Effect of calcium carbonate as pore-forming agent on properties of recycled polyethylene terephthalate masterbatch

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Abstract. In order to study the effect of calcium carbonate particles as pore-forming agent on properties of recycled polyethylene terephthalate(PET) masterbatch, pore-forming agent and PET derived from waste bottle were melt-blended and extruded, and then treated with acetic acid solution to obtain recycled PET masterbatch with micro-cavity structure. The influence of content of pore-forming agent and parameters of twin screw extruder for granulation process on the performance of recycled PET melt and masterbatch were analyzed. The results show that the intrinsic viscosity of recycled PET masterbatch is greatly affected by pore-forming agent and the parameters of the twin screw extruder for granulation process. When the mass ratio of polyester bottle flakes to virgin PET is 9:1 and 3 wt% of pore-forming agent added, with the temperature of the barrel 1~6 of the twin-screw extruder is 240℃, 244℃, 244℃, 244℃, 240℃, 240℃, respectively, and 150 r/min of screw speed, the intrinsic viscosity of the recycled PET masterbatch produced by twin screw extruder can reach 0.613 dL/g. The recycled PET masterbatch could be applied to PET fibers spinning. This method provides a new method for improving moisture regain for PET.

1. Introduction

China has large-scale industrial production of polyester (PET) fibers, and its current production capacity ranks among the top in the world, which made china become the world’s largest consumer of polyester and polyester [1]. With the shortage of global petrochemical resources and textile raw material supplied, with contradiction of textile industry becoming increasingly prominent, the renewable PET industry has gradually changed from "supplement" to "replacement" in industry. At present, there are three main methods for recycling PET, namely energy recovery, chemical recovery and physical recovery of PET [2-4]. Physical recycling is to use them directly after crushing that perform preliminary mechanical separation of waste PET products, or melt and pelletize them to obtain primary raw materials such as recycled polyester masterbatch. The physical regeneration method is simple, fast, energy-saving, and environmentally friendly, which is currently widely used in the polyester recycling industry. Meanwhile, renewable raw PET materials by physical recovery can be used in spinning, filling, non-woven and other industrial.

The main disadvantage of polyester fiber in the application and processing is low moisture regain, which increases the complexity of application processing. At present, the methods to improve polyester moisture regain mainly include grafting hydrophilic macromolecules or groups, biological enzyme technology, hydrophilic copolymerization and other chemical modification methods [5,6], as well as physical methods such as surface etching, densification, fiber profilization, coating method and fiber blending [7-9]. Physical modification is mainly to improve the hydrophilic properties of fibers by
blending hydrophilic substance or changing the shape of fibers. In recent years, etching methods using physical and chemical combination, such as plasma etching, alkali reduction treatment, and inorganic powder pore formation increasing the surface roughness of fibers to improve the hydrophilicity of fibers have attracted great attention [10]. The physical-chemical combination etching method is simple and easy to implement, which has obvious effect of moisture absorption modification with relatively low cost. However, according to the literature, there were quite little reports about recycled PET that mixed with inorganic pore-forming agent by melt extrusion granulation, and then the etching of the surface after post-treatment to produce recycled polyester masterbatch with micro-cavity structure. Studies have found that the addition of pore-forming agent has a greater impact on the structure, performance and application processability of PET polymer and masterbatches production in granulation. Therefore, in order to study mechanism for etching treatment technology of polymer surface to increase the moisture regain of PET, the influence of inorganic pore former on the performance of polyester masterbatch is analyzed.

In this paper, PET derived from waste bottle are used as raw materials, CaCO3 particles used as inorganic pore-forming agent, which are blended, extruded and pelletized sequentially to produce recycled PET masterbatch, and then treated with acid solution to obtain recycled polyester masterbatches with surface micro-cavity structure. The effects of calcium carbonate content and granulation parameters of twin-screw extruder on performance of recycled PET masterbatch were analyzed experimentally. In order to obtain masterbatch applied to fiber spinning, the effects of the the mass ratio of polyester bottle flakes to virgin PET were also analyzed to improve intrinsic viscosity of recycled PET masterbatch. The pore-forming technology of recycled PET on the surface developed in this experiment provides a new method for increasing moisture regain for PET.

2. Experimental

2.1. Materials and reagents
Recycled Polyester bottle (PET, purchased from Anhui Xinde Chemical Fiber Co., Ltd.); spinning grade semi-dull virgin PET (DP=100, purchased from Anhui Xinde Chemical Fiber Co., Ltd.); CaCO3 (analytical grade, China Xilong Chemical Co., Ltd.); ethanol (analytical grade, China Sinopharm Chemical Reagent Co., Ltd.); 1,1,2,2-tetrachloroethane (analytical grade, China Xilong Chemical Co., Ltd.); Phenol (analytical grade, China Xilong Chemical Co., Ltd.); Acetic acid (analytical pure, China Xilong Chemical Co., Ltd.); Deionized water.

