

# Effect of Ultrasound on the Processability and Mechanical Properties of Poly(butylene terephthalate)/Talc Composites

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Received 20 April 2010; accepted 18 July 2010

DOI 10.1002/app.34043

Published online 29 June 2011 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** Poly(butylene terephthalate) (PBT)/talc composites were prepared through a single-screw extruder in the absence or presence of ultrasonic irradiation. A special exit die, which could be regarded as a capillary, was attached to the extruder to measure the effect of ultrasound on the melting temperature and pressure. The experimental results show that with the introduction of ultrasound and with its increasing intensity, the processability of the composites was improved. The morphology of the composites was also investigated by scanning electron microscopy. It was shown that ultrasonic oscillations

improved the dispersion of talc in PBT and, furthermore, increased the crystallinity of PBT. Therefore, the mechanical properties were promoted through ultrasonic extrusion but decreased once the ultrasonic intensity was higher than 200 (or 150) W. This deterioration of the mechanical properties was induced by the ultrasonic degradation of PBT. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 2708–2714, 2011

**Key words:** extrusion; fillers; mechanical properties; melting point; structure property relations

## INTRODUCTION

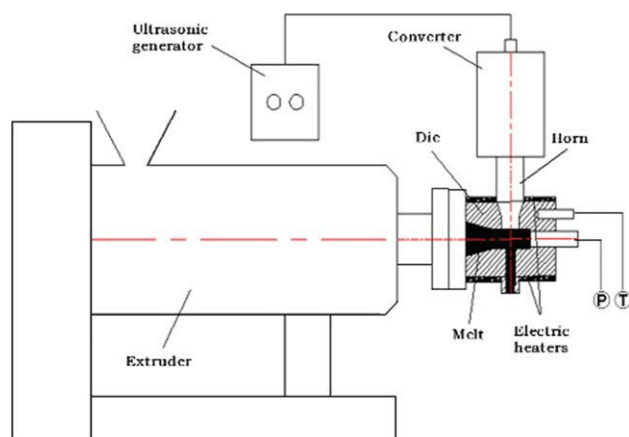
Poly(butylene terephthalate) (PBT) is an important semicrystalline polymer and engineering plastic with excellent heat resistance, weatherability, and mechanical properties, which has been widely used in electric appliance, vehicles, machinery, and other applications. However, its disadvantages, such as low impact strength and heat distortion temperature, limit the applications of PBT.<sup>1</sup> Some reports have shown that the addition of inorganic fillers, such as organoclay,<sup>2,3</sup> carbon nanotubes,<sup>4,5</sup> SiO<sub>2</sub>,<sup>6</sup> carbon fibers,<sup>7</sup> and glass fibers,<sup>8,9</sup> can promote the comprehensive performance of PBT in practical applications. Among them, talc {Mg<sub>3</sub>[Si<sub>4</sub>O<sub>10</sub>](OH)<sub>2</sub>} is a cheap inorganic filler with a trioctahedral layered structure, the use of which leads to a reinforcing effect in polymers.<sup>10,11</sup> Nevertheless, the introduction of inorganic fillers brings two negative effects for the application of PBT materials. On the one hand, unstable flow occurs easily in the exit mold because of the increasing melt viscosity of PBT; this leads to a decrease of processability. On the other hand, the apparent qual-

ity and mechanical properties deteriorate because of the aggregation of inorganic fillers in PBT. Therefore, the question of how to improve the processability and dispersion of inorganic-filler-filled polymer composites has absorbed many researchers' attention.

The traditional methods for improving the extrusion behaviors of high-viscosity polymer materials are the addition of processing aids or plasticizers and the adjustment of the extrusion parameters.<sup>12</sup> However, in many cases, these methods have been found to be insufficient and even inapplicable or to be limited because of the polymer's thermal stability. At the same time, these methods rely on the operators' experience and an improvement in the extruder, which means an increase in the production cost. Moreover, the dispersion of fillers in composites is hardly improved through these methods.

