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ORIGINAL PAPER

# Properties of toughened poly(butylene terephthalate) by blending with reactive ultra-fine full-vulcanized acrylonitrile butadiene rubber particles (UFNBRP)

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**Abstract** The nano-sized ultra-fine full-vulcanized acrylonitrile butadiene rubber particles (UFNBRP) functionalized with carboxyl groups were used to toughen poly(butylene terephthalate) (PBT) through compatibilization of the two components via reactive extrusion in a twin-screw extruder. The impact strength of PBT was greatly improved with the nano-sized UFNBRP which may be attributed to its small particle size and the reactive compatibilization. Reactions between carboxyl groups on the surface of UFNBRP and hydroxyl end groups of PBT were proved with FT-IR spectra. In addition, UFNBRP also exhibited good nucleation effect and promoted the crystallization kinetics of PBT. Incorporation of small amounts of UFNBRP was found to be enough to improve the thermal stability. The maximum temperature of decomposition was increased by 25 °C at 1 wt% UFNBRP in comparison with that of pure PBT.

**Keywords** Poly(butylene terephthalate) (PBT) · Polymer · Composites · Rubber · Toughness

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## Introduction

Poly(butylene terephthalate) (PBT) is an important semi-crystalline engineering thermoplastic with many valuable properties including a high rate of crystallization, good solvent resistance, thermal stability, and excellent processing properties. However, pure PBT has low impact strength, a property not desired in engineering thermoplastics. As a toughening method, PBT/rubber composites have been studied extensively by polymer melt blending [1–6].

Coran et al. [7] investigated the effect of the size of rubber particles on mechanical properties of thermoplastic elastomers. They indicated that the ultimate properties of thermoplastic elastomers were inversely proportional to the size of rubber particles. The minimum size of rubber particles obtained by dynamic vulcanization method was usually about 1–2 μm.

Recently, a new kind of highly cross-linked nano-particle rubbers, ultra-fine full-vulcanized rubber powders (UFRP), by irradiating rubber latex and spray drying has been developed [8]. The particle size of the UFRP is tunable between 30 and 2,000 nm by controlling polymerization conditions of the rubber latex. When the particle size is below 100 nm, the UFRP can be recognized as elastomeric nano-particle (ENP). It has been found that the UFPR could be used in many different plastics as a good toughening modifier [9–14].

In this study, preparation of fully crosslinked UFNBRP/PBT nanocomposites was studied. Comparing with the traditional preparation method, following differences could be found. First, a fully cured carboxy nitrile rubber powder with nanometer scale (50–100 nm) was adopted. Second, the traditional dynamic vulcanization process of the rubber component during blending process was eliminated. And third, functionalized UFNBRP with carboxyl groups was used to improve the compatibility between NBR particles and PBT. The effects of blending ratio and reactive compatibilization on the mechanical properties, morphology, crystallization properties, and thermal properties of UFNBRP/PBT composites were investigated systematically.

## Experimental

### Materials

Commercial grade PBT (trade name: PBT-2090, melt flow index (MFI) 30 g/10 min (250 °C, 2.16 kg)) was purchased from Shanghai Jiacheng Polyester Co., Shanghai. UFNBRP (Narpow$^{TM}$ VP-501) with particle size of 50–100 nm and gel content of 97.1% was supplied by Beijing Research Institute of Chemical Industry, SINOPEC, China.

### Blends preparation

Melt blending was carried out on a co-rotating twin-screw extruder (TSE-35, Nanjing Ruiya) with a diameter of 35 mm and the length to diameter (L/D) ratio of

60 at a barrel temperature with 70–250 °C and a screw speed of 100 rpm. 0.5 wt% antioxidant, Irganox-1010, was added during melt processing. The extruded materials were injection molded to obtain specimens for various mechanical tests. Neat PBT for comparison also went through similar thermal history.

## Characterization

Thermal behavior of the blend samples was investigated by using a Perkin-Elmer DSC-Diamond differential scanning calorimeter (DSC) in the range of 50–250 °C. All samples were heated to 250 °C at 20 °C/min and held for 5 min to eliminate the influence of the thermal history. A scanning rate of 10 °C/min was adopted during second heating and subsequent cooling studies. The weight of a sample was about 4–7 mg.