2.2. Instruments
Twin screw extruder (BP-8171-ZB, China Baopin Precision Instrument Co., Ltd.); scanning electron microscope (S-4800, Hitachi, Japan); Ubbelohde viscometer (0.8-0.9 mm, China Hefei Shenyi Glass Products Co., Ltd.); thermostat heating magnetic stirrer (DS-101S, China Zhengzhou North and South Instrument Co., Ltd.).

2.3. Experiment method

2.3.1. Preparation of recycled PET masterbatch. The PET derived from bottle were pre-dried for 4 hours in a vacuum oven at 80 °C, and the oven temperature was adjusted to 120 °C for another 4 hours to make PET completely dry. The dried PET and CaCO3 powder were mixed in proportion and placed in a vacuum drying oven at 60 °C for 24 h, and then the mixture was stirred evenly. The mixed materials are fed into the screw barrel of twin screw extruder through heating, melting, spinneret extrusion to obtain mixed melt. Water bath solidification and cooling process were carried out to fix shape of PET filaments, with final pellet-cutting process, and the recycled PET masterbatch is prepared.
2.3.2. Surface pore-forming treatment of recycled PET masterbatch. The recycled PET masterbatch was placed in a 2 wt% acetic acid aqueous solution at a ratio of 1:50 and treated at 50 °C for 2 hours. The acid-treated recycled PET masterbatch was dried in a vacuum oven at 60 °C for 4 hours to obtain a recycled PET masterbatch with micro-cavity structure.

2.4. Test method

2.4.1. Intrinsic viscosity of recycled PET masterbatch. According to the standard GB/T 14190-2008 "Test Method for Fiber Grade Recycled Polyester Chips (PET)" Method A: Capillary Viscometer Method. 0.125g sample was accurately weighed and placed in 25ml 1,1,2,2-tetrachloroethane and phenol solution (according to the mass ratio of 1:1). The flask was sealed and shaken at 110 °C in oil bath for 30 min until the sample was completely dissolved. And 10 ml of this solution was filled into an Ubbelohde viscometer, and made the solution equilibrate at 25 °C for about 15 min. Then, the efflux time was measured when the solution flowed between the two marks on the viscometer; the similar procedure was performed to measure the efflux time of solvent of in 10ml 1,1,2,2-tetrachloroethane and phenol solution (according to the mass ratio of 1:1). The intrinsic viscosity could obtained from the following equation:

\[ \eta_i = \frac{t_1}{t_0} \]  \hspace{1cm} (1)

\[ \eta_{sp} = \frac{t_1 - t_0}{t_0} \]  \hspace{1cm} (2)

\[ [\eta] = \frac{\sqrt{1 + 1.4\eta_{sp}} - 1}{0.7c} \]  \hspace{1cm} (3)

Where: \( t_1 \) is the efflux time of the sample solution, s; \( t_0 \) is the efflux time of solvent, s; \( c \) is the concentration of the test solution, g/100mL; \([\eta]\) is the intrinsic viscosity of the sample, dL/g.

2.4.2. Scanning electron microscope (SEM) of recycled PET masterbatch. The recycled PET masterbatchs treated with acetic acid were gold sputter coated for scanning electron microscope (SEM) morphology analysis. The voltage is 3 kV, and temperature and relative humidity is 20 °C, 65%, respectively.

3. Results and discussions

3.1. The effect of pore-forming agent on the granulation process of recycled PET masterbatch

When the PET derived from bottle flakes is blended with inorganic porogen calcium carbonate, in order to ensure that the pore-forming agent is adequately dispersed in the PET particles, the mixture of calcium carbonate and PET need to be dried at 60 °C, for 24 hours with stirring process, which make calcium carbonate adhere to the surface of PET. And then the mixture are fed into extruder barrel for melt blending and extrusion. The purpose of drying of the mixture with stirring process is to promote the adequate blending of PET and calcium carbonate, which obtain the mixture without the phenomenon of jam in between two screws in granulation. On the other hand, this drying method could achieve that the mixture are dried evenly, so moisture in mixture is more uniform. Calcium carbonate is easy to absorb water in the air, but the water content has a great impact on the performance of recycled PET masterbatch during melting extrusion [11]. In a high temperature environment, excessive moisture will cause the ester bond of PET macromolecules to be hydrolyzed and the degree of polymerization will decrease. Therefore, the content of calcium carbonate and drying process are key factor for recycled PET in masterbatch granulation.
3.2. The influence of content of pore-forming agent on the intrinsic viscosity of recycled PET masterbatch

