

Effect of Cryomilling on the Thermal Behaviors of Poly(ethylene terephthalate)

Y. G. Zhu,¹ Z. Q. Li,¹ D. Zhang,¹ T. Tanimoto²

¹State Key Laboratory of Metal Matrix Composites, Shanghai Jiaotong University, Shanghai 200030, People's Republic of China

²Department of Materials Science and Ceramic Technology, Shonan Institute of Technology, Tsujido-Nishikaigan 251, Japan

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ABSTRACT: We have studied the effect of cryomilling (high-energy ball milling under cryogenic temperature) on the thermal behaviors of poly(ethylene terephthalate) (PET) by comparing with original PET and quenched PET. Cryomilling induced the amorphization of crystalline PET, but the thermal behaviors of amorphous PET obtained from cryomilling are significantly different to those of amorphous PET obtained from quenching. Unlike amorphous PET obtained from quenching, the heating curve of amorphous PET obtained from cryomilling shows no cold crystallization peak, but evidences are found that its cold crystallization occurs within a wide temperature range. In addition, the

stability of amorphous PET obtained from cryomilling is higher than that of amorphous PET obtained from quenching. The difference is proved to be attributed to the stored energy in cryomilled PET. The hot crystallization behaviors of PET improve a lot after cryomilling, and the heat stability of cryomilled PET is also better than those of original PET during reheating. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 2868–2873, 2006

Key words: cryomilling; abnormal thermal behaviors; differential scanning calorimetry

INTRODUCTION

Mechanical alloying (MA) is a well-established technique for processing metals and ceramics with fine microstructures since 1960s.¹ It is a high-energy ball-milling process in which the repeated fracture and welding of powder particles, arising from ball-powder collision events, enables true alloy powders to be formed from mixtures of elemental powders.² In 1988 Shaw and Pan^{2,3} explored the concept that MA could be applied in polymer field. To overcome the ductile and viscoelastic nature, mechanical alloying of polymer was modified to process under cryogenic temperature induced by cryogenic media such as liquid nitrogen. This adapted technology was mostly referred as cryogenic mechanical alloying or cryomilling. Cryomilling is to process the polymers in solid state, which avoids the viscosity, infusible, and insoluble problems

of polymers, while has the ability to fabricate polymer materials with special structure and performance, and so it is becoming more prevalent in recent years. Previous researches have not only proved the efficacy of cryomilling to improve blending intimacy and compatibility between polymers,^{4–7} but proved the ability to induce abnormal behaviors such as anomalous phase inversion,⁸ second glass transition in amorphous polystyrene and structural phase transformation in high-density polyethylene.⁹ However, cryomilling of polymers has not yet been fully explored and the fundamental operative mechanisms have not been elucidated. Up to present, only a little attention has been paid to the effect of mechanical milling on the thermal behaviors, although it plays an important role in the microstructure, processing, and properties of the polymers. Joan et al.¹⁰ and Bai et al.¹¹ analyzed only the cold crystallization behaviors (crystallization during heating process) of PET with different crystallinities after ambimilling (ball milling under ambient temperature), but did not analyze the hot crystallization behaviors (crystallization during cooling process) and reheating behaviors, which are also of great values. In this work, we present a thorough study of the effect of cryomilling on the thermal behaviors of PET by comparing with those of original PET and quenched PET during first heating, cooling and second heating of differential scanning calorimetry.

Correspondence to: Z. Q. Li (lizhq@sjtu.edu.cn).

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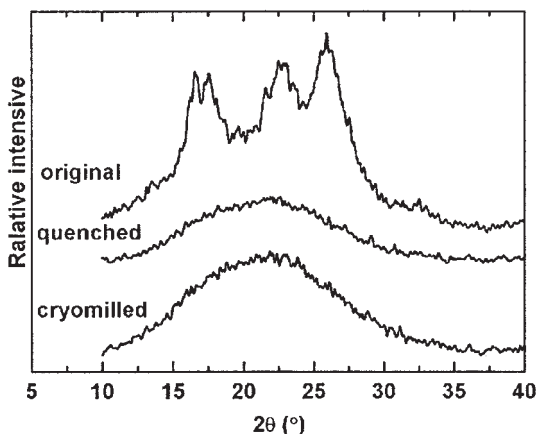


Figure 1 XRD patterns of three different PET samples.