The melting enthalpy ($\Delta H_f$) in the second heating scan was used to measure the degree of crystallization ($X_c$), according to the following equation: $X_c = \Delta H_f / F\Delta H_f^* \times 100\%$ where $\Delta H_f$ is the melting enthalpy of PBT in the sample, $F$ is the homopolymer weight fraction in the blend, and $\Delta H_f^*$ is the melting enthalpy of the matrix polymer of 100% crystallization ($\Delta H_f^* = 142$ J/g [15], $\alpha$ crystal form). Moreover, the degree of supercooling ($\Delta T_d = T_{m2} - T_{c,m}$) values, which were indirectly proportional to the rate of crystallization, were used for the discussion of the influence of blend components on the crystallization rate of PBT, where $T_{m2}$ is the melting point and $T_{c,m}$ is the maximum of the crystallization temperature [16].

Thermal gravimetric analyses (TGA) of the samples were carried out with a Perkin-Elmer Pyris 1 TGA Instrument at a heating rate of 20 °C/min from 50 to 650 °C under a nitrogen atmosphere.

X-ray diffraction (XRD) was performed with a Rigaku D/Max-III XRD diffractometer (Tokyo, Japan) equipped with a copper target ($\lambda = 1.54$ Å) at a scanning rate of 4°/min. The scanning scale is $2\theta = 5°–65°$. XRD data were measured at room temperature.

The dispersion of UFNBRP particles in the composites was characterized using field-emission scanning electron microscopy (FE-SEM; Quanta 200F) at an acceleration voltage of 10 kV.

TEM imaging was performed on a JEOL 100 CX operated at 100 kV accelerating voltage. The samples were microtomed using a Leica Ultracut Cryo-ultramicrotome with a Diatome diamond knife at a sample temperature of −60 °C to obtain ultrathin (about 40–100 nm) sections. The sections were stained with $OsO_4$.

FT-IR spectroscopic studies in transmittance mode were carried out with a Nicolet AVATAR 360 FT-IR spectrometer in the range from 4,000 to 400 $cm^{-1}$, with a resolution of 4 $cm^{-1}$. The specimens for the FT-IR spectroscopy were pressed into ultra-thin films about 0.1 μm.

The notched izod impact strength (ASTM D256) was determined with an impact testing machine (model XJU-22, Chengde Experiment Equipment Company) at room temperature.

## Results and discussion

### Mechanical properties and morphology

Figure 1 shows the notched izod impact strength of PBT/UFNBRP composites with different UFNBRP contents. As can be seen, the impact property was improved greatly with the increasing amount of UFNBRP in the composites comparing with that of pure PBT. This indicates that the nanosized UFNBRP can toughen the PBT matrix effectively.

However, according to the toughening theory [17, 18], the formulation of

$$d_c = \tau_c / \left[ k(\pi/6\Phi_r)^{1/3} - 1 \right]$$

where $d_c$ is the critical rubber particle diameter and $\Phi_r$ is the rubber volume fraction, $k$ is the geometric factor characterizing the spatial package of the particles, $\tau_c$ is the critical face-to-face inter-particle distance or critical thickness of matrix ligaments. The rubber particles which are smaller than 100 nm do not toughen the PP materials [19].

However, in this system, this equation does not seem to work. The nanosized UFNBRP can still well toughen the PBT matrix as reported in other studies [19]. Whereas, the reasons need to be studied further. However, the good interfacial interaction between the two phases may act as an important factor which resulted from the carboxyl groups on the surface of the UFNBRP [1]. During the process of melt blending, the chemical reactions between the carboxyl groups of UFNBRP and the hydroxyl end groups of PBT may take place (as shown in Scheme 1) and thereby improve the compatibility.

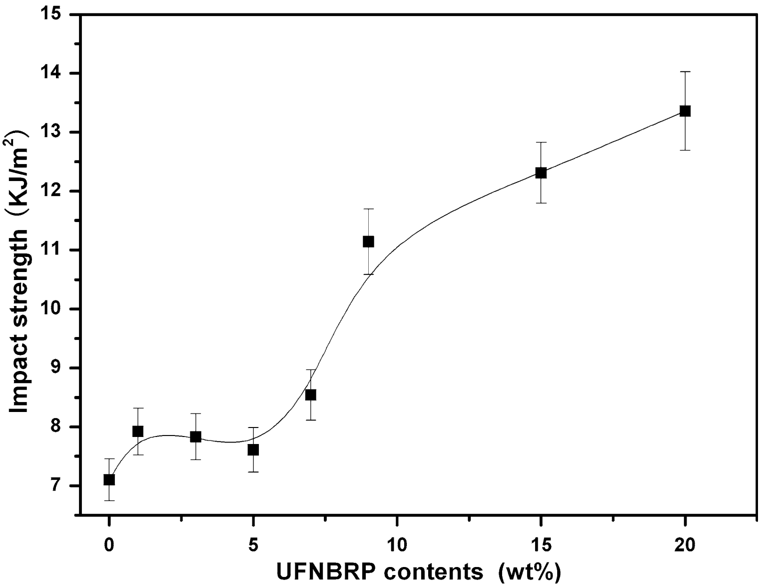
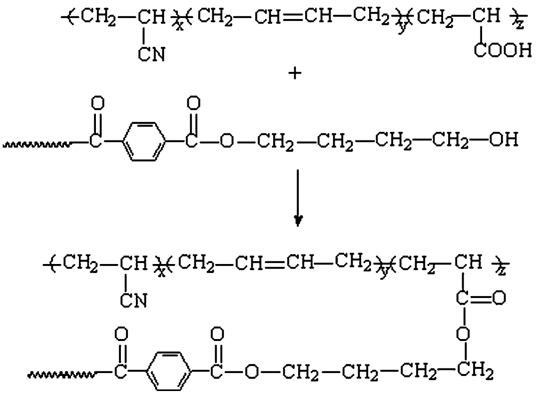


