



## Study on the Crystallization of Poly(ethylene terephthalate)/ SiO<sub>2</sub>/TiO<sub>2</sub> Hybrid Nanocomposites by Sol-Gel Method

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(Received: 14 January 2013;

Accepted: 18 September 2013)

AJC-14139

The hybrid PET/TiO<sub>2</sub>/SiO<sub>2</sub> composites were synthesized *via* the sol-gel method. A polymerization process resulted in the formation of Si-O-Ti bonds in the poly(ethylene terephthalate) (PET) matrix, which was confirmed by the appearance of the small new peak at *ca.* 937 cm<sup>-1</sup> in the fourier transform infrared spectroscopy spectrograms. The SiO<sub>2</sub>-TiO<sub>2</sub> components had a significant effect on the crystalline morphology of the PET in PET/TiO<sub>2</sub>/SiO<sub>2</sub> composites by polarized light microscopy observations from 290-190 °C at a cooling rate of 5 °C/min. The differential scanning calorimeter results exhibited that the crystallization behaviour of the PET was also influenced strongly by the inorganic nanoparticles due to the formation of the Si-O-Ti bonds in the matrix of composites. The X-ray diffraction results were in a good agreement with the polarized light microscopy and the differential scanning calorimeter results, which indicated that the SiO<sub>2</sub>-TiO<sub>2</sub> content affected the perfect degree of the PET crystal.

**Key Words:** Poly(ethylene terephthalate), Sol-gel method, Hybrid composites, Crystallization.

### INTRODUCTION

As one of the important polymers, poly(ethylene terephthalate) (PET) is widely used in everyday life for fibers, films, bottles, packaging materials and engineering plastics. In general PET not only shows the excellent optical and mechanical properties but also is a low-cost polymer. However, when exposed to the natural environments, both its appearance and properties would be weakened, specially for the irradiation of the UV radiation in air<sup>1</sup>. To solve the above problems, the fillers or inorganic particles such as carbon fiber, clay, calcium carbonate and glass fibers have been incorporated into PET matrix to improve the performances of PET resins. Conventionally, the filler particles have been added into PET resin by a mechanical blending process which has yielded some new problems, such as the poor dispersion of the filler particles, phase separation between the resin matrix and filler particles, *etc.*<sup>2</sup>.

Recently, the sol-gel process has received a great deal of attention as a valuable technique for mixing the inorganic precursor with organic monomers, oligomers and even polymers directly, which obtained the molecule-level hybrid composites<sup>3-6</sup>. The hybridization of polymer/inorganic nanoparticles results in the formation of new chemical bonds between the inorganic and organic phase of the composites. So the

composites have some special properties such as high strength, improved barrier properties and thermal stability, meanwhile, avoiding the macrophase separation. Some work have reported that nanoparticles like organo-clay, TiO<sub>2</sub>, BaSO<sub>4</sub>, calcium carbonate and carbon nanotube were used for synthesizing PET nanocomposites by the solution polymerization, the melt polymerization and the *in situ* polymerization<sup>7-15</sup>. Wang *et al.*<sup>16</sup> prepared the PET/SiO<sub>2</sub> hybrid materials *via* adding the nano-SiO<sub>2</sub> solution of ethylene glycol or the solution of SiO<sub>2</sub> into the *bis*(2-hydroxyethyl) terephthalate (BHET) followed by *in situ* polymerization. The results showed that the SiO<sub>2</sub> nanoparticles could play a role of the nucleating agents and effectively increase the crystallization rate of the organic phase. However, there is still dearth of the research on preparing hybrid PET/TiO<sub>2</sub>/SiO<sub>2</sub> nanocomposites through sol-gel method during which PET was substrate directly.

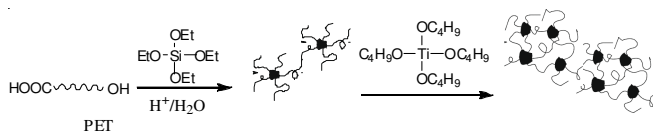
In this paper, one of the objectives was to synthesize such a nanocomposites *via* sol-gel method. Another key objective was to identify the effect of inorganic particles on the crystallization of PET. The purpose of this work is to reveal the crystalline morphology and the crystallization behaviour of PET by PLM, DSC, XRD and FTIR measurements, particularly in the presence of multiple nanoparticles such as TiO<sub>2</sub> and SiO<sub>2</sub>. Further studies on the dispersion of the nanoparticles in the

PET matrix and mechanical properties of PET will be summarized in our next study.