EXPERIMENTAL

The PET pellets were synthesized in the nanoengineering center lab. Before use, PET pellets were pulverized by a commercial pulverator, the average particle size of obtained powders was about $303\ \mu\text{m}$ measured by a SALD-2000 Laser Diffraction Particle Size Analyzer. These powders were treated at 160°C for 3 h to attain the crystalline PET, which is hereafter referred to as "original PET." Original PET had a crystallinity of 31%, determined by Differential Scanning Calorimetry and X-ray Diffraction, and its intrinsic viscosity was $0.663\ \text{dL/g}$. In addition, quenched PET was obtained by heating the original PET to 280°C , and then quenching it using the liquid nitrogen.

Original PET was cryomilled in a stirring mill at a rotating speed of 900 rpm. Appropriate amounts of original PET and stainless steel balls (6 and 8 mm in diameter, a ball-to-powder weight ratio of 60 : 1) were put into a stainless steel vial. The temperature inside the inner vial was maintained at -150°C or so by introducing the liquid nitrogen into the outer vial and the resulting nitrogen gas was introduced into the inner vial to provide a protective atmosphere. The cryomilling duration added up to 10 h. The final powders are hereafter referred to as "cryomilled PET," whose average particle size was $9.6\ \mu\text{m}$ as measured by a SALD-2000 Laser Diffraction Particle Size Analyzer.

The polymer's thermal behaviors were performed on a TA differential scanning calorimeter (DSC) under a nitrogen purge. The powders were heated to 280°C at a rate of $10^\circ\text{C}/\text{min}$, maintained at 280°C for 3 min to erase the thermal and stress history, and then allowed to cool to the room temperature at the rate of $10^\circ\text{C}/\text{min}$, following that the second heating was performed at the same speed rate, recording the heating and cooling curves of whole procedure. The degree of crystallinity of PET before heating in the DSC was

calculated by subtracting the heat of crystallization from the heat of fusion and by dividing the heat of fusion for 100% crystalline PET ($142\ \text{J/g}$). X-ray Diffraction measurement was conducted on D8 Advance Diffractometer with $\text{Cu K}\alpha$ radiation. Intrinsic viscosities of original PET and cryomilled PET were measured using the viscosity meter in phenol-tetrachloroethane (1 : 1) mixture solution at 25°C .

RESULTS AND DISCUSSION

Xrd analysis

The XRD patterns provide additional insight into the effects of cryomilling on PET at the molecular level. The XRD patterns of three different states PET are shown in Figure 1. We can see that the original PET has obvious diffraction peaks, but cryomilled PET only has an amorphous peak, which indicates that cryomilling resulted in amorphization of crystalline PET. This is consistent with the previous researches.^{10–12} We call the amorphous PET obtained from cryomilling as "cryomilled amorphous PET." Quenched PET is amorphous too, and we refer it as "quenched amorphous PET." From Figure 1 we found that although both quenched PET and cryomilled PET are amorphous, their XRD patterns have some difference. We consider that this might be due to the different amorphous formation mechanism from melting state and solid state, respectively. Further research is in progress.

First heating DSC thermograms

The DSC first heating thermograms of three different states of PET are shown in Figure 2, and the thermodynamic data are listed in Table I. Obviously, the thermal behaviors of cryomilled amorphous PET not

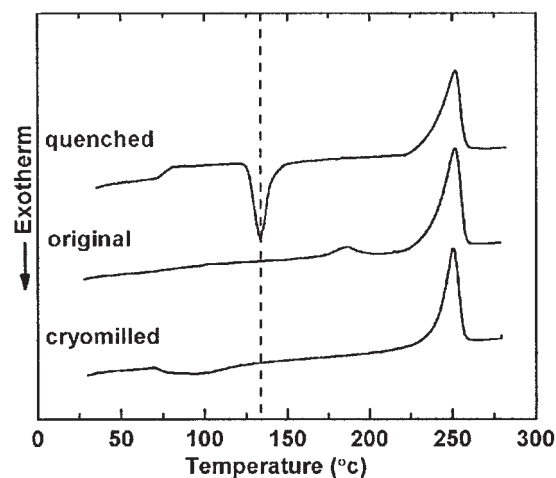


Figure 2 DSC first heating thermograms of three different PET samples.

TABLE I
Thermodynamic Data of DSC First Heating of Different States of PET

Samples	T_g (°C)	T_c^a (°C)	ΔH_c^b (J/g)	T_m (°C)	ΔH_m (J/g)	Crystallinity (%)
Quenched PET	76.1	133.5	33.68	251.22	40.45	4.77
Original PET	–	–	–	251.61	44.31	31.20
Cryomilled PET	–	90	12.51	250.53	39.34	18.89,27.7 ^c

^a T_c represents the exothermal peak temperature.

