

Non-isothermal crystallization kinetics and rheological behaviors of PBT/PET blends: effects of PET property and nano-silica content

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ABSTRACT

PBT and PET are subjected to thermal-oxidative degradation and thermomechanical degradation during the process of melt blending, which affect the polymer structure and properties. The effect of feed properties of PET and the addition of modified nanoparticles on blends are a question worthy of discussion. This work describes the melting and thermal stability, the crystallization behavior and non-isothermal crystallization kinetic, the rheological behaviors and mechanical properties of several PBT/PET blends prepared by twin-screw melt extrusion. Results show that the molecular chain of the polyester blends obtained by stable extrusion are not significantly degraded, there is only one obvious melting peak and crystallization peak on the thermal analysis curves, and the melting point is lower than either of the two polyesters. An appropriate amount of SD can effectively reduce the crystallization rate of the PBT material and extend the crystallization time. The rheological behavior of PBT/PET blends is complicated than PET raw materials and SD, as well as the melt processing temperature and shear rate will all affect the rheological behavior of the blends. For example, at low shear rate, polyester blends with SD exhibit strong shear thinning behavior. In general, the SD content affects the rheological property of blends in a way similar to the law of influence on crystallization behavior. When SD content is 0.3 wt%, a polyester product with higher elongation at break than pure PBT can be obtained. This can provide a useful reference for preparing commercialized polyester blend products with good melt processability and elongation by simple blending.

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1 Introduction

Semi-aromatic polyester has good mechanical properties, chemical stability, melt processability and low price, which can be widely used in industries such as textile, clothing, packaging, auto parts, electrical appliances as one of the most important polymer materials [1]. Among the semi-aromatic polyester family, poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) as well as recently developed poly(trimethylene terephthalate) (PTT), poly(1,4-cyclohexylene terephthalate) (PCT) and poly(ethylene 2,6-naphthalate) (PEN), etc. have been successfully commercialized on a large scale [2]. Where, due to the easy availability of raw materials, mature production technology, outstanding comprehensive product performance, good melt fiber-forming performance, high fiber fabric strength, good crispiness and wearability, PET has become an absolute advantageous variety in the field of chemical fiber. It is more and more used in drinking bottle flakes, film and engineering plastics, becoming the fastest-growing variety in thermoplastic polyester resins. In 2019, the world's polyester production exceeded 85 million tons. The recycling of

PET products has also become an important topic in the field of polymer materials [3]. Generally, in practice, polyester can be divided into three categories according to its intrinsic viscosity. For example, intrinsic viscosity is 0.65 dL/g for clothing fiber, 0.85 dL/g for bottle flakes, and 1.0 dL/g for industrial fiber [4]. The corresponding number average molecular weights (intrinsic viscosities) are 18000 g/mol, 30000 g/mol and 40000 g/mol, respectively.

Compared with PET, the molecular chain of PBT has two more methylene groups than PET. Therefore, PBT has smaller molecular chain rigidity than PET, lower glass transition temperature, melting point and hardness than PET, and superior toughness than PET. PBT macromolecule has a regular structure and appropriate flexibility, which is easier to form a crystalline structure, with significantly faster crystallization rate in processing [5]. Moreover, the crystallization temperature of PET is high (130 ~ 200°C), and the crystallization temperature range is wider. PET can start to crystallize at 40°C, which can meet the needs of high crystalline products at a mold

temperature of about 60°C. Therefore, it is possible to shorten the injection molding time of PBT, increase yield of mold base. Molded products have good stability, making PBT more suitable for use in the field of injection molding as engineering plastics. The crystallization condition determines the mechanical properties, shrinkage properties, optical properties and other physical properties of the thermoplastic polyester. As crystallization is so important for polyester, many researchers have carried out research on the crystallization kinetics of PBT and PET [6–9].

PBT is the latest industrialized but the fastest-growing variety of general engineering plastics. In order to improve PBT usability and facilitate injection processing, PBT is usually filled or blended and modified. For example, researchers have developed measures such as nanotechnology, composite technology, and polymer composite to improve PBT processability and impact resistance, so that their products can be better applied to automotive industrial parts and electrical components [10,11]. For example, PBT/ABS composite is used in the housing of household appliances and automobile interior parts, PBT/polyolefin composite is used in vehicle bumpers, PBT/PPO elastomer is used in vehicle packaging parts, electronic appliances and instrument parts, etc., PBT/EPDM composites are used in vehicle shock-absorbing casings, electric pistons, etc. However, in general, the compatibility of PBT blends with other polymer components needs to be improved. It is necessary to add corresponding compatibilizers in blending to change the compatibility and improve the material properties [12,13]. Xu et al. [14] synthesized a compound with sulfonic acid group and liquid crystal ionomer (SLCL) characteristics using adipic acid, biphenol and p-OH-azobenzenesulfonic acid as raw materials, and added proper amount of this SLCL type compound when blending PBT and PET, which can make the mixed system form a good phase structure, and improves the mechanical properties by increasing the interface adhesion. Ignaczak [15] added a linear triblock thermoplastic elastomer copolymer (SEBS-TPE-MAH) to the PBT/PP blend, thus increasing the toughness of PP/PBT by three times.

As other polyesters have similar structure to PBT, there is a certain degree of natural compatibility, making PBT mixture with other polyesters demonstrate obvious composite advantage. The rheological properties of PET and PBT melts tend to be non-Newtonian, so the melt viscosity is more sensitive to the shear rate than to the temperature. During the processing, the processing fluidity of the polyester can be effectively improved by changing the shear rate. In addition, the melting point of

PBT is relatively close to that of PET. The blending system of PET and PBT has good compatibility, and only a glass transition temperature will appear. Compared to compounding of other polymers and PBT, good development potential is shown. Although studies have shown that two polycondensates with similar structures are prone to transesterification during melt blending, there is no uniform rule in the effect of this reaction on product properties [5,16]. Zhang et al. [17] used differential scanning calorimetry to study the effect of Glass Fiber (GF) on the non-isothermal crystallization process of PBT/PET blends. The study showed that as the cooling rate increases, the crystallization temperature moves towards a lower temperature. The half crystallization time decreased, and the crystallization rate of PBT/PET blends increased with the reduction in GF content. Maksimov [18] used a large amount of hydroxybenzoic acid-modified PET as raw material to blend with PBT, and found that when the content of the modified polyester is high, the viscosity and breaking strain of the blend are significantly reduced, and the modified polyester alternates between the droplet phase and the fibril phase as the dispersed phase. PBT crystalline properties are also affected by additives. The elastic modulus and elastic anisotropy parameters increase monotonically with the increase of the modified polyester content.

In order to improve the usability of PBT products and further reduce the PBT material cost, we selected PET with similar molecular structure, natural compatibility and prominent cost advantages as one of the blending raw materials, compared PET with different molecular weights and recycled melt reprocessing PET in terms of blend performance after mixing with PBT, and tried to add nano-silica to improve the blend performance. Differential scanning calorimetry, thermogravimetric analysis, and rotational rheometer are used to study the effects of non-isothermal crystallization kinetics and melt processing rheology of two kinds of PET and PBT after mixing, and the tensile properties of the blend are analyzed.

2. Experimental section

2.1 Materials

PBT chips ($[\eta] = 0.99$ dL/g) were kindly provided by Sinopec Yizheng Chemical Fiber Co., Ltd., Three different intrinsic viscosities of PET ($[\eta] = 0.68, 0.85, 1.01$ dL/g, marked as PET_{0.68}, PET_{0.85}, PET_{1.01}, respectively) and recycled PET (rPET, $[\eta] = 0.70$ dL/g) were provided by Zhejiang Guxiandao Green Fiber Co., Ltd., China. The modified nano-SiO₂ (SD) (specific surface area 150 m²/g, AR) was provided from Aladdin, and dried in a vacuum oven overnight at 110°C

before used. Other solvents and reagents including 1,1,2,2-tetrachloroethane (AR), phenol (AR) were all provided by Aladdin reagents company.