## EXPERIMENTAL

Poly(ethylene terephthalate) (PET) was prepared in our laboratory, with  $[\eta] = 0.384$  that was measured by the viscosity method. Tetraethylorthosilicate (TEOS, AR), tetrabutyltitanate (TBT, AR), dichloroethane (DCE, AR), phenol (AR) and acetic acid (AR) were supplied by Chengdu Kelong Chemical Reagent Company, China. Other solvent with AP grade were purchased from Bodi chemical Factory (Tianjin, China) and used without further purification.

**General procedure:** Weighed a certain amount of the as-prepared PET, 1 mL phenol and 10 mL DCE into 250 mL glass round bottom flask-3-neck connected with a stirrer and immersed in an oil bath, after nitrogen replacement and protection, heated the oil bath to 120 °C and kept for 1.5 h to completely dissolve the PET in the mixed solvent, then removed the 3-neck flask to a 30 °C water bath, adjusted the pH value of the reaction system to 2-3 using acetic acid, added TEOS with continuous stirring, after stirring for 1 min added distilled water, after stirring for 10 min then added TBT, after stirring for 1.5 h drew out the gel product and washed it by vacuum extraction, finally dried the extracted product in a vacuum oven at 50 °C for 24 h. The proposed mechanism of cohydrolysis-condensation reaction among TEOS, TBT and PET can be described as **Scheme-I**.



**Scheme-I:** Proposed mechanism of cohydrolysis-condensation reaction among TEOS, TBT and PET

**Detection method:** Polarized light microscope (PLM):

The crystalline morphology of samples was characterized by polarized light microscopy (PLM) (Leica DM2500p) connected to a Linkam THMS600 hot-stage (Linkam Scientific Instruments Ltd., UK) and a Pixelink (PL-A662) camera. The samples were heated from room temperature to 290 °C at a heating rate of 30 °C/min and kept the temperature for 5 min to erase any thermal history. Then the samples were cooled to 250 °C at a cooling rate of 30 °C/min, continued to cool at a cooling rate of 5 °C/min to 190 °C and finally cooled to room temperature at a fast cooling rate. The non-isothermally crystallized morphology in the crystallization region of PET was recorded from 250 to 190 °C.

The thermal behaviour and crystallization behaviour of the samples was characterized by DSC (DSC Q20, TA Instruments). About 5 mg fine granular samples in nitrogen atmosphere were heated at a quite fast heating rate from 0-300 °C, then cooled to 0 °C at 5 °C/min cooling rate. This cooling DSC traces were recorded to analyze the crystallization. Heated again to 300 °C at the heating rate of 10 °C/min and recorded the heating process curve to understand the thermal behaviour.

X-Ray diffraction patterns were measured by a DX-1000 diffractometer (Dandong Fangyuan Instrument Co., Ltd,

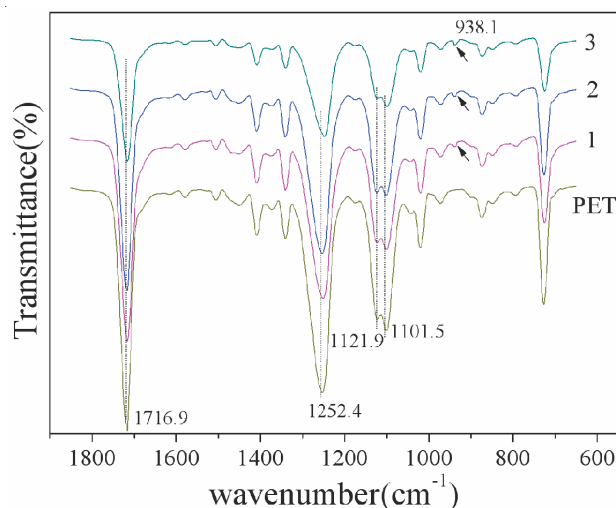
China) using a CuK $\alpha$  radiation. The voltage and current were set to 40 kV and 25 mA, respectively. Diffraction patterns were recorded for 2 $\theta$  values ranging from 10-50° at a scanning rate of 0.06°/s.