^b ΔH_c represents the exothermal heat of the T_c peak.

^c The crystallinity is 18.89% and 27.7%, respectively, when the broad exotherm round about 90°C is induced by the cold crystallization or not.

only differ from those of the original PET, but also differ from those of quenched PET. The DSC thermogram of original PET shows two endothermic peaks: first one is small, corresponding to the annealing treatment¹³; the second corresponds to the melting. Quenched amorphous PET shows an exothermic peak and an endothermic peak, corresponding to the cold crystallization and the melting, respectively. Cryomilled amorphous PET has two abnormal phenomena when compared with quenched amorphous PET: (1) the glass transition deviates towards the exothermal direction, and then shows an unusual broad exotherm round about 90°C, which is different with usual exothermic crystallization peak; (2) has a strong melting peak, which means cryomilled PET has a high crystallinity (referring to Table I), but the XRD pattern of cryomilled PET in Figure 1 appears almost totally amorphous. That is to say, even if the broad exotherm is induced by the cold crystallization, the crystallinity (18.89%) of cryomilled PET deduced from XRD is inconsistent with the DSC measurements.

About the exotherm round about 90°C, some researchers^{10,11} considered that it was induced by the cold crystallization, but they did not give evidence. To validate this viewpoint, we did a series of XRD tests to observe the crystallinities of cryomilled PET at different temperatures during DSC heating. Selecting five temperatures from 90 to 200°C, cryomilled PET was heated to the selected temperature at a heating rate of 10°C/min, respectively, and then immediately cooled to the room temperature, following this XRD test was performed, and the XRD patterns were shown in Figure 3. As shown in the figure, at 90°C, its XRD pattern did not show any change when compared with that of untreated cryomilled PET, which means that the broad exotherm round about 90°C cannot be the crystallization exotherm; at 120°C, it shows some difference, which indicates the crystallization of cryomilled PET occurs about 120°C. The degree of crystallinity is too low to be detected by XRD and so there is no diffraction peaks in its XRD pattern. At 130°C, the diffraction peaks appear, though they are weak; at 160°C, the diffraction peaks are distinct; and at 200°C, they become strong. The changes of the intensity of diffraction peaks indicate that the cold crystallization

proceeds gradually with increase in the heating temperature. From XRD test, we can obtain two conclusions: one is that the exotherm round about 90°C is not induced by the cold crystallization; the other is that the cold crystallization of cryomilled amorphous PET occurs in DSC heating, but its process is slow and its temperature scope is wide from about 120°C to ahead of the melting temperature and so there is no obvious cold crystallization in DSC heating. That is, the right reason that the degree of crystallinity of cryomilled PET deduced from XRD is entirely inconsistent with DSC measurements.

DSC measurements for the treated cryomilled PET at 90 and 120°C, respectively, were done again (shown in Fig. 4). Figure 4 shows that the base line of the cryomilled PET treated at 90°C (Fig. 4(b)) decreases from 90°C, and then overlaps with that of the untreated cryomilled PET (Fig. 4(a)) from about 100°C. If the exotherm round about 90°C is induced by the cold crystallization, the treated sample at 90°C should begin crystallization at the lower temperature than untreated sample, since the crystal nucleus formed during heat treatment can hasten crystallization. But Figure 4(b) is contrary to the assumption, which indicates further that the exotherm cannot be induced by the cold crystallization. The treated sample at 120°C (Fig.

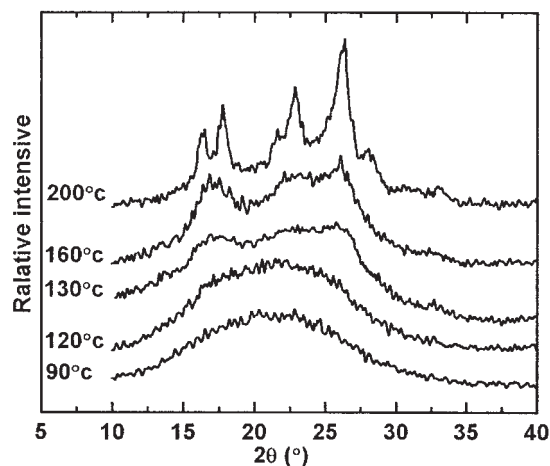


Figure 3 XRD patterns of cryomilled PET treated with different temperatures.