2.2 Preparation of PBT/PET/SD blends

Before blending, PBT and PET should be dried in a vacuum oven at 110°C for 12 h to remove moisture and prevent hydrolysis of the materials during processing. The PBT/PET/SD blend was prepared by blending using a twin-screw extruder (HTGD-20, Hartek Technologies Co., Ltd). When the content of PET is 30%, the impact strength of the system is the largest, and the tensile strength, bending strength, thermal deformation temperature and shrinkage are also better improved, so the blending ratio of PBT/PET was 70:30 [19], and the SD addition amount was 0.1 ~ 0.5 wt% of the total mass of PBT and PET. For convenience, we defined SD with different mass fractions as SD1 (SD = 0.1 wt%), SD2 (SD = 0.3 wt%), SD3 (SD = 0.5 wt%). The temperature from the extruder barrel area to the extrusion die area was set to 230 ~ 265°C, the feeder speed was constant at 6 rpm, and the screw speed was constant at 80 rpm. After the long extrudate was cooled in a water bath, it was cut into aggregates in a pelletizer, and then dried in a vacuum oven at 110°C. The naming of the blends is shown in Table 1.

2.3 Characterization of blends

2.3.1 Intrinsic viscosities

The intrinsic viscosities (IV) testing was performed in constant-temperature water-bathing by using an Ubbelohde viscometer (VISCO-070) with capillary diameter of 0.7–0.8 μm at $25 \pm 0.05^\circ\text{C}$. polyesters and blends were dissolved at 100°C in mixture solution of phenol and tetrachloroethane (mass ratio 1:1), and the testing solution concentration was fixed at 0.5 g/dL. The testing processes and calculation methods of IV were following the typical testing method of intrinsic viscosity as described in public report [20].

Table 1. The component of PBT/PET blends.

Samples	Component	Ratio of components (wt%)
PBT1	PBT/PET _{0.68}	70/30
PBT2	PBT/PET _{0.85}	70/30
PBT3	PBT/PET _{1.01}	70/30
PBT4	PBT/rPET	70/30
PBT2/SD1	(PBT/PET _{0.85})/SD	(70/30)/0.1
PBT2/SD2	(PBT/PET _{0.85})/SD	(70/30)/0.3
PBT2/SD3	(PBT/PET _{0.85})/SD	(70/30)/0.5
PBT4/SD1	(PBT/rPET)/SD	(70/30)/0.1
PBT4/SD2	(PBT/rPET)/SD	(70/30)/0.3
PBT4/SD3	(PBT/rPET)/SD	(70/30)/0.5

2.3.2 Thermal analysis

The melting and non-isothermal crystallization behaviors of the samples were investigated using a differential scanning calorimeter (DSC, Mettler Toledo). Dry nitrogen was used as a purge gas at a rate of 40 mL/min. The samples for all of the measurements were 5–8 mg. The typical testing procedures of simple melt and melting and crystallization were that the sample initially was heated from 25 to 280°C at 50°C min⁻¹, held at the final temperature for 5 min to eliminate the thermal history, and then cooled to 50°C at 10°C/min to determine the crystallization temperature (T_c). Finally, the samples were heated up to 280°C at 10°C/min to determine the melting point (T_m). For recording the non-isothermal crystallization process, the samples were cooled to 25°C at 40, 20, 10, 5°C/min, respectively, after the first time heated to 280°C and held at the final temperature for 5 min.

Thermogravimetric analyzer (TGA, Mettler Toledo) was used to estimate the thermal stability of blends under nitrogen atmosphere of 40 ml/min. About 5 mg of the samples increased from 25°C to 600°C at 10°C/min to provide the decomposition temperature (thermal weight loss of 5%, $T_{5\%}$).

A two-dimensional X-ray diffractometer was used for testing, and the sample powder was spread horizontally on the sample stage and flattened with a glass slide. The voltage used in the test is 40 kV, the current is 40 mA, and the X-ray wavelength is 1.5418×10^{-10} m. Select the scanning type as Coupled Two Theta/Theta. The scanning steps are divided into three steps, two Theta angles are 20°, 40°, and 60°, each step is 70s, and the effective scanning time is 210 s.

2.3.3 Melt processing rheological measurements

Melt processing rheological measurement analyses were performed by using a stress controlled rheometer (Anton Paar MCR 301) with a plate–plate geometry (plate radius = 25 mm; gap = 1 mm). The complex viscosity $|\eta^*|$, storage modulus G' , and loss of modulus G'' data of the various samples as functions of angular frequency were collected. Temperature levels of 260, 265, 270, and 275°C were applied by an Anton Paar CTD convection heating chamber with nitrogen. Samples with loaded angular frequency sweep from 500 rad/s to 0.1 rad/s (decreasing mode). Time-resolved mechanical spectroscopy measurements were also conducted under nitrogen as described in the public work [21].

2.3.4 Mechanical testing

To test the mechanical property of polyesters blends, the round rod samples with diameter of 1.5 mm were stretched on a universal testing machine (Instron 3367,

England) with speed of 10 mm/min, generally, the effective stretch length was about 2 mm, then the tensile strength and elongation at break could be achieved.

3. Results and discussion

The changes in the molecular-chain structure, thermal properties, crystallization behavior and melt flow properties of polyester under heating and mechanical action are the key concerns in processing. This paper focuses on the impact of modified silica nanoparticles and PET types on PBT/PET blend processing performance.

3.1 Intrinsic viscosity of PBT/PET blends

Polyester is a polymer that degrades when heated. Under poor processing conditions, PBT and PET are prone to transesterification, which results in molecular weight reduction, destroys molecular-chain regularity, deteriorates crystallization performance, and lowers the mechanical properties of the final product. Intrinsic viscosity is the most common molecular weight evaluation index in the polyester industry. Table 1 shows the intrinsic viscosity of the PBT/PET blends discussed herein. Since the two polyesters, PBT and PET, have obviously different intrinsic viscosity values (see Table 1), in order to accurately understand the changes in intrinsic viscosity of the blend before and after melt processing, intrinsic viscosity of the two polyesters was tested after full mixture in the same solvent, which is used as the reference value of the intrinsic viscosity of the polyester before melt blending. It can be seen from Table 2 that the intrinsic viscosity of the blends is biased towards the intrinsic viscosity of PBT. The addition of a small amount of PET with a low intrinsic viscosity has a limited effect on the intrinsic viscosity of the polyester blend after blending. This may be because PBT has strong molecular-chain movement ability, and the number of molecular chains is also dominant (70:30 mixing of raw materials). In addition, regardless of whether the blend contains SiO₂, under the set blending process conditions, the thermal oxidation and thermomechanical degradation of the polymer are relatively weak. When the recycled polyester is blended with PBT, the viscosity

Table 2. The intrinsic viscosity of PBT/PET blends with or without modified nano-silica.

Samples	Blending in solvent (dL/g)	Intrinsic viscosity Melt processing by twin-screw extruder (dL/g)			
		Without SiO ₂	0.1 wt% SiO ₂	0.3 wt% SiO ₂	0.5 wt% SiO ₂
PBT2	0.96	0.93	0.94	0.92	0.94
PBT4	0.93	0.90	0.90	0.89	0.90

value also decreases slightly after mixing. It shows that the use of twin-screw extruder in this study and suitable processing conditions can effectively control the molecular weight of the PBT/PET blends.

3.2 Melt behaviors and thermal stability property

The curves of melting thermal behavior and thermal stability analysis of PBT/PET blends using DSC and TG are shown in Figures 1 and Figure 2, respectively. The corresponding important temperature data are listed in Table 3. Figure 1 displays the DSC secondary heating curve after eliminating the thermal history of the blend. The melting point of the blend is lower than that of the two polyester raw materials to a certain extent. For this reason, in the secondary heating process, the polymer chain in the molten state has a strong mutual interaction as the sample is kept at a high temperature for a long time, which is prone to transesterification, leading to decreased regularity of the molecular chain. During the melting process, the entropy change

Table 3. Thermal property parameters of polyesters and blends.