The FTIR spectra of the samples dried in a vacuum oven at 70 °C for 48 h were carried out by a FTIR spectrometer (ThermoFisher Corp., Nicolett 6670, USA), using infrared attenuated total reflection (IRATR) and operating in the wavenumber range 4000-600 cm<sup>-1</sup>.

## RESULTS AND DISCUSSION

**Structural characters of PET/SiO<sub>2</sub>/TiO<sub>2</sub> composites:**

Fig. 1 displays the FTIR spectra of pure PET and the PET/SiO<sub>2</sub>/TiO<sub>2</sub> composites after dried at 70 °C for 48 h in a vacuum oven. It was clear that, there were several characteristic peaks appearing in all IR spectrograms for the pure PET and the PET/SiO<sub>2</sub>/TiO<sub>2</sub> composites-1,2 and 3, e.g., the peak occurring at ca. 1717 cm<sup>-1</sup> assigned to C=O bonds of ester group, a series of peaks from 1600-1450 cm<sup>-1</sup> ascribed to skeleton vibration peaks of the aromatic ring, the three peaks at 1252, 1122 and 1101 cm<sup>-1</sup> corresponded to the stretching vibration absorption peak of C-O bonds, the characteristic peak appearing at 873 cm<sup>-1</sup> attributed to the group of the benzene ring, etc. The results indicated that the all formed PET/SiO<sub>2</sub>/TiO<sub>2</sub> composites were actually the PET production. However, it is worthwhile to note that a small peak at 937 cm<sup>-1</sup>, appearing only in the IR spectrograms for the PET/SiO<sub>2</sub>/TiO<sub>2</sub> composites-1,2 and 3, was primarily attributed to Ti-O-Si bonds<sup>7</sup>. The peak at 1101 cm<sup>-1</sup> would be also assigned to the stretching vibration peak of Si-O bonds in the silica network, overlapping with the characteristic peak of C-O bonds, additionally indicative of the occurrence of the Si-O-Ti bonds in PET/SiO<sub>2</sub>/TiO<sub>2</sub> composites. The FT-IR results could be taken as evidence for the sol-gel reaction mechanism of the PET/SiO<sub>2</sub>/TiO<sub>2</sub> system in before-mentioned experimental section.



**Fig. 1.** Fourier transform infrared attenuated total reflection spectrum of pure PET and PET/SiO<sub>2</sub>/TiO<sub>2</sub> composites-1,2,3. The percentage content of SiO<sub>2</sub> and TiO<sub>2</sub> in samples is: 1, 5.49 wt. %; 2, 10.07 wt. %; 3, 14.05 wt. %

**Polarized light microscopy analysis:** The crystalline morphology of pure PET and PET/SiO<sub>2</sub>/TiO<sub>2</sub> composites-1, 2

and 3 during non-isothermal crystallization in PET crystallization region at a cooling rate of 5 °C/min is shown in Fig. 2. Obviously, the SiO<sub>2</sub>-TiO<sub>2</sub> inorganic components in PET/SiO<sub>2</sub>/TiO<sub>2</sub> composites had a large influence on crystalline morphology of PET in the composites. It was seen that pure PET and the PET/SiO<sub>2</sub>/TiO<sub>2</sub> composite-1 both formed considerable fragmentary crystals, no legible spherulites appearing in Fig. 2(a,b), whereas the PET/SiO<sub>2</sub>/TiO<sub>2</sub> composites-2 and 3 produced spherulites with the distinct Maltese-cross extinction patterns, as displayed in Fig. 2(c,d), in which the size of the spherulites were visibly larger than that of the crystals in Fig. 2(a,b). It should be pointed out that *in situ* observation of the crystallization process could be implemented using polarized light microscopy (PLM) with a hot-stage and the crystallization temperature at any time was also recorded. So based on the comparison of crystallization temperatures in Fig. 2(a-d), with the increase of the SiO<sub>2</sub>-TiO<sub>2</sub> content the crystallization temperature had been trended down *i.e.*, the crystallization temperatures of PET/SiO<sub>2</sub>/TiO<sub>2</sub> composites-2 and 3 were much lower than those of pure PET and PET/SiO<sub>2</sub>/TiO<sub>2</sub> composite-1. Moreover, to further analyze crystallization rate of the samples, the onset crystallization temperature according to the first appearance of PET crystals in the field of polarized light microscope and the complete crystallization temperature based on the whole space of polarized light micrograph filled with PET crystals were listed in Table-1. It was clear that the crystallization rate of pure PET and PET/SiO<sub>2</sub>/TiO<sub>2</sub> composite-1 was evidently faster than that of PET/SiO<sub>2</sub>/TiO<sub>2</sub> composites-2 and 3 and the onset crystallization temperatures and the complete ones of the formers were still higher than those of the latters, respectively. Apparently, the SiO<sub>2</sub>-TiO<sub>2</sub> components not only affected the crystalline morphology but also had a great impact on the crystallization temperature and the crystallization rate of the PET in the composites.