Recently, mechanical<sup>13</sup> or electromagnetized<sup>14</sup> vibrations were introduced into the extrusion of polymer melts to improve the processability of the polymers. As compared to mechanical or electromagnetized vibrations, ultrasonic oscillations have characteristics of high frequency, low amplitude, and noise. Ultrasonic irradiation has been widely applied to the synthesis, degradation, and modification of polymer solutions. Since Isayev and coworkers<sup>15–18</sup> found that high-intensity ultrasonic irradiation can rapidly break up the three-dimensional network in crosslinked rubber through the scission of C–S,

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**Figure 1** Schematic of the ultrasonic extrusion system. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

S—S, and C—C bonds, the application of power ultrasound in the field of polymer processing has become more and more extensive, including the improvement of processing behaviors, the degradation of polymer melts, and the *in situ* compatibilization of polymer blends. Many studies have shown that with the introduction of ultrasonic irradiation, the apparent viscosity, die pressure, and die swell rate decreased, whereas the mechanical properties, die temperature, and productivity increased.<sup>19–23</sup> For melted polymer blends, their compatibility increased because of the *in situ* formation of copolymer by the coupling of ultrasound-induced macromolecular radicals. The improvement of these properties did not depend on the addition of some special materials that were synthesized through the chemical route. It seems that ultrasound-assisted polymer processing is an environmentally friendly and valid method for improving the processability and mechanical properties of a polymer material.

Despite the potential uses of ultrasonic effects on the extrusion processing and modification of polymers, little attention has been focused on the system of filler-filled polymers. Li et al.<sup>24</sup> studied the effects of ultrasonic oscillations on the rheological and viscoelastic properties and morphology of high-density polyethylene/Illite (70/30) composites. The experiment results showed that the die pressure and apparent viscosity were greatly reduced and the dispersion of Illite particles into the high-density polyethylene matrix was improved. Obviously, the researches in this field were very profound work because of the positive effects of ultrasound on the processability and dispersion of filler-filled polymers.

In this study, we prepared poly(butylene terephthalate)/talc (PBT) composites by means of ultrasonic extrusion. The effects of ultrasonic oscillations on the apparent viscosity, die pressure, exit swell, appearance, crystallization, phase morphology, and mechanical properties of the composites were studied.

## EXPERIMENTAL

### Material

The PBT, with a melt index of 22 g/min, used in this study was obtained from YiZheng Chemical Fiber Co., Ltd., Engineering Plastic Factory (YiZheng, China). Talc, with an average diameter of 4.25  $\mu\text{m}$ , was provided by HaiCheng TianHe Chemistry Industry Co., Ltd. (HaiCheng, China).

### Preparation and equipment

The ultrasonic extrusion of PBTT composites were carried out in a special extrusion system, the schematic of which is shown in Figure 1. It consisted of a single-screw extruder (diameter = 30 mm, length/diameter = 30) and a cylinder die. This die was a special capillary with a length/diameter ratio of 8, attached to the single-screw extruder. A horn of ultrasonic oscillation with a maximum power output of 300 W and a frequency of 20 kHz was inserted into the polymer melt of the die, and the oscillation was in the direction parallel to the flow of the polymer melt. A pressure transducer and a thermal couple at the die entry were installed to continuously record the variation of die pressure and temperature during the extrusion process and to indicate the rheological properties of the polymer melt. The set temperature of the extruder and cylinder die was 240°C. The rotation speed of extruder was 20 rpm. The abbreviations and compositions of PBTT are listed in Table I.

### Measurements and characterizations

The rheological properties of the PBTT composites were studied during ultrasonic extrusion. The die of the extruder shown in Figure 1 could be treated as a capillary rheometer, and the shear stress at the capillary wall ( $\tau_w$ ), shear rate ( $\dot{\gamma}_w$ ), and apparent viscosity ( $\eta_a$ ) were calculated as follows:

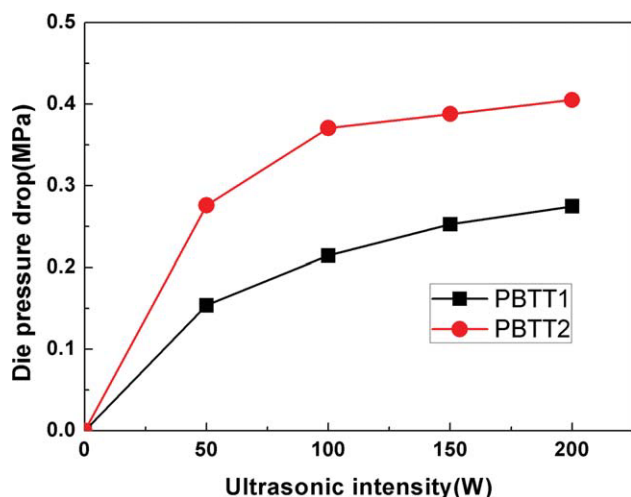
$$\tau_w = \frac{PD}{4L} \quad (1)$$

$$\dot{\gamma}_w = \frac{32Q}{\pi D^3} \quad (2)$$

$$\eta_a = \frac{\tau_w}{\dot{\gamma}_w} = \frac{\pi PD^4}{128QL} \quad (3)$$

**TABLE I**  
Compositions and Abbreviations of the PBTT Composites

Abbreviation	Content (wt %)	
	PBT	Talc
PBTT1	98	2
PBTT2	80	20



**Figure 2** Dependence of the die pressure drop on the ultrasonic intensity. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

where  $P$  is the die pressure,  $L$  is the length of the capillary,  $D$  is the diameter of the capillary, and  $Q$  is the flow rate.

To investigate the appearance and inner morphology of the extrudates, a JEOL JSM-5900LV scanning electron microscope (JEOL, Tokyo, Japan) was used. Before the scanning electron microscopy (SEM) observations, gold was coated onto the liquid- $N_2$ -fractured surfaces of the composites.

The tensile mechanical properties of the composites were studied at room temperature on an SANS CMT4104 universal testing machine (Xinsansi, Shenzhen, China). The measurements of unnotched impact strength were performed with a Charpy impact tester at room temperature. The tensile specimens, with dimensions of  $20 \times 4 \times 2 \text{ mm}^3$ , and the impact specimens, with dimensions of  $80 \times 10 \times 4 \text{ mm}^3$ , were obtained through injection molding on a HAAKE MiniJet (Liangjing, Shanghai, China).

The inherent viscosity of PBT in the absence or presence of ultrasonic irradiation was measured at  $25^\circ\text{C}$  by a capillary viscometer according to ISO 1628/1-1984(E). The diameter, length, and constant of apparatus were, respectively, 0.54 mm, 120 mm, and  $0.0119 \text{ mm}^2/\text{s}^2$ . The solvents used here were phenol and 1,1,2,2-tetrachloroethane (1 : 1 by volume).

The melting behaviors of the PBTT composites were measured on a TA DSC Q20 under a nitrogen atmosphere (TA, US, New Castle). The samples were heated from 25 to  $280^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$ .