**Fig. 1** Impact strength of PBT/UFNBRP composites as a function of UFNBRP content

**Scheme 1** Reaction between UFNBRP and PBT



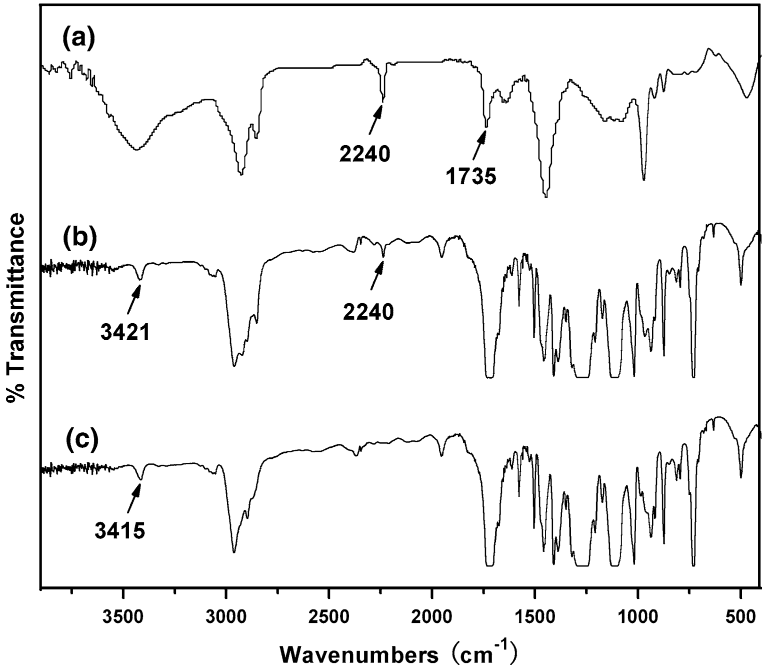


**Fig. 2** FTIR spectra of **a** UFNBRP, **b** PBT/UFNBRP composite (9 wt%) and **c** pure PBT

To better understand the compatibility of UFNBRP and PBT matrix, FTIR and FE-SEM were carried out. Figure 2 shows the FTIR spectra of the UFNBRP and PBT/UFNBRP composites. In Fig. 2a, we can see that the broad peak at 3,000–3,500 $cm^{-1}$ is attributed to stretching vibration of –OH of carboxyl groups. And the shoulder peak appeared at 1,735 $cm^{-1}$ was attributed to carbonyl stretching vibration of –COOH groups. These features revealed the existence of carboxyl groups on UFNBRP molecular chains.