The reasonable explanation for the phenomena was that the viscosity-average molecular weight of the chosen PET was not high in our experiment so most molecular chains of PET were relatively short, which induced that the molecular chain segments had a difficulty in arranging layer by layer into a big spherulite during the growth crystals. So the comparatively short molecular chains were favorable to form a great number of nuclei by means of homogeneous nucleation but not to grow into large spherulites. In addition, it was noteworthy that due to the massive nuclei the space among the adjacent nuclei was really limited so that the neighboring crystals collide with each other quickly during their growth process, leading to many fragmentary crystals and the quite fast crystallization rate in pure PET. In the PET/SiO<sub>2</sub>/TiO<sub>2</sub> composite-1, the SiO<sub>2</sub>-TiO<sub>2</sub> content was so comparatively little that the two inorganic components could not influence the crystalline morphology of the

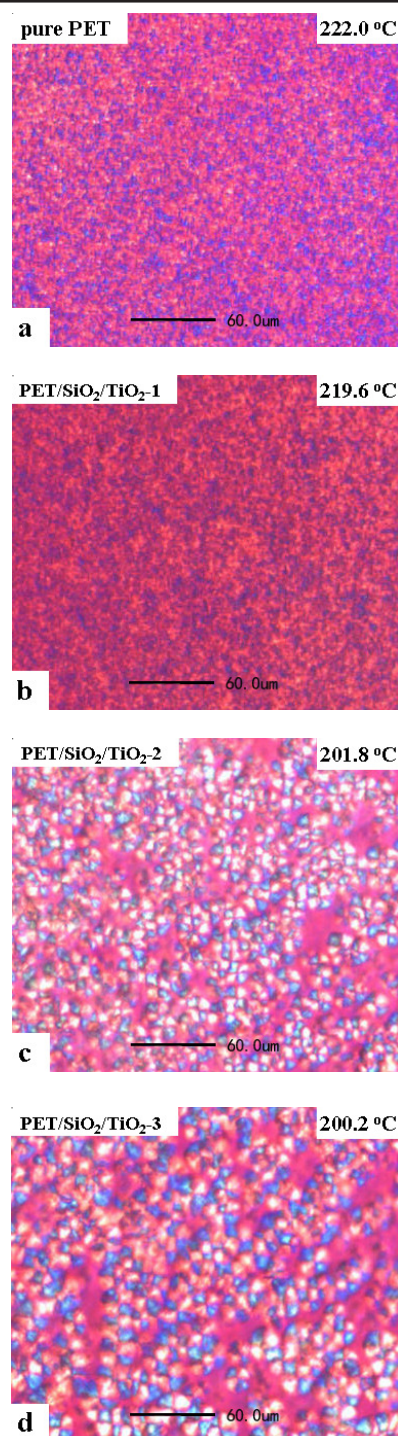


Fig. 2. Polarized light micrographs of pure PET and PET/SiO<sub>2</sub>/TiO<sub>2</sub> composites-1,2,3 during non-isothermal crystallization of PET at a cooling rate of 5 °C/min from 250-190 °C. The temperature during crystallization is indicated in each photo. The percentage composition of SiO<sub>2</sub> and TiO<sub>2</sub> in samples is: a, 0.00 wt. %; b, 5.49 wt. %; c, 10.07 wt. %; d, 14.05 wt. %

TABLE-1

THE ONSET AND THE COMPLETE CRYSTALLIZATION TEMPERATURES OF PURE PET AND PET/SiO<sub>2</sub>/TiO<sub>2</sub> COMPOSITES DURING THE NON-ISOTHERMAL CRYSTALLIZATION

