four district temperature control	260	area temperature control	260
Five district temperature control	260	head temperature control	260
Six district temperature control	260		

1) Speed: 75r/min; Feeding frequency: 3/Hz

2.3.2 Preparation of experimental samples

The granular nylon nanocomposites were dried, placed in a melt index instrument to melt, and then manually pressed, the prepared sheet material will be used for scanning electron microscopy to observe the dispersion of nano-calcium carbonate.

The granular nylon nanocomposite material is heated and melted, and then produced under a certain pressure, natural cooling to room temperature, the prepared sample will be used for polarizing microscope to observe the shape and size of spherules.

The granular nylon nanocomposites were cut into fine particles with a mass of 10 mg or less and dried for DSC and TGA to test their properties.

2.4. Performance test and characterization of nylon 66/nano CaCO3 composites

A) Scanning electron microscopy (SEM)

The dispersion of nano - CaCO3 in the samples was observed by scanning electron microscopy. The acceleration voltage of the scanning electron microscope is 3.0kv, the magnification is 8000 times.

B) Polarization microscopy (PLM)

The morphology and size of spherules were observed by polarizing microscope. The magnification of the selected eyepiece is 10X and the magnification of the objective lens is 20X.

C) Thermogravimetric analysis (TGA)

TGA detection in a nitrogen atmosphere, the temperature was raised at a rate of 10 ° C/min, and the change in sample weight with temperature was recorded.

D) Differential scanning calorimetry (DSC)

DSC analysis was carried out using tzero aluminum as a reference sample under nitrogen at a flow rate of 50.0 mL/min.

Effect of nano-CaCO3 content on the crystal form of nylon 66/nano-CaCO3 composites. The samples were heated at a heating rate of 40.00 ° C/min to 270.00 ° C and then kept at a constant temperature of 3.00 min to eliminate the thermal history and then equilibrated to 50.00 ° C, and finally 40.00 ℃/min heating rate to 320.00 ℃, and recorded during the heating process with the temperature changes in the heat flow.

Effect of isothermal crystallization time on the crystal form of nylon 66/Nano-CaCO3 Composites. Take the sample with a mass fraction of 5%. The sample was heated to 280.00 ° C at a heating rate of 40.00 ° C/min and then kept at a constant temperature of 3.00 min to eliminate the thermal history. The sample was heated to 240.00 ° C at a heating rate of 40.00 ° C/constant temperature of 10.00min (the second constant temperature 30.00min), the material to create a thermal history, followed by a balance to 50.00 ℃, and finally to 40.00 ℃/min heating rate of heating up to 320.00 ℃, and record the heating process with the temperature changes happening.

Effect of heating rate on the crystal form of nylon 66/nano-CaCO3 composites. A sample with a mass fraction of 5% was first heated to a temperature of 300.00 ° C at a heating rate of 40.00 ° C/min and then at a constant temperature of 3.00 min to eliminate the thermal history and then equilibrated to 50.00 ° C. Finally, the samples were heated at 10.00 ° C/min and 40.00 ° C/Min heating rate up to 320.00 ℃, and record the heating process with the temperature changes in temperature.

Effect of cooling rate on the crystal form of nylon 66/nano-CaCO3 composites. Take the sample with a mass fraction of 5%. The sample was heated to 280.00 ° C at a heating rate of 40.00 ° C/min and then kept at a constant temperature of 3.00 min to eliminate the thermal history. The samples were cooled at 10.00 ° C/min and 40.00 ° C/min The temperature from 250.00 ℃ down to 50.00 ℃ and finally to 40.00 ℃/min heating rate to 320.00 ℃, and record the heating process with the temperature changes in temperature.