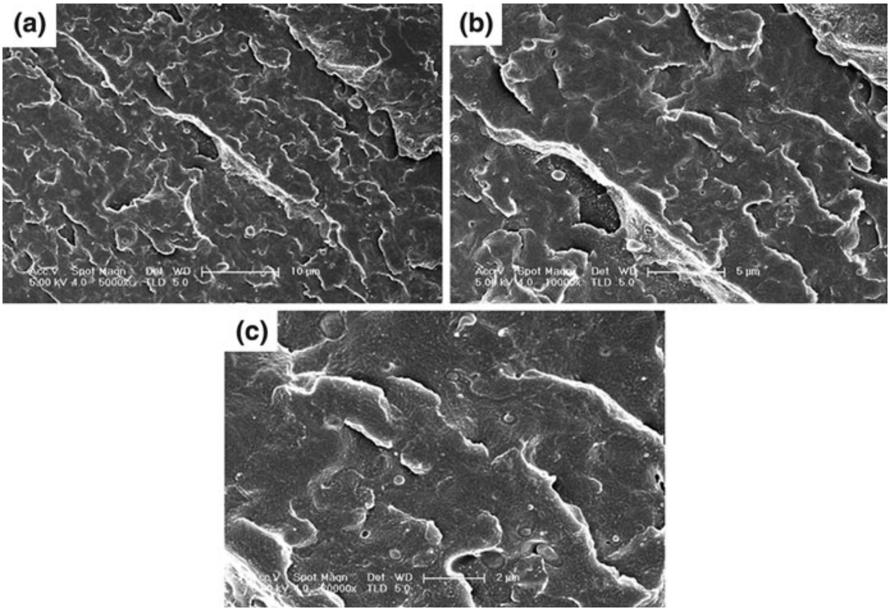


**Fig. 3** FE-SEM micrographs of cryofracture surfaces of PBT/UFNBRP (9 wt%) nanocomposite: **a** ×5000, **b** ×10000, **c** ×20000

In Fig. 2b, it can be found that the characteristic peaks of PBT still exist at 1,700 $\mathrm{cm}^{-1}$ and 1,105 $\mathrm{cm}^{-1}$ for C=O and C–O–C stretching vibration, respectively. Meanwhile, the 2,240 $\mathrm{cm}^{-1}$ for the $\mathrm{C}\equiv\mathrm{N}$ of NBR particles also appeared in the PBT/UFNBRP 9 wt% curve. Especially, the hydroxyl stretching vibration of PBT shifts from 3,415 to 3,421 $\mathrm{cm}^{-1}$ for the composite with 9 wt% UFNBRP. All of these indicate that the reactions between the PBT matrix and the UFNBR particles actually happened during the extrusion process in twin-screw extruder.

Figure 3 shows the FE-SEM micrographs of the PBT/UFNBRP composites. From the cryofracture surfaces, we can see that there is no obvious separation in the interface of UFNBRP particles and the PBT matrix which indicates good compatibility of the two components. At the same time, it also confirmed the interfacial reactions of the carboxyl groups on UFNBRP surface and the hydroxyl end groups of PBT chains.

From the TEM micrograph in Fig. 4, it can be seen that some of the UFNBRP aggregated together; but most of the UFNBRP were well dispersed in the PBT matrix at the nanoscale size which ensured the larger interface between UFBNRP and PBT polymer. Hence, more interaction occurred between the two phases in the composites which results in good compatibility. This also leads to the increased toughness of PBT/UFNBRP composites.

## Crystallization properties

Since PBT is a semi-crystalline polymer, the incorporation of rubber particles into the PBT could affect the crystallinity of the plastic. This could influence on the