Sample No.	PET (g)	TEOS (g)	TBT (g)	SiO <sub>2</sub> -TiO <sub>2</sub> content (wt %)	Onset T <sub>c</sub> (°C)	Complete T <sub>c</sub> (°C)
PET	0	0	0	0	228.0	220.0
PET/SiO <sub>2</sub> /TiO <sub>2</sub> -1	2.531	0.260	0.442	5.49	227.3	218.0
PET/SiO <sub>2</sub> /TiO <sub>2</sub> -2	1.503	0.261	0.442	10.07	222.5	198.0
PET/SiO <sub>2</sub> /TiO <sub>2</sub> -3	1.002	0.262	0.441	14.05	220.0	196.0



PET constituent in the composite. The possible reason was that during the synthesis process of the PET/SiO<sub>2</sub>/TiO<sub>2</sub> composite-1, the PET solution concentration was relatively high as well as the addition amount of TEOS and TBT was relatively low, which had more or less impact on co-hydrolysis-condensation reaction among the PET and TEOS as well as TBT components; thus in the PET/SiO<sub>2</sub>/TiO<sub>2</sub> composite-1 the PET molecular chains maybe underwent a relatively slight influence resulting in only a lot of fragmentary crystals and the speedy crystallization rate, similar to the crystallization behaviour of the pure PET.

Nevertheless, during the synthesis process of the PET/SiO<sub>2</sub>/TiO<sub>2</sub> composites-2 and 3, the increment of the amount of TEOS and TBT as well as the decrease of the PET solution concentration might be beneficial for the composite system to yield Si-O-Ti or Si-O-Si or Ti-O-Ti bonds that would probably develop into some slight cross-links, joining the neighboring PET molecular chains up. Consequently, part of the PET molecular chains were potentially lengthened, which was good for the longer molecular chains to arrange and pile up layer by layer into comparatively bigger spherulites. What is more, the cross-links dispersing in PET chains always affected the movement of the macromolecular chains or chain segments to some extent, hindering the orderly arrangement of the chain segments and then prolonging the nucleation and growth process<sup>17</sup>. These conditions induced the depression of the crystallization rate and the crystallization temperature. Additionally, due to the decrease of nuclei number the growth space among the nuclei became relatively extended, maybe making the spherulites larger, too. In sum, there was an interesting changing trend: the more the SiO<sub>2</sub>-TiO<sub>2</sub> content in the composite, maybe the more the three bonds, the more the cross-links, the bigger the spherulites, the slower the crystallization rate, the lower the crystallization temperature.

**DSC analysis:** Fig. 3 presents the DSC cooling traces of pure PET and PET/SiO<sub>2</sub>/TiO<sub>2</sub> composites-1, 2 and 3 during the non-isothermal crystallization at a cooling rate of 5 °C/min and the corresponding crystallization parameters are listed in Table-2. Clearly, the exothermic peaks of the PET in the PET/SiO<sub>2</sub>/TiO<sub>2</sub> composites shifted to lower temperature and the crystallization temperatures as well as the enthalpy values also gradually reduced with the increase of the SiO<sub>2</sub>-TiO<sub>2</sub> content. The main reason for these phenomena was that the formed Si-O-Ti or Si-O-Si or Ti-O-Ti bonds and the cross-link structure in the ternary composite system always had some effect on the movement of the macromolecular chains or chain segments so that the non-isothermal crystallization process of the PET in the composites was somewhat restricted, leading to the depression of the crystallization temperatures as well as the enthalpy values. Especially in the PET/SiO<sub>2</sub>/TiO<sub>2</sub> composites-2 and 3, the comparatively more SiO<sub>2</sub>-TiO<sub>2</sub> components

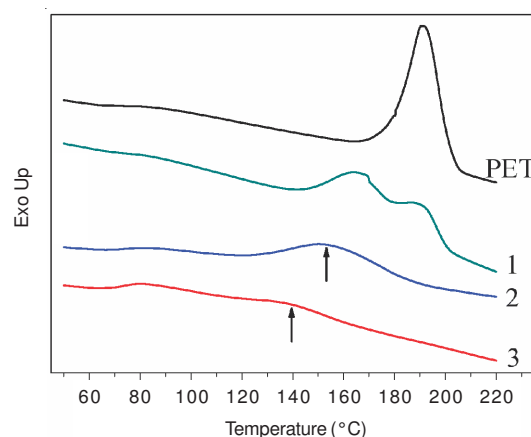


Fig. 3. Differential scanning calorimetry cooling traces of pure PET and PET/SiO<sub>2</sub>/TiO<sub>2</sub> composites-1,2,3 at a cooling rate of 5 °C/min from 300-0 °C. The percentage composition of SiO<sub>2</sub> and TiO<sub>2</sub> in samples is: 1, 5.49 wt. %; 2, 10.07 wt. %; 3, 14.05 wt. %