3. Results and discussion

3.1. Dispersed morphology of nanometer CaCO3 in nylon 66

Figure 3-1 shows a scanning electron microscope image of the PNC-01 section showing the dispersion of nano-calcium carbonate in nylon 66, where the spherical particles are dispersed nano-calcium carbonate in the nylon 66 matrix. It can be seen from the figure that the effect of nano-calcium carbonate dispersion in the nylon 66 matrix is not ideal, mainly in the form of aggregates. The scale in the figure shows that the nanometer calcium carbonate aggregates have a particle size of about 1000 nm to 2000 nm, which is much larger than the size required for the nanocomposites (1 nm to 100 nm), and a significant interface boundary can be observed, calcium in the nylon 66 matrix was agglomerated, nano-calcium carbonate and nylon 66 matrix interface adhesion is very weak. There are two reasons for the agglomeration of nano-calcium carbonate: First, nylon 66 melt and nano-calcium carbonate particles interface is relatively weak; second, nano-calcium carbonate particles surface area is very large, exposed to the outer layer of particles in the high atomic activity, so there is higher than the surface energy of ordinary particles, in order to reduce the surface energy, the interaction between particles agglomeration.

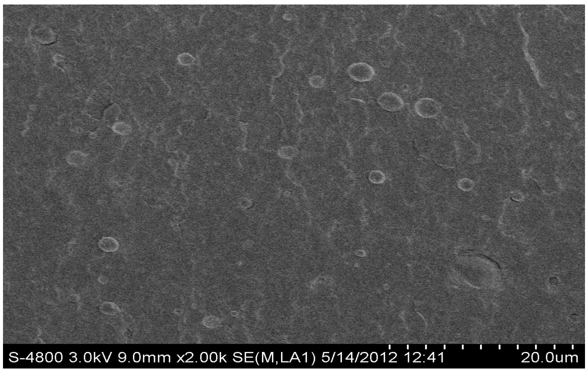

Figure 3-1 SEM image of PNC-01 section

The dispersion of nano-calcium carbonate particles in nylon 66 matrix and the interfacial adhesion of nylon 66 to nano-calcium carbonate are very important for the properties of the materials. In order to disperse the nanoparticles evenly and have some interface adhesion, the most common the method is to surface treatment of nanoparticles. The nano-calcium carbonate is subjected to organic surface treatment, that is, the intercalation of the organic reagent into the layers of the nanoparticles can not only make the hydrophilicity of the surface of the nano-calcium carbonate particles become lipophilic and increase the interface adhesion with the nylon 66; will increase the interlayer spacing of nano-calcium carbonate, is conducive to nylon 66 into the interlayer, nylon 66 and nano-calcium carbonate in the nano-uniform mixing; the same time, non-reactive surface treatment will reduce the surface tension of nylon 66, and then make between the nanoparticles, the interaction between the nanoparticles and the polymer decreases. The results show that different kinds of intercalation agent, amount of intercalation agent and organic time will affect the effect of nano-particles on the surface treatment of nano-particles.

As the nano-calcium carbonate particles used in this experiment were not surface treated, the nanoparticles were easily agglomerated, which affected the properties of nylon 66/nano CaCO3 composites. In order to prevent the agglomeration of nano-calcium carbonate particles, in addition to organic surface treatment, but also from the following aspects can be improved: first, without causing nylon 66 decomposition of the case, as far as possible to extend the mixing time; second, improve the twin screw extruder screw structure, or the use of a combination of screw with a mixer to enhance the cutting effect; third, change the process parameters, such as barrel temperature, screw speed, so that the performance of the material to achieve better.