Sample	T_m (°C)	ΔH_m (J/g)	$T_{d,5\%}$ (°C)	T_{max} (°C)
PBT	223.3	49.11	380	409
PET _{0.85}	252.6	29.82	411	446
rPET	254	35.57	410	445
PBT2	215.6	28.63	384	412
PBT2/SD1			383	415
PBT2/SD2	215.7	31.64	384	411
PBT2/SD3			385	413
PBT4	216.6	32.19	386	412
PBT4/SD1			384	411
PBT4/SD2	218	37.18	388	414
PBT4/SD3			385	412

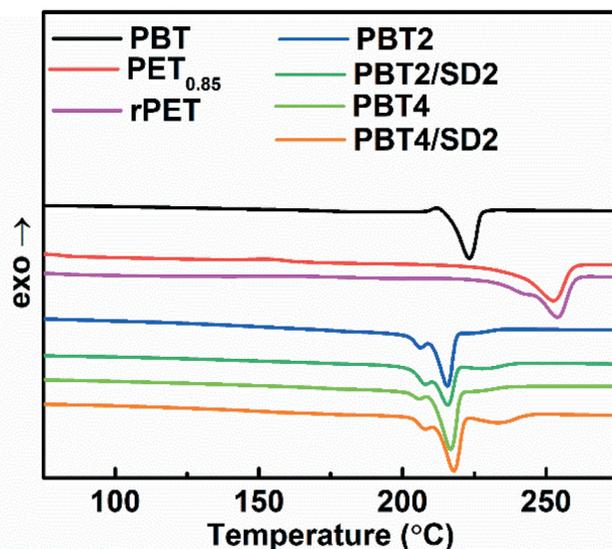


Figure 1. DSC thermograms of polyesters and PBT/PET blends.

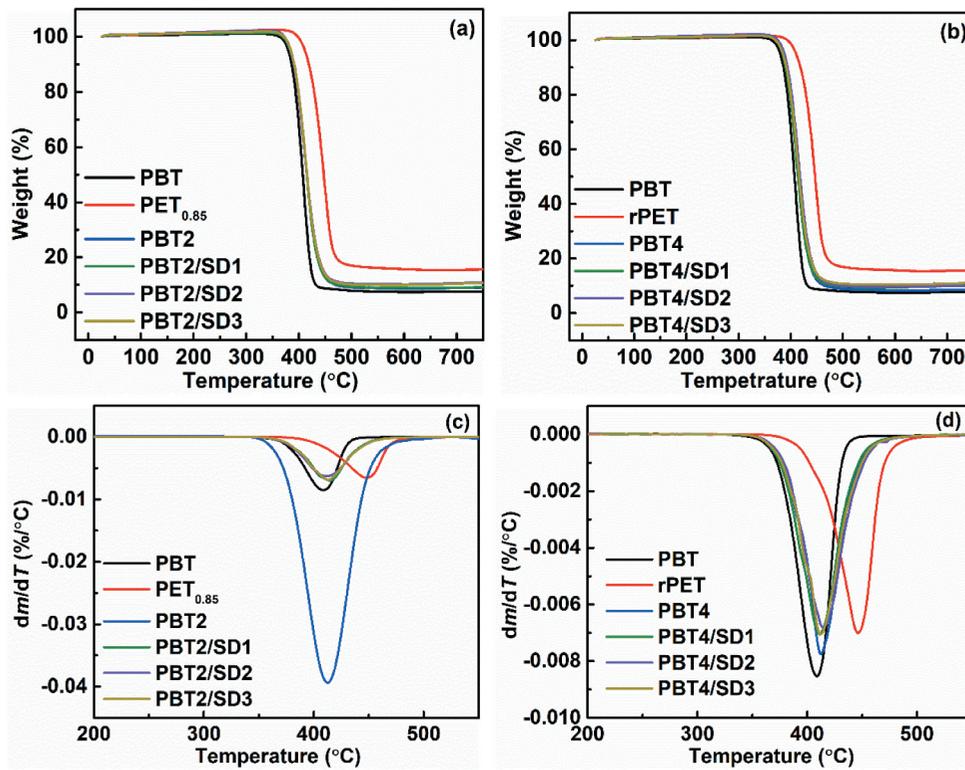


Figure 2. TGA (a), (b) and DTG (c), (d) graphs of polyesters and PBT/PET blends.

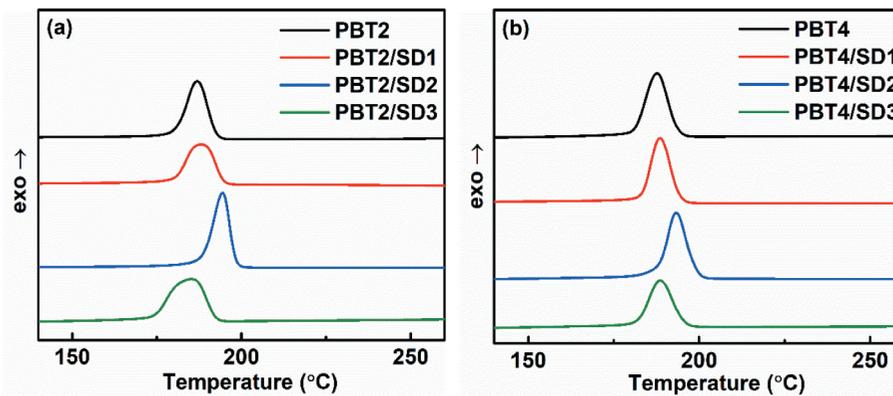


Figure 3. Effect of SD content on crystallization properties of PBT2 (a) and PBT4 (b).

ΔS increases, so the melting point decreases. In the first melting, PBT and PET are incompatible in the crystalline region. The two peaks at low temperature are the melting peaks of PBT [22]. The reason for the additional melting peak is that another crystalline form is formed during the slow cooling process. PBT of the two crystalline forms melts, generating two melting peaks. The blend PBT4 containing rPET has slightly higher melting enthalpy than PBT2. This is because rPET has undergone multiple melt processing treatments, and its molecular chain has a slight cross-linking behavior,

which increases the melting enthalpy. The melting enthalpy of the blend after adding modified nano-SiO₂ (SD) also rises slightly. The main reason for this phenomenon is that SD has a good heterogeneous nucleation effect, which promotes the crystallization of PBT and PET and further improves crystalline, so higher melting enthalpy is needed to melt and collapse the crystal structure.

Figure 2 shows the thermal weight loss (TG) and thermal decomposition rate curves (DTG) of different types of polyester blends. Regardless of what kind of

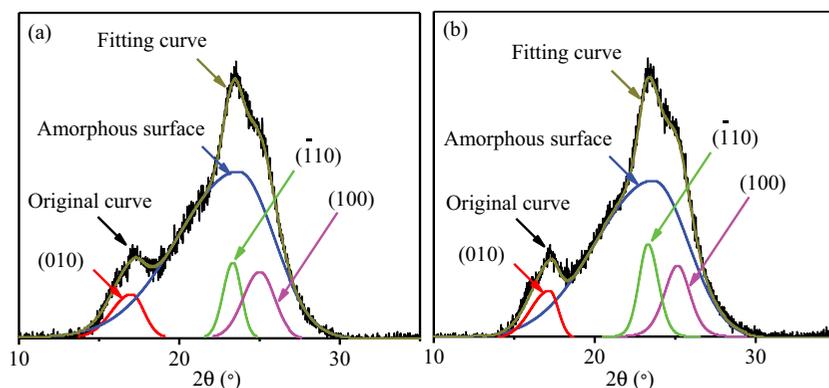


Figure 4. The effect of SD on the crystallinity of PBT2 (a) and PBT2/SD2 by XRD analysis.

Table 4. Crystallization temperature of PBT/PET blends.

Sample	T_c (°C)	$X_{c, DSC}$ (%)	$X_{c, XRD}$ (%)
PBT2	187.18	20.08	22.84
PBT2/SD1	188.34		
PBT2/SD2	194.77	24.75	26.59
PBT2/SD3	185.35		

PET is used, the decomposition curve of its blend with PBT lies between the two raw materials, indicating that PBT and PET are completely physically compatible after blending. In general, there is relatively small thermal stability difference between different blends. In order to specifically quantify and compare the differences between them, two temperature parameters characterizing thermal stability are defined, namely the initial decomposition temperature obtained based on the TG curve at 5% decomposition ($T_{d,5\%}$) and the maximum thermal decomposition rate temperature (T_{max}) obtained based on the DTG curve, are shown in Table 3. The several blends have very similar thermal weight loss curves, indicating that the addition of PET raw materials and SiO₂ has no effect on the thermal stability of PBT/PET blends. For the thermal weight loss rate curve, material containing rPET has obviously faster thermal weight loss rate, which is related to the easy degradation of rPET after multiple melting.