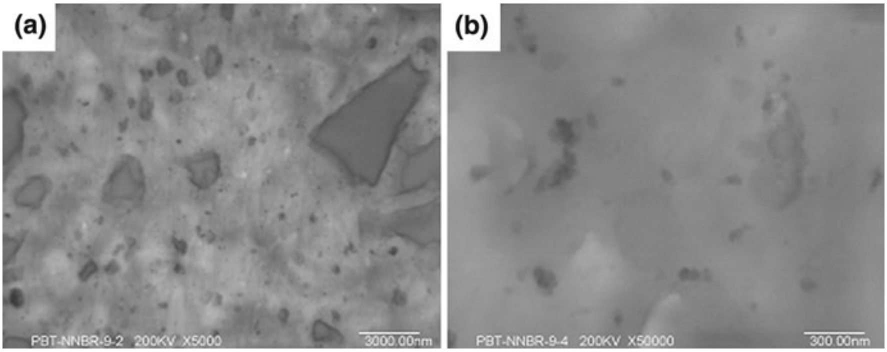


**Fig. 4** TEM micrographs of PBT/UFNBRP nanocomposite with 9 wt% UFNBRP: **a** ×5000, **b** ×50000

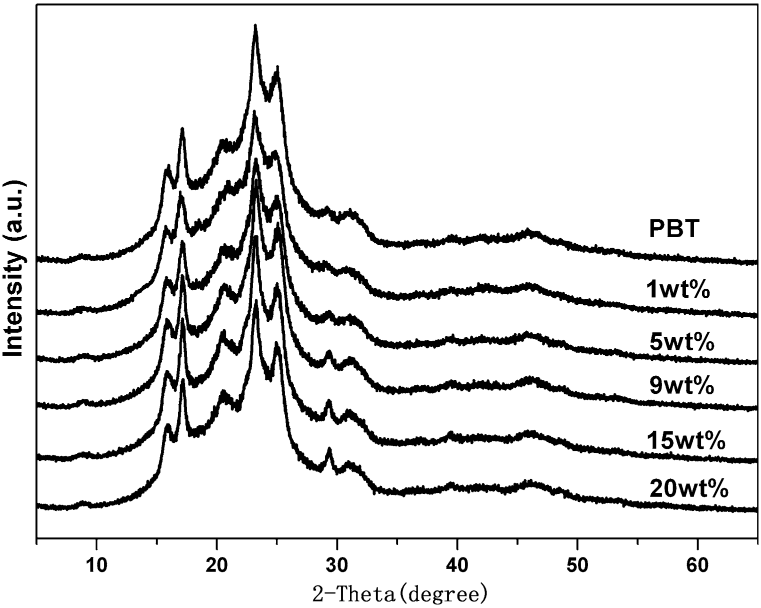


**Fig. 5** XRD of pure PBT and PBT/UFNBRP composites with various UFNBRP contents

mechanical properties of the composites. In order to assess the influence of rubber dispersion and reactive compatibility on the crystal structure of PBT, XRD, and DSC were employed. Figure 5 displays the XRD patterns of PBT/UFNBRP composites with various amounts of UFNBRP. The PBT diffractions do not change owing to the addition of the dispersed phase components and essentially remain located at the same $2\theta$ values. This indicates that the existence of UFNBRP has no effect on the crystalline form of PBT [19]. However, for the PBT/UFNBRP composites, it can be seen that the peaks become evidently sharper with the increasing content of UFNBRP than that of pure PBT, especially at $2\theta = 29.16°$

**Table 1** Crystallite sizes of the PBT crystals estimated from the fwhm of the X-ray diffraction at $2\theta = 29.16°$ using the Scherrer equation

| UFNBRP contents (wt%) | 0 | 1 | 5 | 9 | 15 | 20 |
|---|---|---|---|---|---|---|
| Crystallite sizes (nm) | 13.6 | 13.8 | 14.5 | 15.8 | 16.9 | 17.3 |

which corresponds to the (101) crystal plane of PBT. According to the Scherrer equation ($L = (k\lambda)/(\beta \cos \theta)$ [20], where $k$ is a constant, $\lambda$ is the wavelength, $\beta$ is the full width at half-maximum (fwhm) of the peak, and $\theta$ is the peak angle), this indicates that the size of the crystallite becomes larger with the increase of UFNBRP content than pure PBT (Table 1). Possibly the UFNBRP acts as a nucleating agent in the PBT matrix [4, 12, 21, 22] and promotes the crystals to be perfect.

The heating and cooling thermograms of neat PBT and its nanocomposites with different UFNBRP contents are compared in Fig. 6. The data of DSC diagrams were summarized in Table 2.

It can be seen that both $T_{c,m}$ and $T_{m2}$ of the composites, especially the $T_{c,m}$ value, clearly increases, and $\Delta H_f$ of the composites, which has taken the fraction of the rubber nanoparticle weight into account, is also larger than that of pure PBT. Meanwhile, compared with the pure PBT, $\Delta T_d$ of the composites become smaller as well. All of these data show that UFNBRP may not only be a toughening agent, but also is a nucleating agent in affecting the crystallization kinetics of PBT. This is in agreement with the XRD result. The same phenomenon has also been reported by other study [19].

From Fig. 6, it can be seen that both $T_{c,m}$ and $T_{m2}$ of PBT are increased by the presence of UFNBRP at all proportions in comparison with pure PBT. However, they decrease gradually with the increasing percentage of UFNBRP in the samples.

This may be as reported in [4] that the UFNBRP played two competitive roles in this system. On the one hand, the UFNBR powders acted as heterogeneous nuclei in the nucleation of crystallization and promoted the crystallization process. On the other hand, the UFNBR powders confined the PBT chains to hinder the crystallization because the activation energy and nucleation parameters of PBT/UFNBRP are higher than those of neat PBT. That is, higher contents of UFNBRP induce large numbers of heterogeneous nuclei and increase the crystallization rate, whereas, increasing contents of UFNBRP will also hinder the crystallization. Therefore, the $T_{cm}$ of PBT/UFNBRP composites are higher than that of pure PBT; nevertheless, with further increase of UFNBRP content, they decrease slightly.

Additionally, the small reduction of $T_m$ ($T_{m1}$ and $T_{m2}$) in composites could be attributed to the good compatibility of UFNBRP in the PBT matrix, which let the UFNBRP act as a compatible additive and thereafter decreased the $T_m$ slightly [22].