3.2. Effect of nano-CaCO3 on the crystal morphology of composites

Figure 3-2 nylon 66 molecules in the presence of hydrogen bonds, hydrogen bonding of the positioning of the material to show anisotropy, the crystal has a birefringence effect of the crystal, so that the morphology of the crystal can be observed by a polarizing microscope. Figure 3-2 shows a picture of the natural cooling of the material after melting the observed material under a polarizing microscope. It can be seen from the figure that the nucleating agent has a significant effect on the crystal morphology of nylon 66. The crystal of pure nylon 66 has a clear black extinction phenomenon, and the spherules are radially grown from the center along the radial direction to the surroundings, the spherical interface is clear and larger (see 3-2a). When the nanometer calcium carbonate nucleating agent was added, the size of the spherule became smaller. When the nucleating agent content was 1% (see 3-2b), the size change of the spherule was less obvious. With the increase of the nucleating agent content, the size of the spherules is getting smaller and smaller until the added content is 5% (see 3-2d), and the complete spherules have not been seen, just some fine crushed crystals. It is clear that the size of the spherule is significantly reduced as the amount of calcium carbonate nucleating agent increases. This is because the nanometer calcium carbonate nucleating agent in the crystallization process from the nucleus, can increase the probability of heterogeneous nucleation, change the crystallization behavior of the polymer to promote the formation of spherules, and the increase in grain crystal of the distance becomes smaller, the spherules squeeze each other to make the size of the spherules smaller, therefore, the addition of nano-calcium carbonate nylon spherule size and uniform shape.

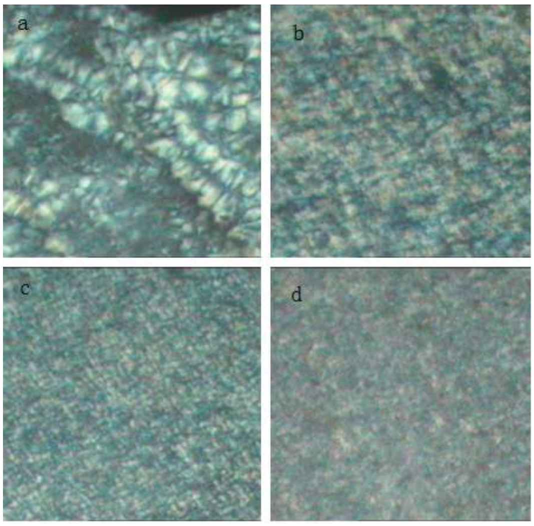

Figure 3-2 Polarization microscope of nylon 66/nano CaCO3 composites

A (PNC-05) b (PNC-01) c (PNC-03) d (PNC-04)

3.3. Thermal stability of nylon 66/nano CaCO3 composites

TGA was used to study the thermal stability of composites. Figure 3-3 shows the thermal weightlessness curves for nylon 66 and PNC-04. It can be seen from the figure that nylon 66 and PNC-04 have only one weight loss stage, between 0 ° C and 400 ° C, the quality of nylon 66 decreases slightly as the temperature increases and decreases from about 100 ° C Initially, the decrease in the quality of nylon 66 is due to the evaporation of water. After 400 ° C, the mass of nylon 66 decreased rapidly due to the decomposition of nylon 66; from 470 ° C to 600 ° C, the mass change of nylon 66 was zero and the residue was carbonized by nylon 66. For PNC-04, the mass change at 520 ° C is zero due to the decomposition temperature of nanometer calcium carbonate of 897 ° C and the last remaining 5% of nanometer calcium carbonate.

The TGA curve of the PNC-04 is somewhat higher than the TGA curve of the nylon 66 to the low temperature region. The decomposition temperature of nylon 66 is about 400 ℃, while the decomposition temperature of PNC-04 is about 380 ℃, which is lower than that of nylon 66, which indicates that the addition of nano-CaCO3 particles reduces the thermal stability of the composites. Under normal circumstances, the nylon 66/nano CaCO3 composite material than the pure nylon 66 decomposition temperature is higher, because when the nano-calcium carbonate particles dispersed evenly into the nylon 66 matrix, with nylon 66 will have a strong interface reaction; and dispersed nano the particles can block the heat conduction and gas diffusion effect, to prevent heat transfer can protect the polymer section, so that it is not easy to break down, thereby reducing the generation of combustible gas, while the polymer particles can prevent combustible gas diffuse into the object The thermal properties of the nylon 66/nano CaCO3 composites are improved by reducing the surface heat and reducing the combustion heat, thereby preventing excess segments from decomposing to produce combustible gases.