3.3 Crystallization behaviors and non-isothermal crystallization kinetics

Before comparing and analyzing the non-isothermal crystallization kinetics of PBT/PET blends, the effect of different SD addition amounts on the blend crystallization properties was first discussed. As shown in Figure 3 and Table 4, when the SD addition amount is 0.3 wt%, the crystallization temperature is increased by 7.59°C and 5.5°C, respectively, compared with the blends

without SD, and when the SD addition content is 0.1 wt% and 0.5 wt%, the crystallization temperature and the crystallization peak position are almost unchanged, which indicates that An appropriate amount of SD acts as a nucleating agent in the blend system to significantly increase the crystallization temperature of the PBT/PET polyester blend. When the SD addition amount is 0.1 wt%, it may not function as a heterogeneous nucleating agent or crystallization inhibitor due to the low content of additives, which only exists in the form of inorganic reinforcing particles. On the other hand, agglomeration of SD may occur at high content such as 0.5 wt%, and the impact is very limited. Compared with protogenetic PET, the crystallization peak of the product blended with recycled PET and PBT is higher and narrower, indicating that the molecular chains of the PBT/rPET mixture are more likely to be concentrated into crystals. In order to further analyze the effect of SD on the crystallinity, the crystallinities of PBT2 and PBT2/SD2 calculated from XRD were provided representatively to compare with DSC methods. It is noted that the $X_{c, XRD}$ is slightly higher than $X_{c, DSC}$ as XRD can reflect All crystalline regions including dispersed polycrystalline, while the results of DSC method only indicates the relatively complete large crystal. It also can be seen from Figure 4 and Table 4 that the intensity of each diffraction peak increases and the crystallinity of blends with SD increases, which agree with that of results in DSC.

The crystallization behavior of PBT/PET has great research value in the industry. Generally, the crystallization behavior of polymers is mostly studied according to Avrami equation under isothermal conditions. Crystallization is limited to ideal conditions, but since non-isothermal crystallization is closer to production practice, study on the non-isothermal crystallization process of polymers carries better

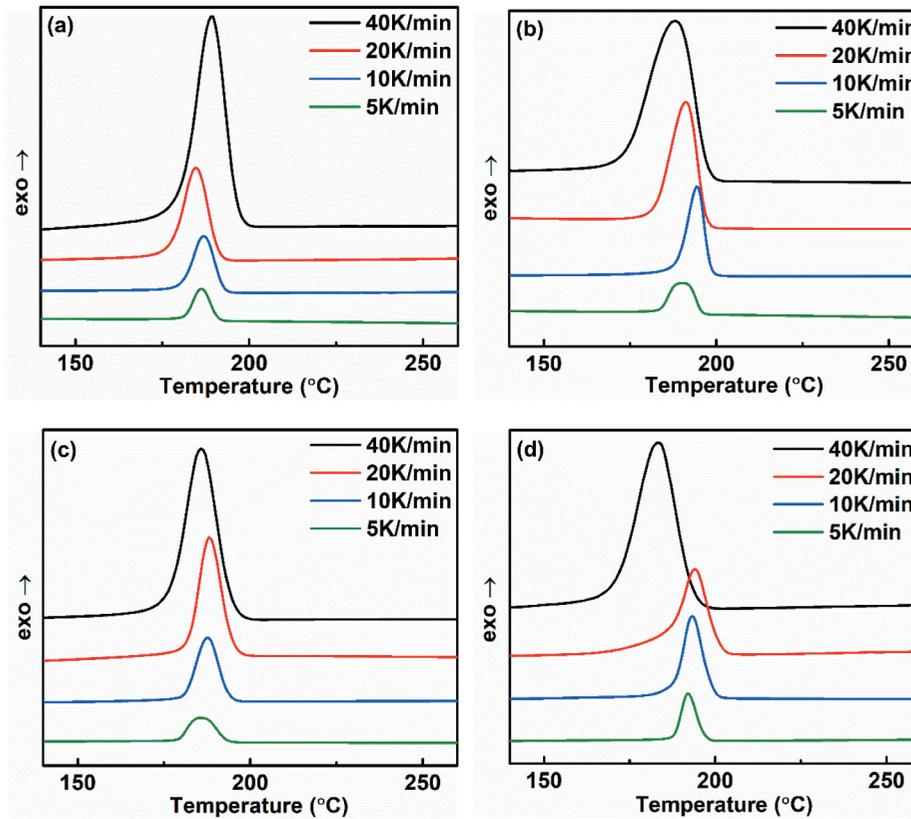


Figure 5. Crystallization curves of PBT/PET blends at different cooling rates, (a) PBT2, (b) PBT2/SD2, (c) PBT4, (d) PBT4/SD2.

guiding significance for actual production [22–24]. The crystallization curves of PBT/PET blends at different cooling rates are shown in Figure 5. The change of cooling rate has roughly the same effect on the non-isothermal crystallization process of different types of polyester blends. As the cooling rate increases, both the crystallization temperature and the crystallization peak move toward the low temperature, and the crystallization peak gets wider. This is because when the cooling rate is low, before the molecular chain is frozen, the polymer molecular chain has sufficient time to move and is regularly arranged, which can complete crystallization in a short time with relatively perfect crystallization. However, at a higher cooling rate, molecular chain has too short residence time at a higher temperature, the molecular chain is frozen before it is rearranged, and it takes longer time to reach the crystallization equilibrium. In addition, PBT4 has wider crystallization peak than PBT2. This is because rPET has undergone more melting processes, and its molecular-chain structure is more complex compared to protogenetic PET. During the crystallization process, PBT molecular chain inhibits the nucleation process, thereby reducing the crystallization rate.

Jeziorny method is a common method for non-isothermal crystallization analysis [25,26]. It takes into account the effect of cooling rate, and corrects the crystallization rate constant using cooling rate based on Avrami equation to obtain the rate constant of non-isothermal crystallization. Figure 6 shows the relationship curve between relative crystallinity and crystallization time of different PBT/PET polyester blends at different cooling rates. It can be seen from the figure that all the curves are S-shaped, and each sample has a clear nucleation process at the initial stage of crystallization. At a lower cooling rate, it takes a longer time to complete crystallization. As the cooling rate increases, the crystallization time shortens.

Avrami equation can be expressed as

$$1 - X_t = \exp(-Z_t t^n) \quad (3.1)$$

$$\lg[-\ln(1 - X_t)] = \lg Z_t + n \lg t \quad (3.2)$$

Where, X_t is the relative crystallinity related to time; n is the Avrami index related to nucleation and growth parameters; Z_t is the crystallization rate constant.

Plot the $\lg[-\ln(1 - X_t)]$ - $\lg t$ diagram for Equation (3.2), the slope is n , the intercept is $\lg Z_t$. Correct the rate constant Z_t using Equation (3.3) based on Jeziorny