In order to study the effect of content of pore-making agent on properties of the recycled PET masterbatch, PET derived from waste bottle containing 1 wt%, 2 wt%, 3 wt%, 4 wt% and 5 wt% of calcium carbonate were blended in the experiment, respectively. And then the mixtures were extruded to obtain the recycled PET masterbatch. The screw speed of the extruder is set to 150 r/min, and the temperature of zone one to six of the screw barrel is 260 °C, 264 °C, 264 °C, 264 °C, 260 °C, and 260 °C, respectively. Intrinsic viscosity of recycled PET masterbatch is shown as in Figure 1. It can be seen that with content of calcium carbonate increased, the intrinsic viscosity of the recycled PET masterbatch decreases firstly, then that increases. The change of the intrinsic viscosity of the recycled PET masterbatch is related to the content and dispersion of the calcium carbonate particles in the mixture. When the content of calcium carbonate is lower, the calcium carbonate is easily dispersed in the matrix, and the addition of pore-forming particles promotes the flow of the polymer, thereby reducing the intrinsic viscosity of the recycled polyester masterbatch; with the increase of calcium carbonate content, the pore-forming particles are prone to agglomeration, which hinders the flow of the polymer, resulting in an increase in the intrinsic viscosity of the PET composite system. When the calcium carbonate content is 3 wt%, the intrinsic viscosity of recycled PET masterbatch is 0.474 dL/g, which is close to that of virgin PET (0.476 dL/g). When the content of calcium carbonate continues to increase, that is over 3 wt%, the intrinsic viscosity of recycled PET masterbatch will begin to decline. It is found that a large number of agglomerated calcium carbonate particles in the reclaimed polyester masterbatch will aggravate the interface separation between PET and calcium carbonate, and the calcium carbonate particles will have a “dilution” effect on PET particles, resulting in the decrease of intrinsic viscosity [12]. In summary, when the calcium carbonate as pore-forming agent is added at 3 wt%, it is beneficial to granulation process of the recycled PET masterbatch.

![Figure 1](image-url)  
**Figure 1.** The influence of calcium carbonate content on the intrinsic viscosity of recycled PET masterbatch

3.3. The influence of barrel temperature on the intrinsic viscosity of recycled PET masterbatch

The PET derived from bottle containing 3 wt% of calcium carbonate were blended and extruded through the twin screw extruder. The screw barrel temperature is set with three schemes in Table 1. Meanwhile, the screw speed of the extruder was set to 150 r/min. The intrinsic viscosity of the recycled PET masterbatch is shown in Table 1 in different setting temperature. It can be seen that increasing the barrel temperature will cause a decrease in the intrinsic viscosity of the recycled PET masterbatch, which indicates that a high temperature may cause thermal degradation of the recycled PET masterbatch. The melting temperature of PET is 250 °C-260 °C [13], and the twin screw of the extruder will generate heat due to friction during operation. When the screw temperature is set near
240 °C of Plan 1, the PET bottle sheet is extruded by melting normally, but when the screw temperature is set below this temperature, the bottle sheet cannot be extruded by melting PET. When the temperature is higher than 240°C, PET will have a certain thermal degradation in the screw barrel, and the intrinsic viscosity decreases continuously, which is not conducive to masterbatch molding and spinning. Therefore, in order to ensure the normal extrusion of mixture and pelleting of the recycled PET masterbatch with better properties, the 240°C of screw temperature in screw barrel is selected as the better temperature for following experiment.

Table 1. Effect of screw temperature on characteristic viscosity of reclaimed polyester master batch

| Zone temperature of screw barrel | Zone 1 / (°C) | Zone 2 / (°C) | Zone 3 / (°C) | Zone 4 / (°C) | Zone 5 / (°C) | Zone 6 / (°C) | Intrinsic viscosity (dL/g) |
|----------------------------------|--------------|--------------|--------------|--------------|--------------|--------------|-----------------|
| Plan 1                           | 240          | 244          | 244          | 244          | 240          | 240          | 0.556           |
| Plan 2                           | 250          | 254          | 254          | 254          | 250          | 250          | 0.512           |
| Plan 3                           | 260          | 264          | 264          | 264          | 260          | 260          | 0.474           |