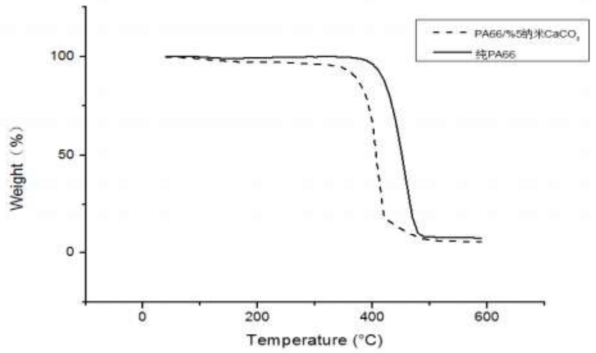

Figure 3-3 TGA curves for nylon 66 and PNC-04

This experiment is not the same as the results obtained from predecessors may be nano-calcium carbonate particles scattered uneven, occurred reunion, as observed by scanning electron microscopy. The nano-calcium carbonate particles used in the experiment were subjected to non-thermodynamically stable state without surface treatment. In order to reduce the surface energy, the atomic interaction was agglomerated together. The agglomerates of nanoparticles have two effects: first, nano-calcium carbonate particles have hydrophobic oleo phobic surface heat, weak affinity with nylon 66, the formation of large aggregates will make defects in the material, thermal stability decreased the second, the agglomerates of nanoparticles improve the thermal conductivity of the composites, so that heat can easily be transferred to the polymer matrix, resulting in the rapid decomposition of the segment, while the decomposition of the segment will increase the combustion gas to further accelerate the decomposition of materials. Therefore, in order to prepare the nylon 66/nano-CaCO3 composite with good thermal stability, the key is to improve the dispersion of nano-calcium carbonate in nylon 66.

3.4. Melt crystallization behavior of nylon 66/nano CaCO3 composites

Study on the melting crystallization behavior of composites by DSC. Figure 3-3 shows the DSC curve of the composite. In the melt crystallization process, the nucleating agent content, constant temperature time, heating rate and cooling rate will have an impact on the crystallization of nylon 66.

3.4.1 Effect of different mass fraction of nylon 66/nano CaCO3 composites on crystallization

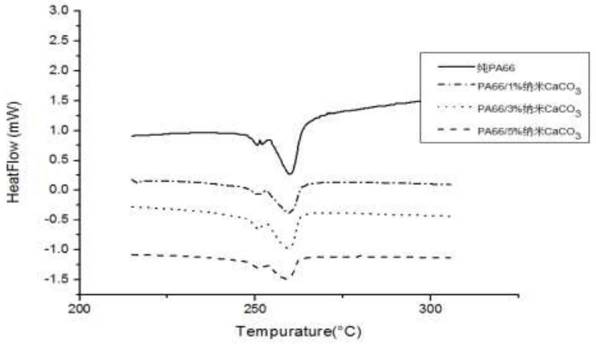

Figure 3-4 DSC curves of nylon 66/nano CaCO3 composites with different mass fractions

Figure 3-4 shows the composite DSC curves of nylon 66 and different mass fraction of nano-calcium carbonate, with heating rates of 40 ° C/min. Bill has pointed out that nylon 66 has α and β two crystal form, under normal circumstances nylon 66 is α crystal form, α crystal form is more stable. Nylon 66 can form a different crystal form, is due to the presence of nylon 66 amide groups to make a strong hydrogen bond between the molecular chain, the different arrangement of molecular chains so that the formation of hydrogen bonds in different ways, so nylon 66 produced a polymorphic phenomenon the as can be seen from the figure, all the curves are bimodal, they correspond to nylon 66 alpha crystal form and β crystal form. However, the shape of the peaks and the crystallization temperature are different. With the increase of the content of nano-CaCO3, the increase of the nano-CaCO3 increases the crystallization temperature of the material, and the crystallization temperature range widen. The crystallization temperature of nanocomposites decreases with the increase of nano-CaCO3 content because a large amount of nano-calcium carbonate particles cannot be uniformly dispersed in the matrix leading to the final agglomeration. And these reunited particles cannot promote nucleation.