## Thermal stability

Dong et al. [23] has reported that the thermal stability of PA6/UFPRM (ultra-fine full-vulcanized powdered rubber/montmorillonite) composites is lower than pure

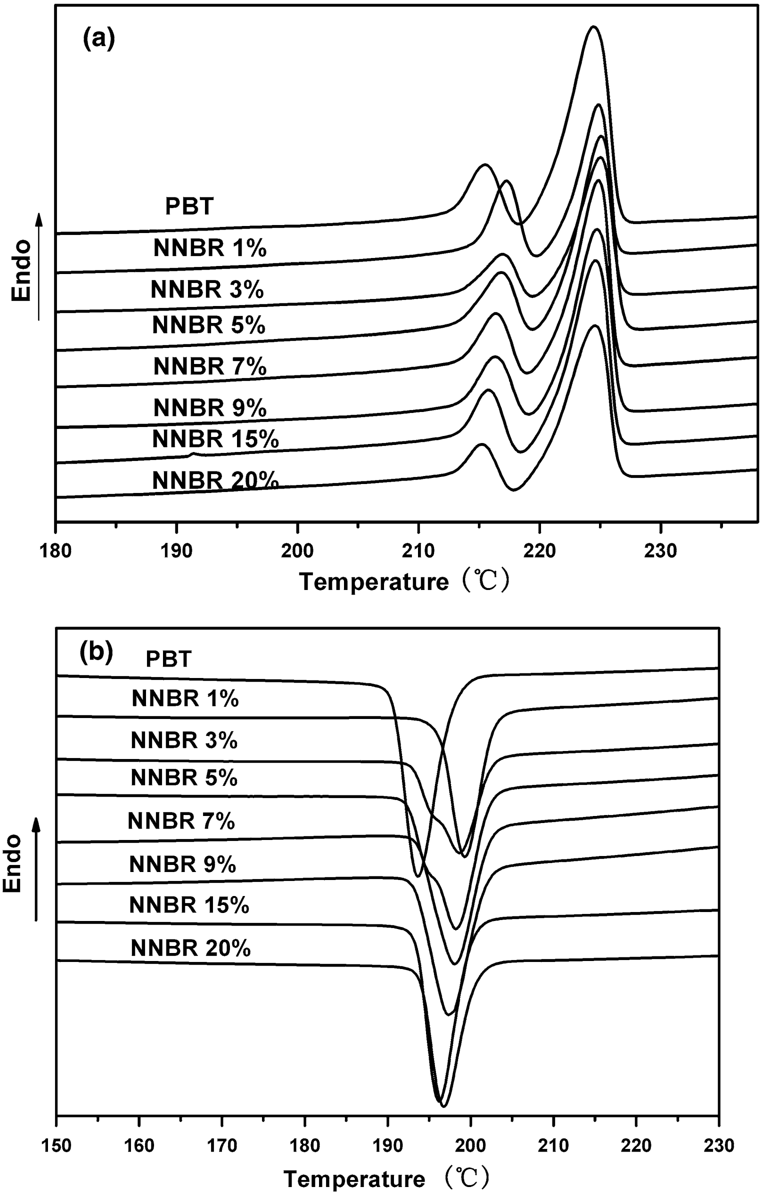


**Fig. 6** DSC scans of PBT/UFNBRP composites with different UFNBRP contents: **a** second heating, **b** cooling

PA6. To investigate the effect of rubber particles on the thermal stability of the PBT/UFNBRP composites, the thermal gravimetric analyses (TGA) were carried out. Typical TGA curves of PBT and PBT/UFNBRP nanocomposites with various amounts of UFNBRP in a nitrogen environment are shown in Fig. 7. It can be seen that the maximum decomposition temperatures of PBT/UFNBRP composites are

**Table 2** Characteristic values of crystallization and melting behavior of PBT/UFNBRP composites

| UFNBRP content (wt%) | Heating (2nd) | | | | Cooling | |
|---|---|---|---|---|---|---|
| | $T_{m1}$ (°C) | $T_{m2}$ (°C) | $\Delta H_f$ (J/$g_{PBT}$) | $\Delta H_c$ (J/$g_{PBT}$) | $T_{c,m}$ (°C) | $\Delta T_d$ (°C) |
| 0 | 215.5 | 224.4 | 34.2 | −41.1 | 193.6 | 30.84 |
| 1 | 217.3 | 224.8 | 46.0 | −42.7 | 199.2 | 25.6 |
| 3 | 217.0 | 225.0 | 41.2 | −40.2 | 198.6 | 26.4 |
| 5 | 216.9 | 225.0 | 43.5 | −43.0 | 198.2 | 26.8 |
| 7 | 216.5 | 224.9 | 42.6 | −41.7 | 198.1 | 26.8 |
| 9 | 216.3 | 224.8 | 34.8 | −41.5 | 197.3 | 27.5 |
| 15 | 215.9 | 224.7 | 33.5 | −35.6 | 196.2 | 28.5 |
| 20 | 215.3 | 224.6 | 29.6 | −35.0 | 196.7 | 27.9 |