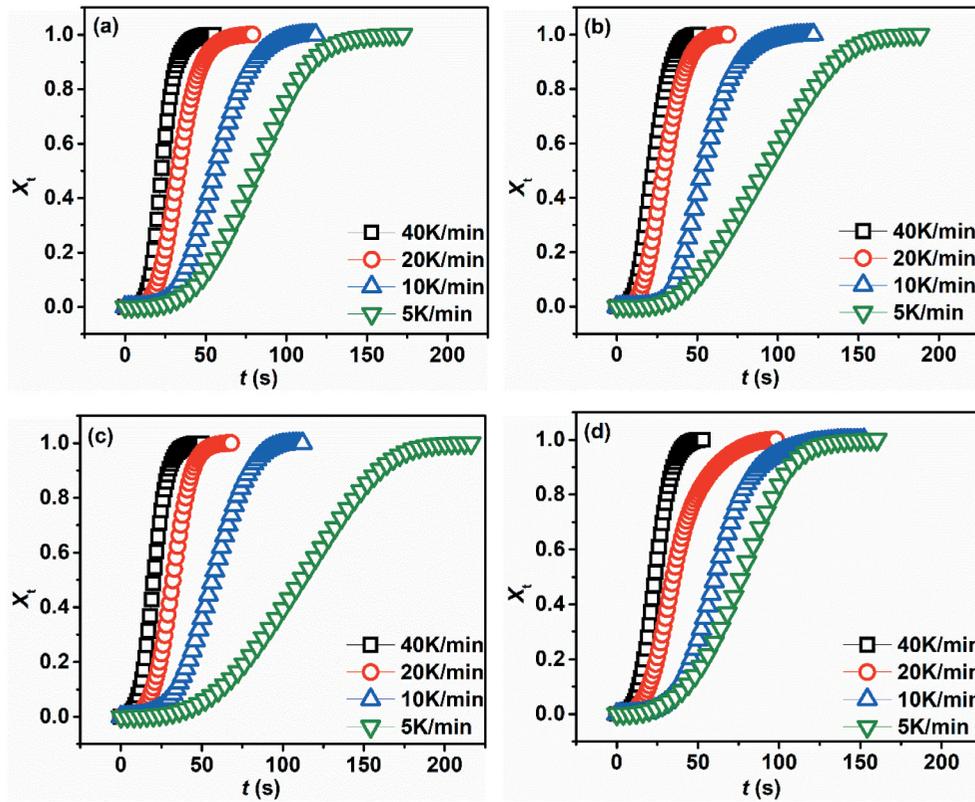


Figure 6. Relationship between relative crystallinity (X_t) and crystallization time of PBT/PET blends at different cooling rates, (a) PBT2, (b) PBT2/SD2, (c) PBT4, (d) PBT4/SD2.

method, and the time required for X_t to reach 0.5 is defined as the half crystallization time ($t_{1/2}$), which is calculated by equation 3.4.

$$\lg Z_c = \lg Z_t / \phi \quad (3.3)$$

$$T_{1/2} = (\ln 2 / Z_t)^{1/n} \quad (3.4)$$

Figure 7 shows the relationship curve of $\lg[-\ln(1 - X_t)]$ vs. $\lg t$ for polyester blends treated by the Jeziorny method at different cooling rates. In the early stage of crystallization, the curve is approximately linear, and there is a slight deviation in the later stage of crystallization. This is because the physical meaning of Z_c and n values of the non-isothermal crystallization process is different from that of the isothermal crystallization process. Both the nucleation rate and crystal growth process are related to temperature. Under non-isothermal conditions, the temperature constantly changes, which will affect the nucleation and growth of crystals. A faster cooling rate will increase the degree of subcooling, making the crystallization temperature move towards the low temperature direction, which will speed up

the movement of polymer molecular chains and increase the crystallization rate, leading to greater curve deviation.

The non-isothermal crystallization kinetic parameters derived from the relationship curve in Figure 6 are listed in Table 5. It can be seen that the Avrami index n of both general polyester and blends is between 3 ~ 4, indicating that heterogeneous nucleation is dominant, homogeneous nucleation and heterogeneous nucleation exist simultaneously, and the crystallization process is complicated. Compared with pure PBT, polyester blend with PET has greater $t_{1/2}$, which makes the crystallization rate smaller. For this reason, PET itself has a slow crystallization rate, and there is excellent compatibility between PBT and PET, resulting in lower crystallization rate of PBT blends with PET. As the cooling rate increases, Z_c increases and $t_{1/2}$ decreases, indicating that the crystallization rate of polyester blends increases with the increasing cooling rate. Under a constant cooling rate, after introducing SD, Z_c of the modified polyester blend decreases slightly and $t_{1/2}$ increases. This is because SD addition interferes with the regular arrangement of polyester molecular chains, leading to lower

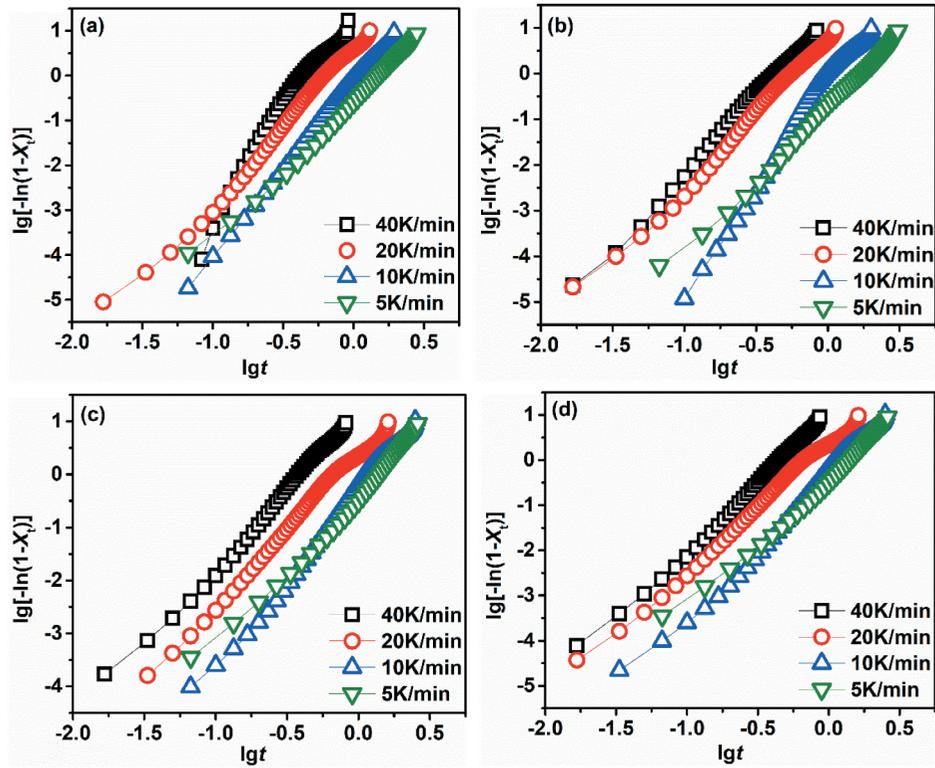


Figure 7. Plots of $\lg[-\ln(1-X_t)]$ versus $\lg t$ for non-isothermal crystallization of PBT/PET blends, (a) PBT2, (b) PBT2/SD2, (c) PBT4, (d) PBT4/SD2.

Table 5. Non-isothermal crystallization kinetic parameters of PBT/PET blends.

Sample	Heat rate (°C/min)	n	Z_t	Z_c	$t_{1/2}$ (min)
PBT	40	3.11	21.7	1.08	0.32
	20	3.02	5.60	1.09	0.47
	10	3.01	1.22	1.02	0.78
	5	3.11	0.254	0.76	1.31
PBT2	40	3.09	45.5	1.10	0.258
	20	3.98	7.22	1.10	0.555
	10	4.13	0.985	0.999	0.918
	5	3.26	0.239	0.751	1.39
PBT2/SD2	40	3.47	1.78	1.01	0.484
	20	3.69	10.1	1.12	0.762
	10	5.55	1.55	1.05	0.864
	5	3.26	0.200	0.725	1.42
PBT4	40	3.34	1.47	1.01	0.587
	20	3.20	3.82	1.07	0.799
	10	3.79	0.616	0.953	1.03
	5	2.73	0.278	0.774	1.40
PBT4/SD2	40	3.26	1.39	1.01	0.591
	20	3.17	3.68	1.07	0.809
	10	3.73	0.601	0.950	1.04
	5	2.60	0.254	0.761	1.47

crystallization rate. The different types of PBT4 in Table 5 have longer $t_{1/2}$ compared to PBT2, which also coincides with the phenomenon that the crystallization peak of PBT4 is wider.