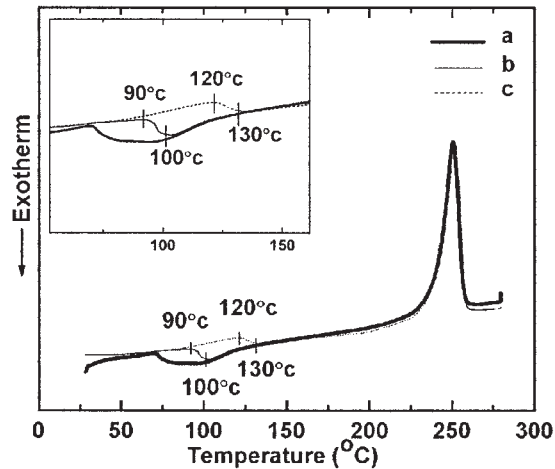


Figure 4 DSC heating thermograms of cryomilled PET: (a) without heat treatment (thick solid line), (b) with heat treated to 90°C (thin solid line), (c) with heat treated to 120°C (short dash line).

4(c)) shows no exothermic peak during DSC heating, and decreases from 120°C, and then overlaps with that of untreated sample from about 130°C. These indicate that the heat treatment at 120°C cannot eliminate completely the effects of cryomilling on PET, but only some effects. From Figure 4, we can surmise that the heat treatment at different temperatures may eliminate part effects of cryomilling on the cryomilled PET through releasing the heat quantity. During cryomilling, PET powders suffered continuously deformation, fracture, and cold-welding because of the high-frequency collision and grinding coming from steel balls, which not only made the molecular chain abrupt and produced free radicals, but produced a lot of defects and stress. So cryomilling not only induced the molecular chains to produce physical interpenetration and crosslinkage, but made powders own large surface energy, defect energy, and strain energy. That is to say, cryomilled PET is in the semistable state due to the high stored energy. During heat treatment, cryomilled PET released the stored energy by releasing the heat quantity. When heated to the glass transition temperature, the molecular segments can move, and the heat capacity should make the base line to move towards endothermic direction, but the base line of the cryomilled PET deviates to exothermic direction, which just proves the existence of the stored energy. The broad exotherm round about 90°C is the stress relaxation, not the cold crystallization. When heated to the cold crystallization temperature, quenched amorphous PET crystallizes and shows a sharp and strong exothermic peak at 133.5°C, but cryomilled amorphous PET did not show any crystallization peak, but its cold crystallization occurs undoubtedly upon heating in DSC (refer Fig. 3). We consider that the stored energy may restrain the molecular segments from get-

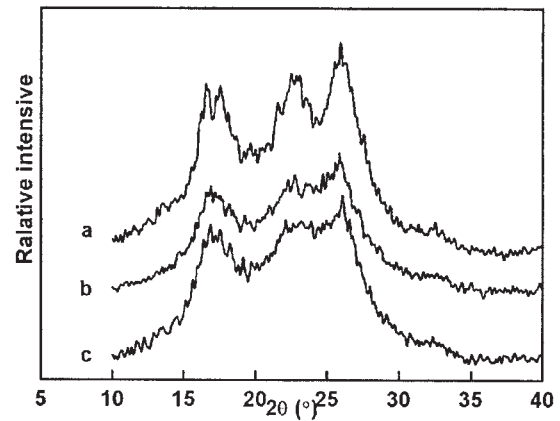


Figure 5 XRD patterns of (a) original PET (treated at 160°C for 3 h), (b) cryomilled PET treated at 160°C for 3 h, (c) cryomilled PET treated at 160°C, and then cooled.

ting arranged into the crystal lattice: the different kinds of stored energies release at different temperatures. That is to say, the stored energy release slowly and the molecular segments arrange gradually into the crystal lattice with increase in heating temperature. This shows that the crystallization of cryomilled amorphous PET is a slow process with a wide temperature scope (from about 120°C to ahead of the melting temperature). These results suggest that the cold crystallization of cryomilled amorphous PET is harder, and its amorphous stability is higher than that of quenched amorphous PET.