and more new bonds as well as more cross-links in the system would surely have a larger impact on the orderly arrangement of the PET molecular chains or chains segments and hinder the crystallization more strongly, appearing as a dramatic decline in the crystallization parameters (Table-2). It was notable that a double-peak appeared in the DSC cooling curves for the PET of the PET/SiO<sub>2</sub>/TiO<sub>2</sub> composites-1. This result could be probably ascribed to the fact that due to the relatively less SiO<sub>2</sub>-TiO<sub>2</sub> components and less cross-links in the composite only part of the PET molecular chains or chains segments were affected but some PET molecular chains still not, which caused that the non-influenced molecular chains crystallized at higher temperature similar to the condition of the pure PET resulting in the higher exothermic peak (around *ca.* 192 °C) as well as the influenced molecular chains underwent the limited crystallization at lower temperature leading to the lower peak.

After the samples were non-isothermally crystallized at the cooling rate of 5 °C/min, they were heated again at a heating rate of 10 °C/min favorable to further analyze their crystallization behaviour. The DSC heating curves of pure PET and PET/SiO<sub>2</sub>/TiO<sub>2</sub> composites are displayed in Fig. 4 and the data of *T<sub>m</sub>* and  $\Delta H_m$  are showed in Table-2. Similarly, the melting points and the endothermic enthalpy values decreased gradually as the content of the SiO<sub>2</sub>-TiO<sub>2</sub> increased, which was in good agreement with the non-isothermal crystallization behaviour of the samples. This result still implied the effect of the SiO<sub>2</sub>-TiO<sub>2</sub> components on the crystallization process of the PET in the composites. Interestingly, except the melting peak there was a small cold crystallization peak around *ca.* 155 °C occurring in the DSC heating trace of the PET/SiO<sub>2</sub>/TiO<sub>2</sub> composite-3. The reason why yielded the cold crystallization peak might be that the PET molecular chains or chain

TABLE-2  
THERMAL CHARACTERISTICS OF PURE PET AND PET/SiO<sub>2</sub>/TiO<sub>2</sub> COMPOSITES-1,2,3

Sample No.	<i>T<sub>m</sub></i> (°C)	$\Delta H_m$ (J/g)	<i>T<sub>c</sub></i> (°C)	<i>T<sub>sc</sub></i> (°C)	$\Delta H_c$ (J/g)
Pure PET	249.23	33.04	192.14	202.63	37.77
PET/SiO <sub>2</sub> /TiO <sub>2</sub> -1	245.31	25.53	191.88, 165.19	201.00	23.00
PET/SiO <sub>2</sub> /TiO <sub>2</sub> -2	244.78	25.97	159.75	189.47	15.48
PET/SiO <sub>2</sub> /TiO <sub>2</sub> -3	242.46	18.68	140.37	163.70	13.00

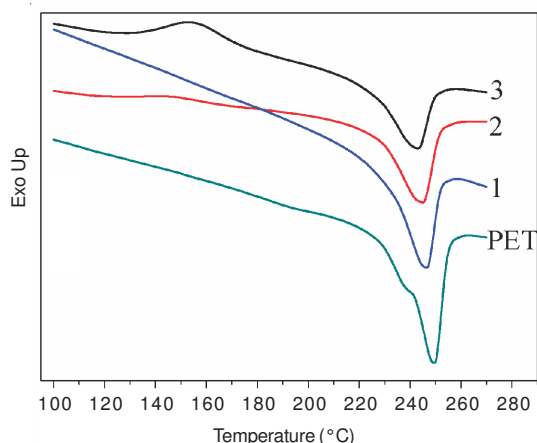


Fig. 4. Differential scanning calorimetry heating traces of pure PET and PET/SiO<sub>2</sub>/TiO<sub>2</sub> composites-1,2,3 at a heating rate of 10 °C/min from 0-300 °C. The percentage composition of SiO<sub>2</sub> and TiO<sub>2</sub> in samples is: 1, 5.49 wt. %; 2, 10.07 wt. %; 3, 14.05 wt. %

segments were restricted by the comparatively more cross-links so seriously that the PET molecular chains had no time to arrange orderly and finish the crystallization during the cooling process. Only during the re-heating process could the molecular chains commence to move as well as arrange regularly so as to form the cold crystallization. The DSC results still implied that the SiO<sub>2</sub>-TiO<sub>2</sub> components would severely retard the crystallization behaviour of the PET in the composites, generally consistent with the PLM results in previous section.