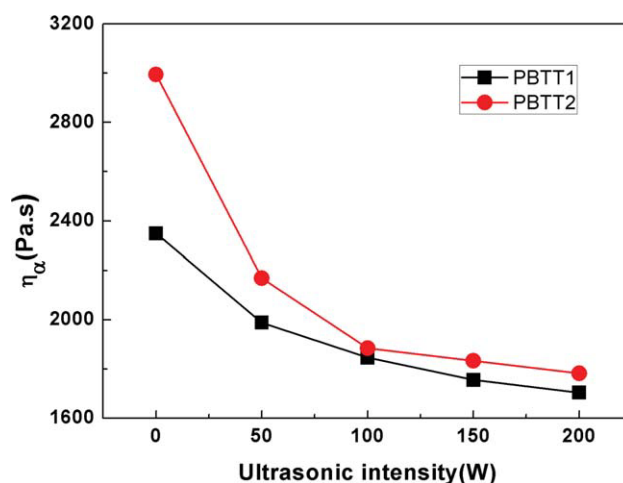
## RESULTS AND DISCUSSION

### Processing properties

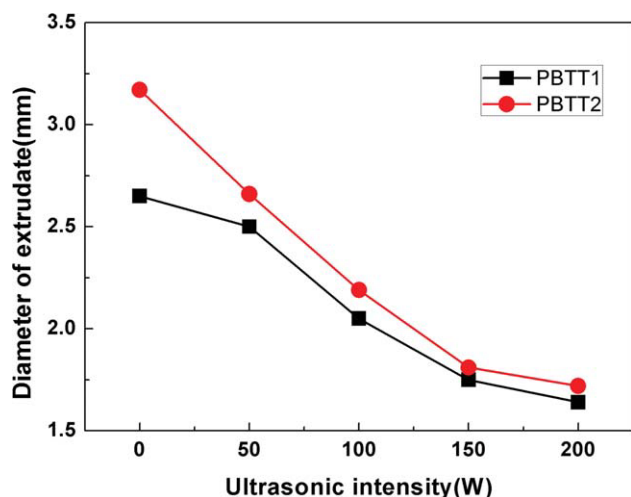
First, we investigated the effect of ultrasound on the die pressure of the polymer melt. The die pressure

was recorded by the pressure transducer installed at the die entry, as shown in Figure 1. The relative die pressure drop ( $\Delta P$ ) in the presence of ultrasonic irradiation can be expressed as  $\Delta P = \frac{P_0 - P_u}{P_0} \times 100\%$ , where  $P_0$  and  $P_u$  are the die pressures in the absence and presence of ultrasonic irradiation, respectively. Figure 2 reveals the dependence of  $\Delta P$  on the ultrasonic intensity. It could be found that  $\Delta P$  increased substantially with the growth of ultrasonic intensity; this indicated that the die pressure decreased greatly during the ultrasonic extrusion. For example,  $\Delta P$  of PBTT2 amounted to 41% when the ultrasonic intensity was 200 W. Compared with that of PBTT1,  $\Delta P$  of PBTT2 was higher when the ultrasonic intensity was the same; this implied that ultrasonic oscillations could more obviously affect polymer melts with a higher melt viscosity.

According to eqs. (1)–(3), the apparent viscosity is proportional to the die pressure. Therefore, the apparent viscosity of polymer melts would depend strongly on the die pressure. As clearly shown in Figure 3, the apparent viscosity of the PBTT composites decreased greatly with the rise of ultrasonic intensity. Our previous works<sup>25–27</sup> revealed that the ultrasound-assisted decrease of apparent viscosity was a physical process, not a chemical process induced by degradation of PBT in the presence of ultrasonic irradiation. The die of the extruder was vibrated by the drive of ultrasonic oscillations. This could have conduced the decrease in friction force between the polymer melts and die wall; this implies that ultrasonic irradiation decreased the apparent viscosity of the polymer melts during extrusion. On the other hand, a high frequency and low amplitude are the features of ultrasonic irradiation; they make it easy to act with the microstructure of polymer. An



**Figure 3** Apparent viscosity versus the ultrasonic intensity for the PBTT composites. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