Cryomilled PET was heated to 160°C at a rate of 10°C/min, maintained at 160°C for 3 h, and its XRD pattern is shown in Figure 5. The XRD pattern of both cryomilled PET (which is only treated to 160°C and then cooled immediately to the room temperature) and original PET is shown in Figure 5 for comparison. It is easy to found that, the crystallinity of cryomilled PET does not increase with the longer heat treatment

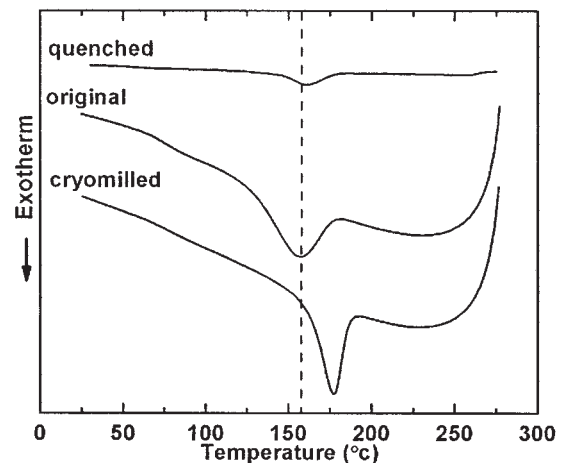


Figure 6 DSC cooling curves of three different PET samples.

TABLE II
Values of Crystallization Parameters of Different PET Samples

Samples	T_p (°C)	ΔW (°)	ΔH_c (J/g)	Crystallinity (%)	ΔT (°C)
Quenched PET	159.00	25.4	27.36	19.3	89.56
Original PET	157.11	26.7	25.84	18.2	91.71
Cryomilled PET	176.89	13.7	36.73	25.9	72.40

time, and its obtainable crystallinity is given at the given heat treating temperature. Furthermore, the crystallinities of cryomilled PET and original PET are obviously different, even if treated at the same condition (160°C for 3 h), and the crystallinity of cryomilled PET is evidently smaller than that of original PET. These results also prove that the stability of cryomilled amorphous PET is higher than that of quenched amorphous PET.

Cooling DSC thermograms

To analyze the effect of cryomilling on the hot crystallization of PET samples, we obtain the DSC cooling curves of three different samples (shown in Fig. 6), and the values of crystallization parameters are shown in Table II. The hot crystallization behaviors can be analyzed from the temperature (T_p) of the exothermic peak, the full width at half maximum (ΔW) of the exothermic peak, the crystallization enthalpy (ΔH_c) and the degree of supercooling (ΔT). T_p is the function of the cooling speed, and can measure the degree of supercooling. ΔW can estimate the distribution of the crystal sizes, and the smaller the ΔW is, the narrower the distribution of the crystal sizes is. ΔH_c can characterize the degree of crystallinity. ΔT is the differential value of the melting temperature in the second heating DSC and T_p . It can judge the rate of crystallization, and the smaller ΔT is, the bigger the rate of the hot crystallization is. We used the T_m in the second heating curves other than that in the first heating curves, since T_{m1} may subject to the effect of the cryomilling history.

From Table II we can see that the values of crystallization parameters of original PET and quenched PET are similar, since the melting treatment has eliminated the heat history. T_p of cryomilled PET moves towards the higher temperature obviously, besides from the changes of the ΔW , ΔT , and ΔH_c , we can all infer that the distribution of the crystal sizes become narrow, the crystallinity and the rate of crystallization increase after cryomilling. These are advantageous to PET processing and application: the narrower distribution of the crystal sizes is benefit to the mechanical performance; the decreased ΔT can reduce the processing temperature of the mold; the increased rate of crystallization can shorten the processing time. We consider the improvement of the hot crystallization behaviors in cryomilled PET, may be explained from two aspects: one is the molecular weight; the other is con-

taminations. The intrinsic viscosities of original PET and cryomilled PET are 0.663 dL/g and 0.580 dL/g, respectively. We counted the viscosity average molecular weight using the Mark-Houwink equation¹⁴ given by:

$$\eta = kM_\eta^\alpha,$$

where η is intrinsic viscosity; k and α are system constants with relation to the polymer, solvent, and temperature ($k = 1.27 \times 10^{-4}$, $\alpha = 0.86$); M_η is the viscosity average molecular weight. The viscosity average molecular weight of original PET and cryomilled PET are 21,034 and 18,004 g/mol, respectively. That is to say, cryomilling reduces the molecular weight of PET, and increases the mobility of molecular chains; consequently, the hot crystallization behaviors of cryomilled PET improve.¹⁵ In addition, we measured the content of contaminations in cryomilled PET, and the contents of Fe and Cr are 0.1594 and 0.005%, respectively. The contents of contaminations introduced by cryomilling are small, but they are inevitable. The contaminations may play a heterogeneous nucleation effect during the hot crystallization, and therefore, the rate of crystallization of cryomilled PET increases. In cryomilled PET, the slow cold crystallization is not contrary with the fast hot crystallization. The cold crystallization has been restrained by the stored energy, and the melting treatment has elim-