3.4 Rheological analysis

Simple blending between homopolyesters does not significantly improve the performance of the composite material. Adding modifiers to the blend is already the most important way for researchers to improve the material performance [27–30]. Nanofillers can be used as reinforcement materials for unsaturated polyesters. The information on the interaction between the filler and the matrix can be collected through rheological behavior analysis, and flow characteristics of polyester blends are studied using dynamic scanning method [28]. Chirayil et al. [30] investigated the reinforcing effect of nanocellulose on the unsaturated polyester matrix, and the results show that nanocellulose can be uniformly dispersed in the unsaturated resin. Due to the large surface area of nanocellulose, there is a strong interface interaction between the filler and the matrix, which lowers mobility of the polymer chain. Figure 8 shows the effect of SD content on the rheological properties of polyester blends when the shear rate drops from 500 to 0.1 rad/s under a fixed temperature. For blends without SD, at a lower shear rate, the rheometer detects the movement behavior of the local molecular chains in the

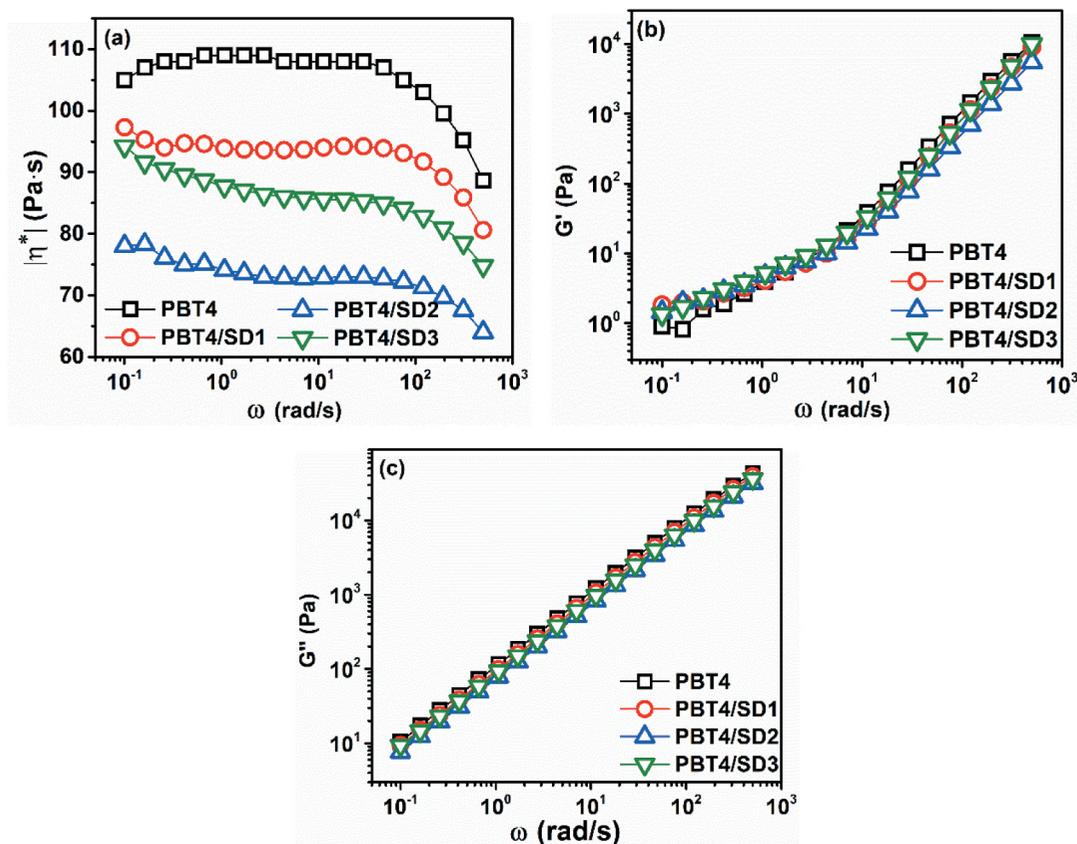


Figure 8. Rheological behaviors curves of PBT/PET blends with different content of SD, (a) complex viscosity, (b) storage modulus, (c) loss modulus.

blend, which does not reflect the true viscosity value of the blend system. When the shear rate is increased from the medium range to the high shear rate range, the polyester blend changes to a normal shear-thinning fluid rather than maintaining Newtonian behavior. This is consistent with the results of our previous rheological analysis of PET with different intrinsic viscosities [4]. When a small amount of SD is added, since the surface of the modified nano-silica has hydroxyl groups, there is a bridging effect between the polyester molecular chains, which weakens the molecular-chain mobility and increases the shear viscosity of the blend. When the SD content is increased, SD exerts a certain plasticizing effect on the polyester molecular chains and reduces the viscosity of the blend system. If SD content continues to increase, SD itself will aggregate and reduce the plastic effect. The loss modulus and storage modulus curves in Figure 8 also indirectly confirm this law. Due to the use of logarithmic coordinates, there is an insignificant apparent difference in modulus between different blends.

The curves describing the influence of SD and PET sources on the rheological properties of polyester blends under different temperatures are shown in

Figures 9–12. Generally speaking, the viscosity of polymer melt decreases with the increase in experimental temperature. The viscosity and modulus of the sample PBT2 follow this principle when the test temperature rises from 265 to 275°C, but at 260°C, the sample viscosity and modulus are higher than 275°C (Figure 8). For this reason, when the PET melting point temperature (260°C) is slightly exceeded, its molecular-chain mobility is weak. At this time, there will be no entanglement between PBT molecular chain and PET molecular chain. After the temperature rises, PET activity increases. Due to the natural affinity of the two molecular chains, transesterification or entanglement may occur. Therefore, the blend has a higher viscosity at 265°C than at 260°C. As the temperature further rises, the rigid polyester exhibits normal temperature-sensitive behavior, with its viscosity decreased. Seen from the modulus curve, the elastic modulus between blends at different temperatures has a greater difference than the loss modulus, which also confirms the temperature effect on the movement behavior of molecular chains. It is worth noting that in the low shear rate range, the shear thinning behavior of polyester blends weakens with increasing temperature.

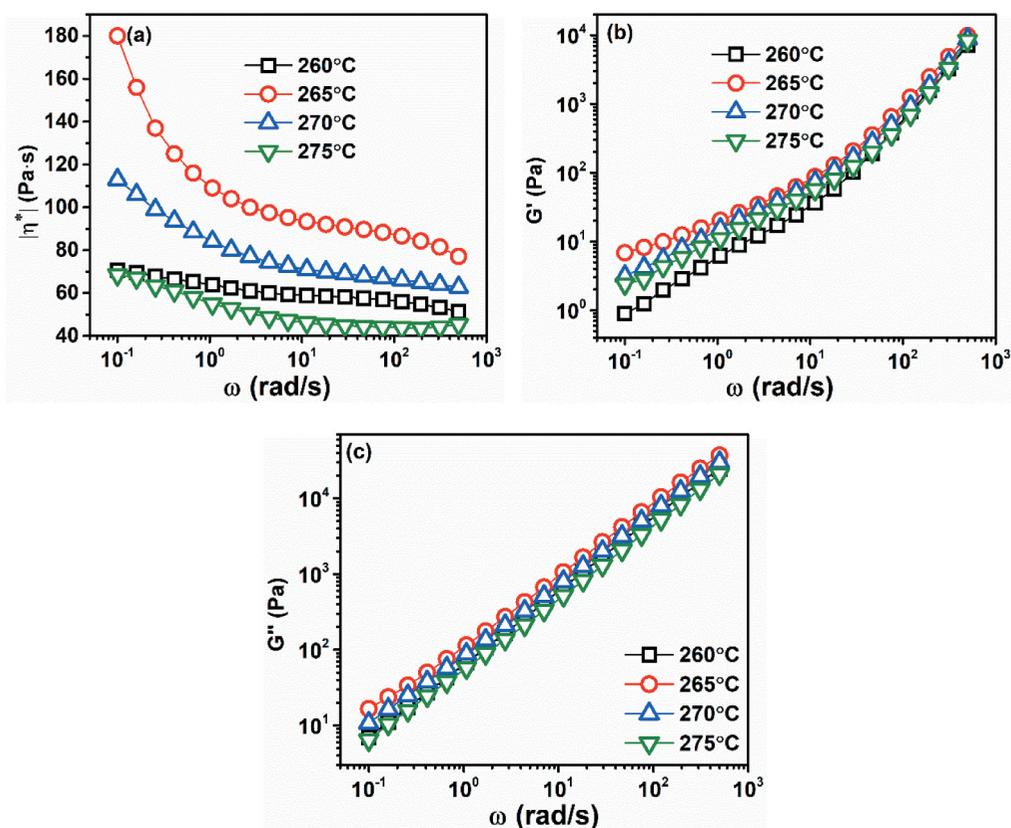


Figure 9. Effect of temperature on the rheological behaviors of PBT2, (a) complex viscosity, (b) storage modulus, (c) loss modulus.