not decreased, the value for PBT/UFNBRP (1 wt%) is even much higher than that of pure PBT matrix. This suggests that the addition of UFNBRP not only toughened the PBT but also improved the thermal stability. There is almost 14 °C increment (Table 3) in the onset temperature of degradation for 1 wt% UFNBRP composite, and 25 °C increment in the maximum decomposition temperature compared with the values for pure PBT. It means that small amount of UFNBRP has a good retarding effect on the thermal degradation of PBT and is capable of improving the thermal stability of PBT. However, with further increase of UFNBRP percentage in the nanocomposites, the thermal stability decreases significantly (Fig. 7) in a nitrogen atmosphere, but they are still not lower than pure PBT. The specific degradation mechanism in this system needs to be further investigated.

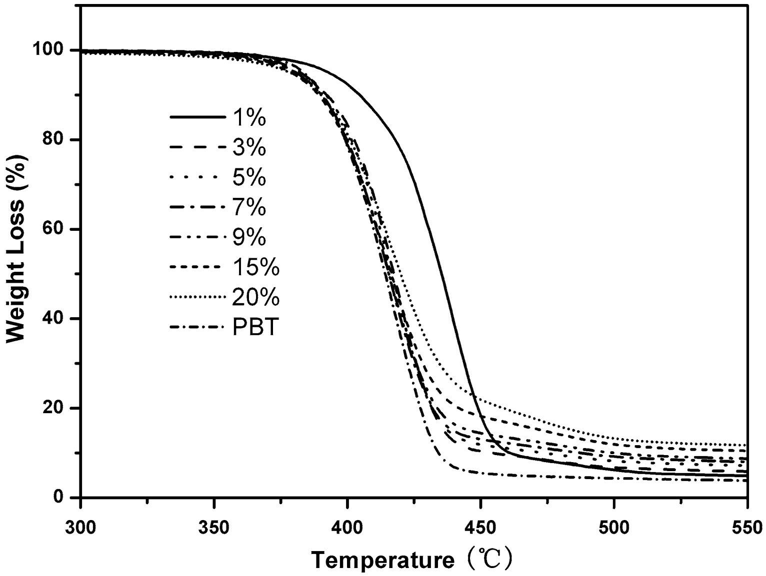


**Fig. 7** TGA curves of PBT/UFNBRP composites with various UFNBRP contents

**Table 3** TGA data of PBT and PBT/UFNBRP composites

| UFNBRP content (wt%) | $T_{10\ \mathrm{wt\%}}$ (°C) | $T_{\max}$ (°C) | Char yield at 650 °C (wt%) |
|---|---|---|---|
| 0 | 390.7 | 415.7 | 3.0 |
| 1 | 404.0 | 440.8 | 3.8 |
| 3 | 392.4 | 420.7 | 5.0 |
| 5 | 392.0 | 419.3 | 6.2 |
| 7 | 390.1 | 417.0 | 7.0 |
| 9 | 390.2 | 415.5 | 7.6 |
| 15 | 389.2 | 412.4 | 9.5 |
| 20 | 390.1 | 415.3 | 10.6 |

## Conclusions

In this study, the toughened PBT was prepared with nanoscale ultra-fine full-vulcanized acrylonitrile butadiene rubber particles (UFNBRP) via reactive extrusion in a twin-screw extruder. The izod impact strength, morphology, and crystallization properties of the nanocomposites were investigated.

These results showed that the nano-sized UFNBRP can improve the impact strength of PBT effectively which increased from 7.1 to 13.4 kJ/m$^2$. This may be attributed to the reactive compatibility of UFNBRP and the PBT matrix. The TEM and SEM micrographs indicated that the UFNBRP was well dispersed in the PBT matrix and had a good interfacial compatibility with the latter. Meanwhile, the FTIR spectra also proved the reactions between the carboxyl groups on the surface of the UFNBRP and the hydroxyl end groups of PBT which confirmed the reactive compatibility. The incorporation of UFNBRP also exhibited good nucleation effect in the PBT matrix. Moreover, small amount of nano-sized UFNBRP was found to be enough to improve the thermal stability of the composites. The maximum temperature of decomposition was increased 25 °C for UFNBRP 1 wt% comparing with that of pure PBT.