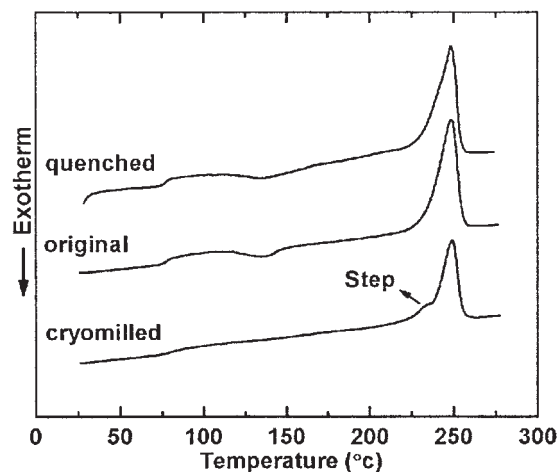


Figure 7 DSC second heating thermograms of three different PET samples.

TABLE III
Thermodynamic Data of DSC Second Heating of Three Different States of PET

Samples	T_g (°C)	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)	Crystallinity (%)
Quenched PET	76.5	133.8	10.56	248.56	40.1	20.8
Original PET	77.0	134.3	12.38	248.82	40.36	19.7
Cryomilled PET	–	–	–	249.29	37.33	26.3

inated the heat and stress history so that the hot crystallization is only affected by the molecular weight and the contaminations.

Second heating DSC thermograms

To research the effect of cryomilling on the thermal behaviors during the reheating, we obtain the second heating DSC thermograms of three different PET samples (shown in Fig. 7). The thermograms of quenched PET and original PET are similar, and they have an obvious glass transition and a small cold crystallization peak, which indicates that their crystallization was incomplete while cooling at a rate of 10°C/min, and so when the temperature exceeds T_g during the reheating process, the molecular segments move and rearrange to crystallize, and when the temperature exceeds the melting point, the crystals melt completely. However, cryomilled PET has no obvious glass transition and cold crystallization peak, which should attribute to its higher crystallinity before the reheating. When the heating temperature exceeds T_g , the molecular segments cannot move because of the higher limiting effect of the crystal lattice, and so cryomilled PET does not show obvious glass transition and cold crystallization peak, which suggests that the cryomilled products will have good size stability during application, and its serviceable temperature will have a big improvement.

In addition, there has a step-type double melting peaks in cryomilled PET. The reasonable explanation should be that cryomilled PET forms incomplete crystals when cooling from the melting state because of the fast rate of crystallization, and these incomplete crystals will rearrange to crystallize during reheating process. The crystallinities of original PET and quenched PET are small, and the limiting effect of crystal lattice is small. Their molecular segments easily move when the heating temperature is higher than T_g , and so their crystallization rearrangement occurs at the lower temperature. Cryomilled PET has high crystallinity after cooling from the melting (see Tables II and III); so the limiting effect of crystal lattice is much higher. Only when the heating temperature reaches the melting temperature of these incomplete crystals, they melt and the molecular chains move, and then form the more intact crystals, which will melt at the higher temperature and,^{16,17} therefore, cryomilled PET shows the double melting peaks in the second DSC heating thermogram.

CONCLUSIONS

Cryomilling resulted in amorphization of crystalline PET, but the thermal behaviors of cryomilled amorphous PET have some abnormal phenomena, comparing with that of quenched amorphous PET. Unlike quenched amorphous PET, whose cold crystallization shows an obvious centralized exotherm, the cold crystallization of cryomilled amorphous PET is a slow process with a wide temperature scope (from about 120°C to ahead of the melting temperature) because of the stored energy induced by cryomilling. These results indicate that the cold crystallization of cryomilled amorphous PET is harder and its amorphous stability is higher than those of quenched amorphous PET. Besides, the hot crystallization behaviors of cryomilled PET have a remarkable improvement: (1) the rate of crystallization and the degree of crystallinity increases; (2) the distribution of crystal sizes becomes narrower. Moreover, cryomilled PET has good size stability in the reheating process, that is to say, the serviceability temperature of cryomilled PET will have a big improvement.

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