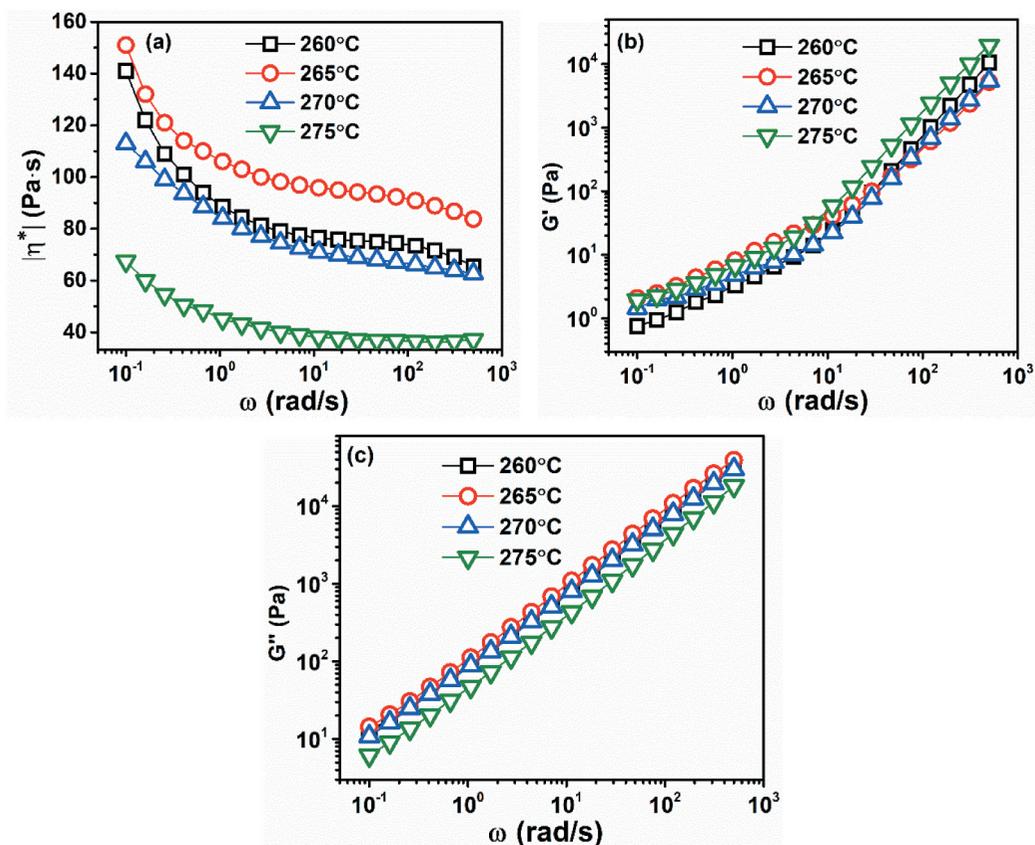


Figure 10. Rheological behaviors of PBT2/SD2 at different temperatures, (a) complex viscosity, (b) storage modulus, (c) loss modulus.

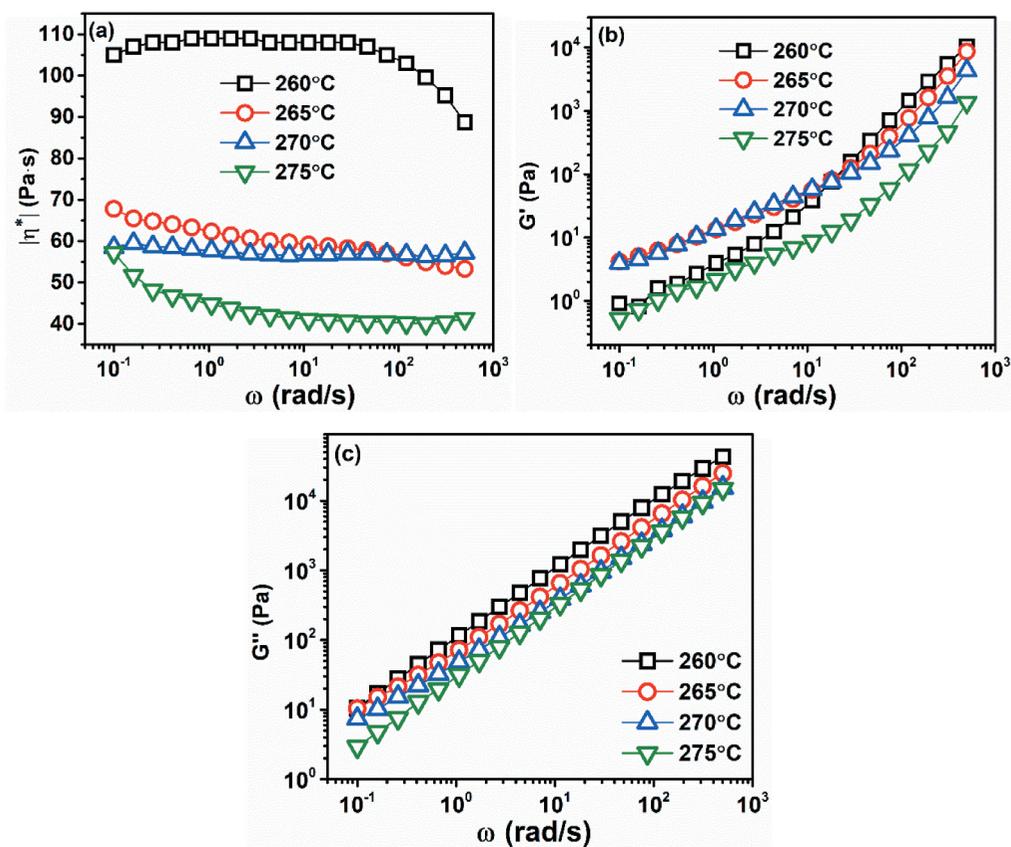


Figure 11. Rheological behaviors of PBT4 at different temperatures, (a) complex viscosity, (b) storage modulus, (c) loss modulus.