## References

1. Phinyocheep P, Saelao J, Buzare JY (2007) Mechanical properties, morphology and molecular characteristics of poly(ethylene terephthalate) toughened by natural rubber. Polymer 48:5702–5712
2. Loyens W, Groeninckx G (2002) Ultimate mechanical properties of rubber toughened semicrystalline PET at room temperature. Polymer 43:5679–5691
3. Loyens W, Groeninckx G (2003) Rubber toughened semicrystalline PET: influence of the matrix properties and test temperature. Polymer 44:123–136
4. Huang WJ (2007) Effect of nanoscale fully vulcanized acrylic rubber powders on crystallization of poly(butylene terephthalate): isothermal crystallization. Eur Polym J 43:4188–4196
5. Huang WJ (2007) Effect of nanoscale fully vulcanized acrylic rubber powders on crystallization of poly(butylene terephthalate): nonisothermal crystallization. J Appl Polym Sci 106:2031–2040
6. Xu D, Karger-Kocsis J, Apostolov AA (2009) Effect of nanoscale fully vulcanized acrylic rubber powders on crystallization of poly(butylene terephthalate): nonisothermal crystallization. Eur Polym J 45:1270–1281

7. Coran AY, Patel R (1983) Rubberthermoplastic compositions. VIII: nitrile rubber polyolefin blends with technological compatibilization. Rubber Chem Technol 56:1045–1060
8. Qiao J, Wei G, Zhang X, Liu Y (2002) Preparation of size-controllable fully cured powered rubbers and its application. PCT/CN00/00281
9. Liu Y, Zhang X, Wei G, Gao J, Huang F, Zhang M, Guo M, Qiao J (2002) Special effect of ultra-fine rubber particles (UFRP) on plastic toughening. Chin J Polym Sci 20:93–98
10. Qiao JL, Zhang XH, Liu SY, Wei G, Zhang SH, Zhang M, Gao J, Huang F (2001) Study on the fully cured thermoplastic elastomers prepared by blending with ultrafine powdered rubbers and plastics. Symp Polym Sci Chin G:243
11. Wang QG, Zhang XH, Liu SY, Gui H, Lai JM, Liu YQ, Gao JM, Huang F, Song ZH, Tan BH, Qiao JL (2005) Ultrafine full-vulcanized powdered rubbers/PVC compounds with higher toughness and higher heat resistance. Polymer 46:10614–10617
12. Liu YQ, Zhang XH, Gao JM, Huang F, Tan BH, Wei GS, Qiao JL (2004) Toughening of polypropylene by combined rubber system of ultrafine full-vulcanized powdered rubber and SBS. Polymer 45:275–286
13. Huang F, Liu YQ, Zhang XH, Wei GS, Gao JM, Song ZH, Zhang ML, Qiao JL (2002) Effect of elastomeric nanoparticles on toughness and heat resistance of epoxy resins. Macromol Rapid Commun 23:786–790
14. Peng J, Qiao JL, Zhang SJ, Wei GS (2002) A novel impact modifier for nylon 6. Macromol Mater Eng 287:867–870
15. Vendramini J, Bas C, Merle G, Boissonnat P, Alberola ND (2000) Commingled poly(butylene terephthalate)/unidirectional glass fiber composites: influence of the process conditions on the microstructure of poly(butylene terephthalate). Polym Compos 21:724–733
16. Jafari SH, Pötschke P, Stephan M (2002) Thermal behavior and morphology of polyamide 6 based multicomponent blends. J Appl Polym Sci 84:2753–2759
17. Wu S (1988) A generalized criterion for rubber toughening: the critical matrix ligament thickness. J Appl Polym Sci 35:549–561
18. Wu S (1985) Phase structure and adhesion in polymer blends: a criterion for rubber toughening. Polymer 26:1855–1863
19. Zhang ML, Liu YQ, Zhang XH, Gao JM, Huang F, Song ZH, Wei GS, Qiao JL (2002) The effect of elastomeric nano-particles on the mechanical properties and crystallization behavior of polypropylene. Polymer 43:5133–5138
20. Pralay M, Kazunobu Y, Masami O, Kazue U, Kazuaki O (2002) New polylactide/layered silicate nanocomposites: role of organoclays. Chem Mater 14:4654–4661
21. Abhijit JH, Bhowmick AK (1997) Thermoplastic elastomeric blends of poly(ethylene terephthalate) and acrylate rubber: 1. Influence of interaction on thermal, dynamic mechanical and tensile properties. Polymer 38:4337–4344
22. He MJ, Chen WX, Dong XX (1993) Polymer physics, 1st edn. Fudan press, Shanghai, p 96
23. Dong WF, Zhang XH, Qiao JL et al (2006) Effect of rubber on properties of nylon-6/unmodified clay/rubber nanocomposites. Eur Polym J 42:2515–2521