3.4. The effect of virgin PET added on the intrinsic viscosity of recycled PET masterbatch

After studying parameters in granulation process, in order to further improve the properties of recycled PET masterbatch, the experiment adds virgin PET to the mixture of PET derived from bottle and calcium carbonate. The blended mass ratios of the virgin PET to the PET derived from bottle were 1:9, 2:8, 3:7, 4:6, 5:5, respectively, and the calcium carbonate were all 3 wt% in samples. All samples were melted and extruded at 240°C of plan 1. The intrinsic viscosity of recycled PET masterbatch is shown in Figure 2. It can be seen that as the content of virgin PET increases within a certain range, the intrinsic viscosity of the recycled PET masterbatch begins to increase. When the mass ratios of the virgin PET to the recycled polyester is 1:9, the intrinsic viscosity of the recycled PET masterbatch reaches to 0.613dL/g; however, when the content of virgin PET exceeds 10 wt% (e.g. the mass ratios of the virgin PET to PET derived from bottle is 1:9), high content of virgin PET will lead to the decline of the intrinsic viscosity of recycled PET masterbatch. When a small amount of virgin PET is added to the mixture of PET derived from bottle and calcium carbonate, condensation polymerization occurs between the molecular chains of the two polymers in the twin-screw extrusion equipment, which increases the molecular weight of the recycled polyester masterbatch and thus leads to the improvement of the intrinsic viscosity of the recycled PET masterbatch [14]. At the same time, the recycled PET masterbatch after reaction with virgin PET by condensation polymerization will be entangled in the dissolving system, which further enhances the intrinsic viscosity of the recycled PET masterbatch. When the amount of virgin PET added is greater than 10%, with poor compatibility between PET derived from bottle and virgin PET in the mixture, virgin PET added will led to the decrease of the polymer intrinsic viscosity. When the PET derived from battle is 40 % (e.g. the mass ratios of the virgin PET to PET derived from bottle is 6:4), the recycled PET masterbatch is mainly composed of virgin PET, and its intrinsic viscosity will remain basically unchanged.

In summary, the better preparation parameters of recycled PET masterbatch obtained in this experiment is that the mass ratio of virgin PET to PET derived from bottle is 1:9, and the content of calcium carbonate as pore-forming agent is 3 wt%. Meanwhile, the temperature of the barrels from 1-6 zone is 240°C, 244°C, 244°C, 244°C, 240°C, 240°C, respectively, and the screw speed is 150 r/min. At above conditions, the intrinsic viscosity of the recycled PET masterbatch reaches to 0.613dL/g. The recycled PET masterbatch could be applied to PET fibers spinning.
3.5. Microporous treatment on the surface of recycled PET masterbatch

To observe effects of the pore-forming agent on the surface of recycled PET masterbatch after acid solution treatment. In the experiment, the recycled PET masterbatch prepared by the above-mentioned better process was treated with an acetic acid solution. The microporous structure of the PET surface is shown in Figure 3. It can be seen from the electron micrograph that the acetic acid solution will dissolve pore-forming agent blended on the surface of recycled PET masterbatch, thereby generating microcavities on the surface of PET. Due to the difference in the size of the calcium carbonate particles distributed on the PET surface, the size of the micropores on the PET surface will significantly vary. Through the magnified picture, it can be seen that the calcium carbonate particles on the polyester surface have “pulling out” traces in dissolution process. Compared with recycled PET masterbatch without calcium carbonate, recycled PET masterbatch have still smooth surface on PET. Therefore, in order to obtain recycled PET masterbatch with uniform micro-cavity sizes, it is necessary to further homogenize the particle sizes of calcium carbonate as pore-forming agent. Making micro-cavities on the PET surface will improve the moisture regain of PET [15].
4. Conclusions

1) In this article, the better preparation parameters of recycled PET masterbatch obtained is that the mass ratio of virgin PET to PET derived from bottle is 1:9, and the content of calcium carbonate as pore-forming agent is 3 wt%. Meanwhile, the temperature of the screw barrels from 1-6 zone is 240°C, 244°C, 244°C, 244°C, 240°C, 240°C, respectively, and the screw speed is 150 r/min. At above conditions, the intrinsic viscosity of the recycled PET masterbatch reaches to 0.613dL/g. The recycled PET masterbatch could be applied to PET fibers spinning.

2) The recycled PET masterbatch containing the pore-forming agent after acid treatment have a clear micro-cavity structure on PET masterbatch surface. In order to further improve the uniformity of pore size and distribution, the calcium carbonate particle size and blending method need to be optimized. Etching on the polyester surface produces a microcavity structure, which provides a new method for increasing the moisture regain of PET.

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