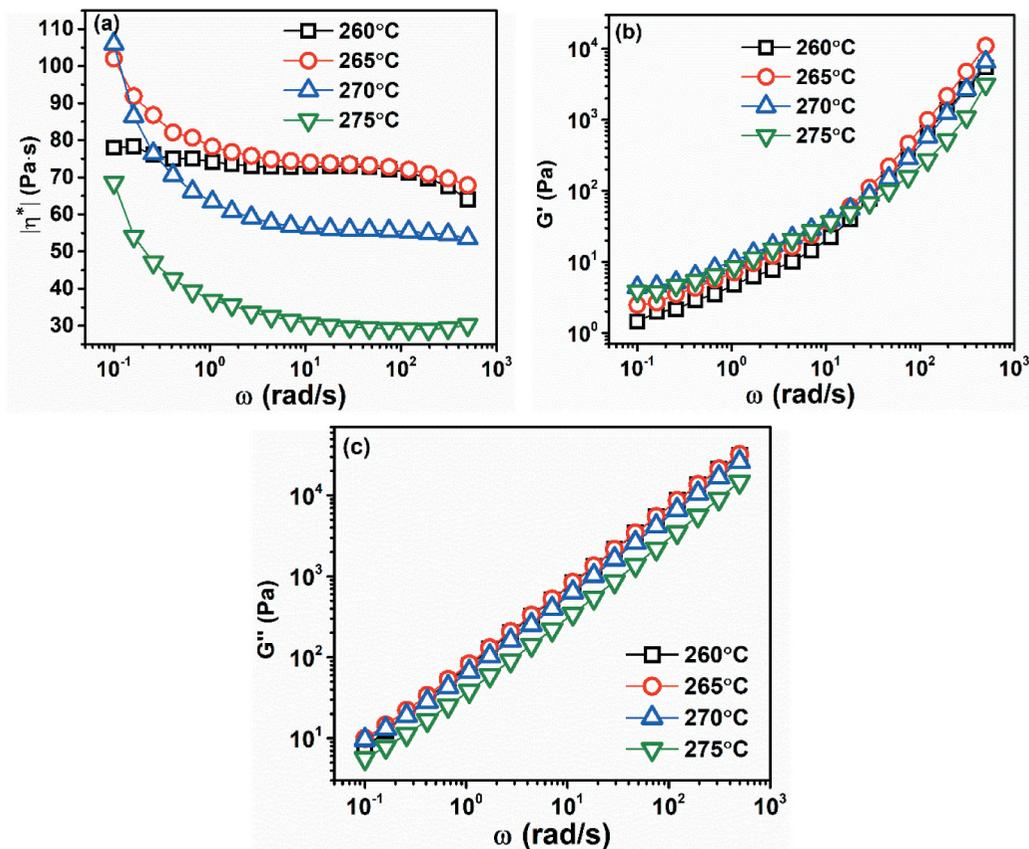


Figure 12. Rheological behaviors of PBT4/SD2 at different temperatures, (a) complex viscosity, (b) storage modulus, (c) loss modulus.

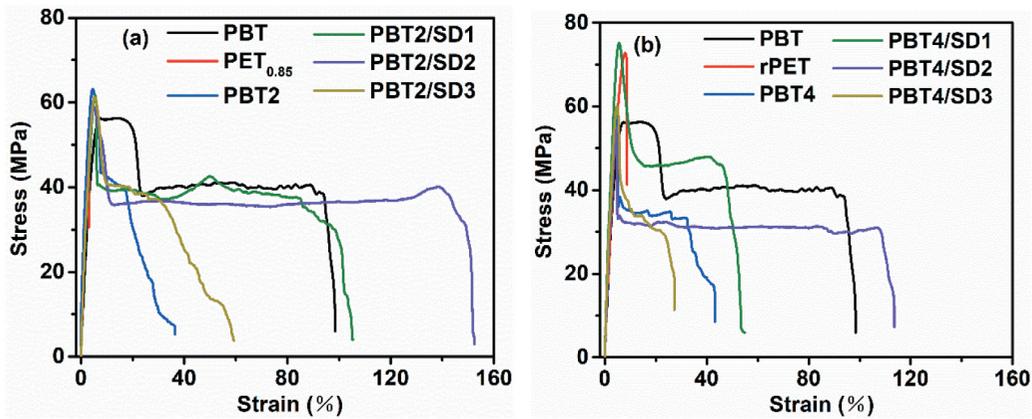


Figure 13. The tensile properties of PBT/PET blends with different content of SD, (a) PBT2, (b) PBT4.

Figure 10 is a blend of PBT containing SD and PET_{0.85}. After SD addition, the rheological parameters of the copolymer decreases under different temperatures, indicating that SD exerts lubrication effect, and reduces the entanglement between the two polyester molecular chains, so that the mobility of the polyester molecular chains is higher. Another feature is that, compared with the blends without SD (refer to Figure 9), blends with SD demonstrate more pronounced shear thinning properties at low shear rates. At 260°C, the system viscosity increases after adding SD. This is because when the temperature is not high, SD acts as a bridge between the two molecular chains, so that the blend viscosity increases rather than decreases.

Figure 11 shows the blend rheological curve of recycled PET and PBT when SD is added. Since PET has undergone multiple melt processing, its molecular-chain structure is damaged to a certain extent. In addition, PET used in this study has higher intrinsic viscosity than rPET. Therefore, the molecular weight of PET is higher among PBT2 copolymers. Owing to the two factors, blend with rPET has significantly lower rheological parameters than blend using protogenetic PET. Surprisingly, the complex viscosity of the blend returns to the general rule that the polymer viscosity decreases with increasing temperature. The possible reason is that rPET undergoing more melting processes has a wider melting range (as shown in the DSC curve in Figure 1), some molecular chains have strong activity at low temperatures, but the entanglement with PBT reduces their mobility. In the storage modulus curve, the blends at low temperature (260°C) have great changes at low shear rates and high shear rates, indicating that blends containing rPET have poorer elasticity at low shear rates, which indirectly confirms that the rPET molecular chain is previously destroyed.

Figure 12 is the rheological curve of the blend of PBT containing SD and rPET. The addition of SD enriches the rheological behavior of blends at different temperatures. Compared with the PBT4 sample without SD,

the blend has lower complex viscosity at low temperature (260°C) and high temperature (275°C), and the complex viscosity value increases in the medium processing temperature range, indicating that SD lubrication effect or bridging action relates to the processing temperature. Under low temperature and low shear rate, the polyester blend exhibits Newtonian properties, which is different from the rheological behavior of the blend with protogenetic PET polyester. At higher temperatures and lower shear rates, it turns to obviously non-Newtonian type. This has important reference significance for selecting optimized processing temperature and shear rate of copolyester.

3.4 Mechanical property

Figure 13 shows the effect of PET variety and SD content on the tensile properties of the blend. In general, due to the small performance difference between the two polyesters and small SD addition amount, there is an insignificant difference in strength between the two series of polyester blends: PBT2 and PBT4. Protogenetic PET has relatively high intrinsic viscosity and small elongation at break, while recycled PET has a higher stress value because its molecular-chain structure is not as pure as protogenetic PET. PBT obviously has greater extensibility due to the better flexibility of the molecular chain. PBT4 has longer elongation than PBT2 after the two are blended. This may be because rPET is distributed as a dispersed phase in the continuous phase of PBT, which makes it easier to entangle with the PBT molecular chain and renders better elasticity. However, when equal amount of SD is added, the elongation of PBT4/SD sample gets lower. This is because the hydroxyl group on the SD can act as a bridge between the two polyesters and produce

entanglement effect, while protogenetic PET obviously has more long-chain molecules, leading to better elasticity of PBT/SD blends. With the increase of SD content, the blend elongation exhibits an interesting phenomenon of first increase and then decrease. A possible reason is that when the SD in the blend increases from 0.1 wt% to 0.3 wt%, more SD can exert bridging action and render better blend elasticity, but when even more SD exists, it cannot play a connecting role due to its own characteristics of easy aggregation. In fact, many inorganic particles can exert a toughening effect on polymer blends under a small amount, but when the content is excessive, the mechanical properties will decrease instead [31].

4 Conclusions

The blended materials of protogenetic PET and recycled PET with PBT were prepared by twin-screw extrusion, and the effect of adding different contents of modified silica on the melt processing performance of PBT/PET blends was analyzed. Thermal analysis shows that the polyester blend has excellent compatibility. The blend has only one melting peak and a crystallization peak. After blending, its melting point is lower compared to the two polyesters, and there is a small melting peak. The thermal decomposition temperature of the blend is between that of the two polyesters, while the maximum thermal decomposition rate of the blend using protogenetic polyester is small. The analysis of non-isothermal crystallization kinetics shows that an appropriate amount of SD can effectively promote the blend crystallization, while the results will be opposite when SD is too low or too high. The addition of SD can reduce the crystallization rate of PBT materials with PET and extend the crystallization time. Experiments show that the rheological behavior of PBT/PET blends is complicated. The addition of PET raw materials, SD, as well as melt processing temperature, and shear rate values will all affect the rheological behavior of the blends. At a low shear rate, the addition of SD will cause the polyester blend to exhibit strong shear thinning behavior. The effect of SD content on the rheological property of the blend is similar to its effect on the crystallization behavior. There is an ideal addition amount in both cases. When the melt processing temperature is higher than 265°C, the blend will show conventional temperature sensitivity, while it is not the case when the temperature is too low. In addition, the test results of the mechanical properties of the blends show that the tensile strength of blends of different compositions is not greatly different, while the elongation at break increases from 0.1 wt% to 0.3 wt% with the increasing

SD content, but drops significantly under 0.5 wt% SD content. It can be seen that by selecting suitable PET raw materials and adding SD in an appropriate amount, a polyester blend product with further improved melt processability and elongation can be obtained.

Disclosure statement

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