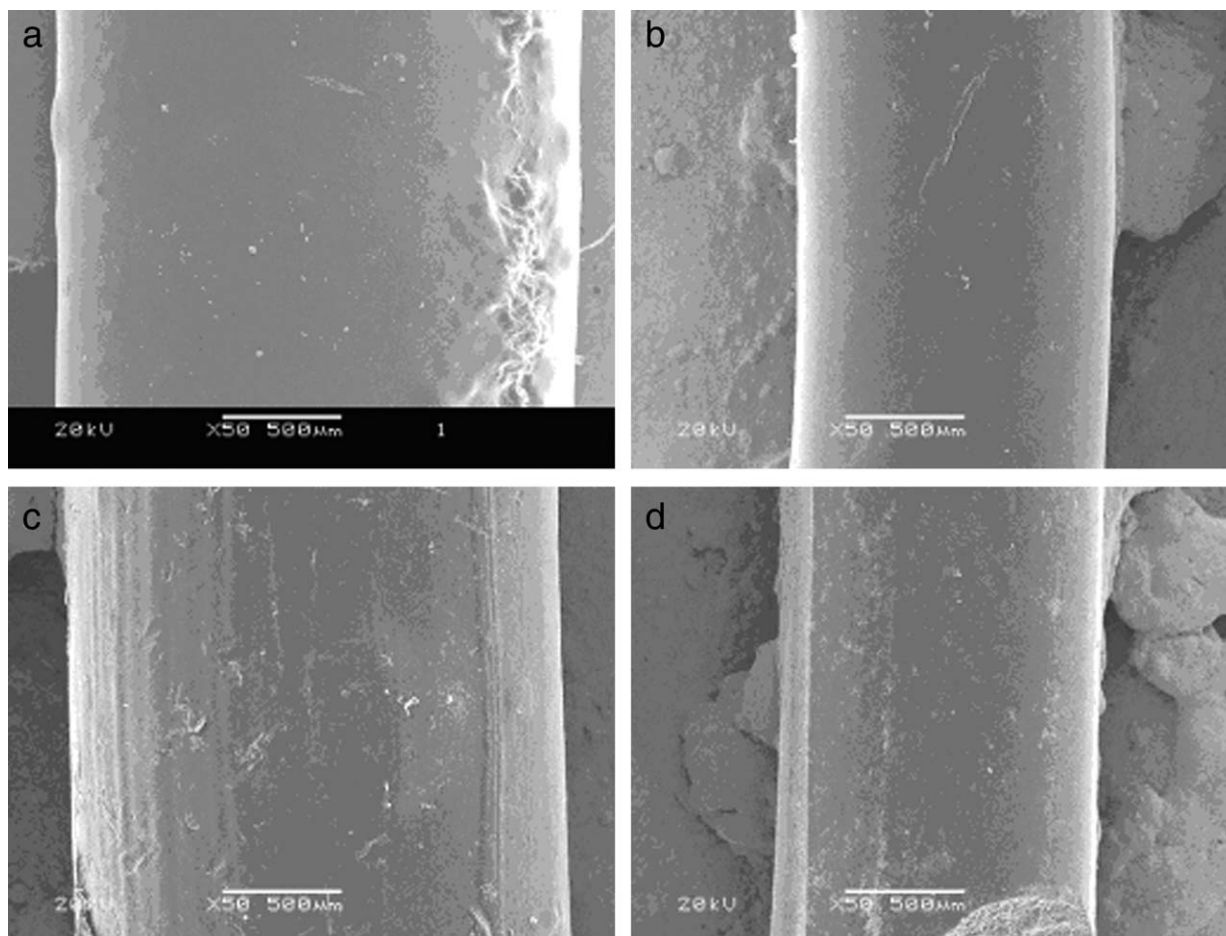


**Figure 4** Dependence of the diameter of the extrudates on the ultrasonic intensity. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