The increase in the endothermic peak of the nanocomposite may be due to two reasons:

The first reason may be the increase in the viscosity of the nanocomposite melt system, which is caused by the interaction of nanometer calcium carbonate with the molecular chains in the nylon 66 matrix. The addition of nanometer calcium carbonate limits the diffusion of the nylon 66 molecular chain, resulting in PA66 crystal growth rate decreased. Due to the heterogeneous nucleation of nano-calcium carbonate, the crystal growth rate plays a decisive role in the total crystallization rate. Thus, a decrease in crystal growth rate means a decrease in the total crystallization rate. That is, the crystallization needs to be in a wider temperature range, and thus the endothermic peak increases.

The second reason may be the uneven dispersion of nano-calcium carbonate, which will lead to uneven growth of the crystal, different content of nano-calcium carbonate nylon 66 molecular chain between the different crystal growth rate.

3.4.2 The effect of different constant temperature on the crystallization of the material

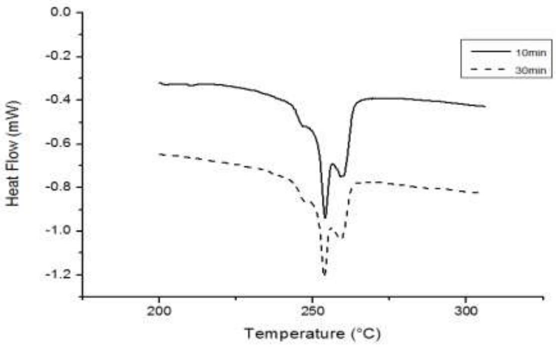

Figure 3-5 DSC curves for PNC-04 for different constant temperature times

Figure 3-5 for the different temperature of the PNC-04 material DSC curve, the solid line at 240.00 ℃ constant temperature 10min, dotted line at 240.00 ℃ constant temperature 30min. Compared to the two curves found that the temperature of the crystallization of nylon 66 did not have much impact. According to the theoretical analysis, the longer the thermostatic time, the longer the nylon chain has a more sufficient time to form a stable α crystal form, but from the two curves found that with the increase in temperature, α melting peak and β melting The area of the peak did not change, that is, the alpha crystal did not increase. This may be due to uneven dispersion of nano-calcium carbonate caused by the two selected PNC-04 material, nano-calcium carbonate content of 5%, but doing constant temperature 30min experiment, the selected material may contain of the nano-calcium carbonate is more, it is conducive to the formation of β crystal form, α crystal growth trend cannot be revealed.

3.4.3 Effect of cooling rate on crystallization of composites

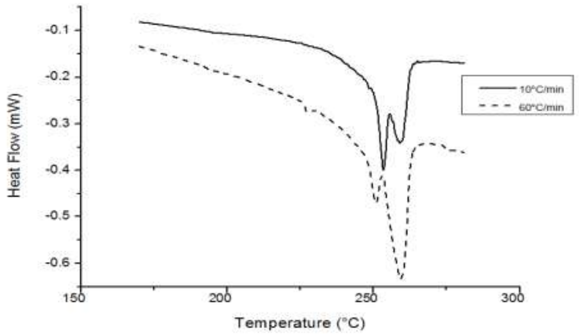

Figure 3-6 DSC curves for PNC-04 at different cooling rates

Figure 3-6 shows the DSC curves of the PNC-04 composites at different cooling rates. The solid line is the cooling rate of 10 ° C/min and the dotted line is the cooling rate of 30 ° C/min. Compared with the two curves, two melting peaks were found on the two DSC curves, and as the cooling rate increased, the curve moved toward the low temperature and the peak shape became broad.