**XRD analysis:** Fig. 5 shows the XRD patterns of pure PET and PET/SiO<sub>2</sub>/TiO<sub>2</sub> composites-1, 2, 3. Obviously, three intense Bragg diffraction peaks occurring at  $2\theta = 17.4$ ,  $23.1$  and  $26.3^\circ$  in the pattern of all samples, corresponded to (100), (10) and (010) lattice planes of triclinic crystal of PET<sup>18</sup>. It indicated that the SiO<sub>2</sub>-TiO<sub>2</sub> components had nearly no influence of on crystal form of the PET component in the composites. Although the PET in all PET/SiO<sub>2</sub>/TiO<sub>2</sub> composites still formed the triclinic crystal, the intensity of three characteristic diffraction peaks of the PET gradually declined with the increment of the SiO<sub>2</sub>-TiO<sub>2</sub> content. Especially in the PET/SiO<sub>2</sub>/TiO<sub>2</sub> composites-3 the intensity of the peaks was the weakest as well as the characteristic diffraction peaks at  $17.4$  and  $23.1^\circ$  were both comparatively slight, indicative of the imperfect crystals of the PET in the composites. The reason might be that the SiO<sub>2</sub>-TiO<sub>2</sub> content was relatively higher and so did the cross-links in this system so as to affect the perfect degree of the PET crystal. So it was clear that the XRD results were in a good agreement with the PLM and the DSC results.

### Conclusion

Through the sol-gel method, the hybrid composites based on PET/SiO<sub>2</sub>/TiO<sub>2</sub> were prepared in the presence of tetraethyl-orthosilicate (TEOS) and tetrabutyltitanate (TBT). Attributed to the formation of Si-O-Ti bonds in the PET matrix, the crystalline morphology and the crystallization behaviour of the PET in PET/SiO<sub>2</sub>/TiO<sub>2</sub> composites were affected significantly by the SiO<sub>2</sub> and TiO<sub>2</sub> inorganic nanoparticles.

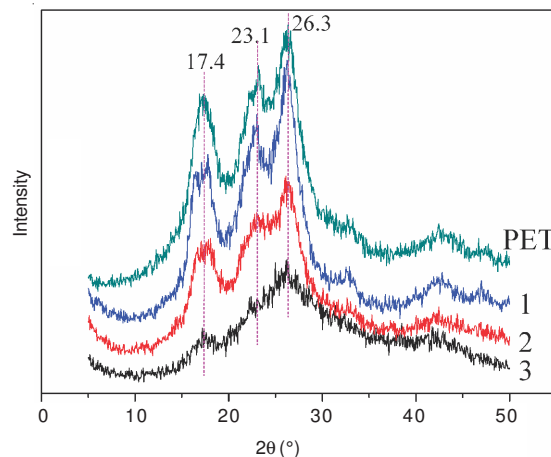


Fig. 5. X-Ray diffraction patterns of pure PET and PET/SiO<sub>2</sub>/TiO<sub>2</sub> composites-1,2,3. The percentage content of SiO<sub>2</sub> and TiO<sub>2</sub> in samples is: 1, 5.49 wt. %; 2, 10.07 wt. %; 3, 14.05 wt. %

### ACKNOWLEDGEMENTS

The authors appreciated the financial supports of (1) the Opening-project Fund for Chongqing Key Laboratory of Micro/Nano Materials Engineering and Technology through contract grant number: KFJJ1105 ; (2) the Local Fund for Chongqing University of Arts and Sciences through contract grant number: R2012CH08; (3) the Opening-project Fund for Chongqing Key Laboratory of Micro/Nano Materials Engineering and Technology through contract grant number: KFJJ1209 ; (4) the Local Fund for Chongqing University of Arts and Sciences through contract grant number: Y2011CL48

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