These phenomena can show that there are α crystal form and β crystal form in the nylon 66 nanocomposite matrix, and the crystallization temperature decreases and the crystallization temperature range increases with the increase of the cooling rate. This may have two causes: one is undercooling, each material has a theoretical crystallization temperature, but because the cooling rate is too fast, the actual crystallization temperature of the material than the theoretical crystallization temperature is lower, the difference between them value is undercooled. An increase in the cooling rate causes the degree of sub cooling to rise, so that the crystallization temperature at 30 ° C/min is lower. Second, because the material molecular chain from the chaotic into a regular order, from the amorphous state or semi-crystalline state into a complete crystalline state, take some time to complete, the faster the cooling rate, the same temperature range to stay less time, the more obvious the temperature hysteresis, so the curve to the low temperature movement and the shape of the curve widened.

3.4.4 Effect of heating rate on crystallization of composites

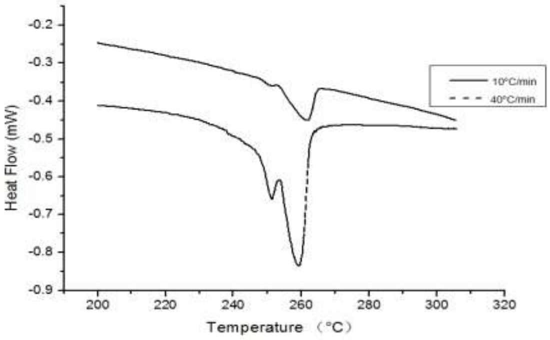

Figure 3-7 DSC curve for PNC-04 at different heating rates

Figure 3-7 shows the DSC curves of PNC-04 composites at different heating rates. The solid line represents the heating rate of 10 ℃/min and the dotted line represents the heating rate of 40 ℃/min. Compared with the two curves, it can be found that although there are two melting peaks, the two peaks are different in area, and the material with the heating rate of 10 ℃/min is basically α crystal (designated as material 1), and the heating rate For the material at 40 ° C/min, there are α crystal form and β crystal form (designated as material 2), which shows that although the two experimental materials are the same, the crystallization rate is the same when the thermal history is eliminated, but the resulting material is not complete the same. Theoretically speaking, the faster the rate of temperature rise, the stronger the temperature hysteresis, the higher the temperature of the crystal melted, but the reaction in Figure 3-7 is just the opposite, which is due to the two different materials used in the experiment caused. Material 1 is mostly stable because of its large α crystal form, until the temperature is high when the melting peak occurs; and material 2 due to β crystal form, at a lower temperature β crystal will melt, β crystal melt will make The heat of the material increases, and the melting of the α crystal is accelerated, so that the temperature of the melting peak is lowered.

4. Conclusiond

The nylon 66/nano CaCO3 composites were successfully prepared and the polycrystalline behavior and thermal properties of the nanocomposites were characterized. The electron microscope image shows that the nano-calcium carbonate particles are dispersed in nylon 66 in the form of aggregates, because the nano-calcium carbonate has not been surface modified, the surface can be high and hydrophilic oleo phobic, the atoms easily interact with the polymer binding capacity is weak, easy to use to form aggregates. Through the TGA image shows that the addition of nano-calcium carbonate nylon composite materials to reduce the decomposition temperature, the thermal stability of the material decreased.

The thermal behavior of PA66 and PA66/nano-CaCO3 composites shows that the thermal history has a strong influence on the polycrystalline transformation behavior of the samples. For PA66/m calcium carbonate composites, after heat treatment at 280 °C for 3 minutes, there was a significant change at different cooling rates. PA66/nano-calcium carbonate composite material in the molten state heat treatment led to β crystal form to become the main crystal type and higher cooling rate of this phenomenon is more obvious, probably because of nano-calcium carbonate with heterogeneous nucleation, can make the material crystal The size of the material decreases and the melting temperature of the material is reduced.

The difference of polymorphism between pure PA66 and PA66/nano-calcium carbonate composites reflects the complexity of the melting behavior of PA66/nano-calcium carbonate composite system. The addition of nanocomposite will limit the movement of nylon 66 molecular chain, induce the formation of β crystal form, increase the crystallization rate and crystallinity, and decrease the crystallization temperature.

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