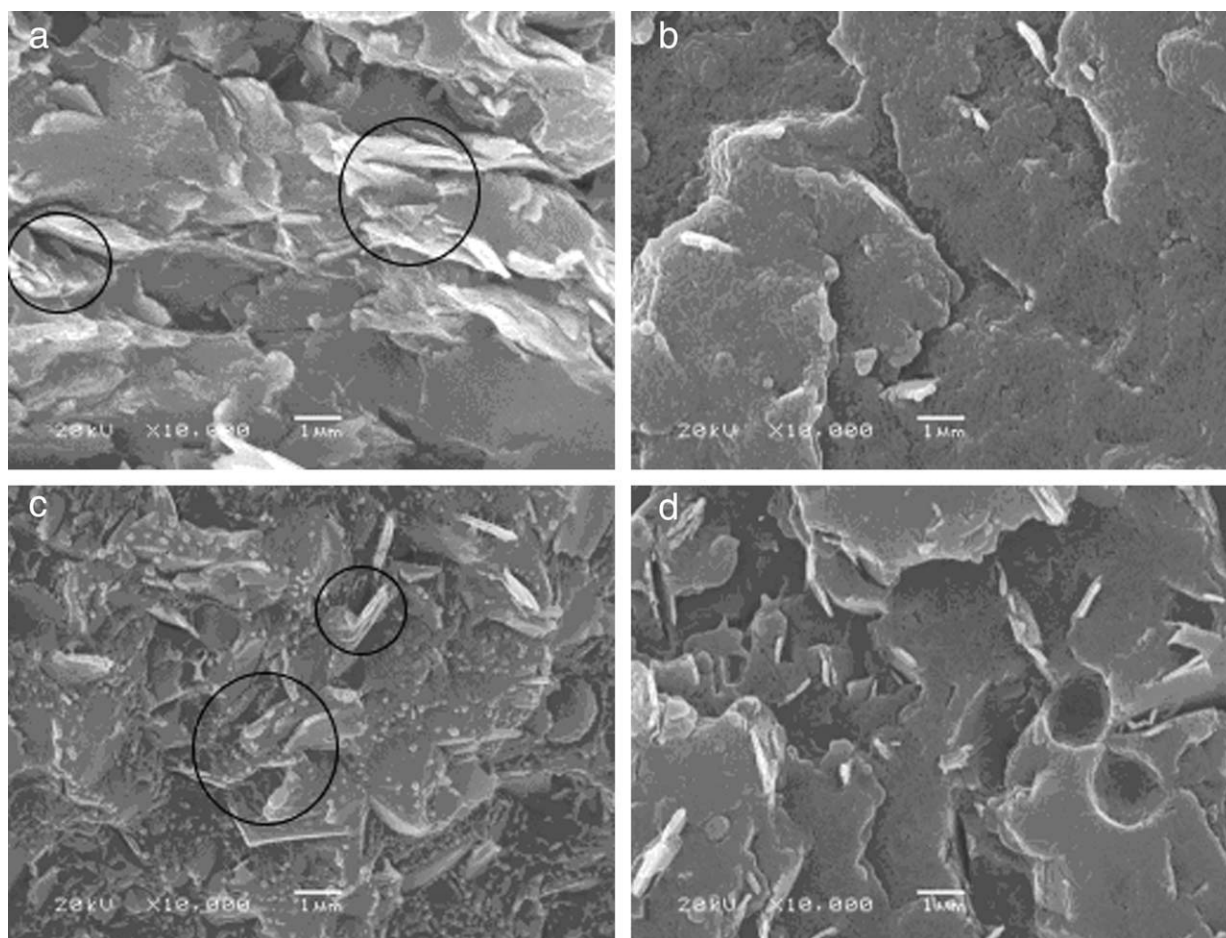
ultrasonic shake wave activated the molecules of the polymer, and hence, it enhanced macromolecular motion ability and shortened the relaxation time of macromolecules, which led to an increase in the

flowability of polymer melts. This shorter relaxation time brought a change in the die swell of the extrudate, which was caused by the deformation of polymer in the die and the sequential relaxation of melt molecules at the exit of the die. Figure 4 shows that the average diameter of extrudates decreased greatly with the increase of ultrasound intensity. The larger diameter of PBTT2 compared to that of PBTT1 was due to its higher viscosity.

The decrease of die pressure was in favor of the processing of high-viscosity melts and could prevent the occurrence of unstable flow, a rough surface of extrudate. Generally, a rough surface appears at a low critical shear stress or shear rate for high-viscosity polymer composites. This is a major obstacle to increasing the rate of production in polymer processing operations. Therefore, increasing the critical shear stress or shear rate for high-viscosity melts was the focused task to increase productivity. As revealed in Figure 5, when the shear rate was  $24.2 \text{ s}^{-1}$  and the ultrasonic intensity was 0, PBTT1 and PBTT2 both showed an apparently rough appearance. However, the surfaces of the PBTT1 and PBTT2 extrudates in the presence of 150 W of ultrasonic irradiation



**Figure 5** SEM image of the appearances of the PBTT composite extrudates untreated and treated at a 150-W ultrasonic intensity: (a) PBTT1, 0 W; (b) PBTT1, 150 W; (c) PBTT2, 0 W; and (d) PBTT2, 150 W.



**Figure 6** SEM images of the brittle fracture surfaces of the PBTT composite extrudates untreated and treated at a 150-W ultrasonic intensity: (a) PBTT1, 0 W; (b) PBTT1, 150 W; (c) PBTT2, 0 W; and (d) PBTT2, 150 W.

became smooth at the same shear rate. This indicated that the introduction of ultrasound increased the critical shear rate and restrained the occurrence of rough surfaces.

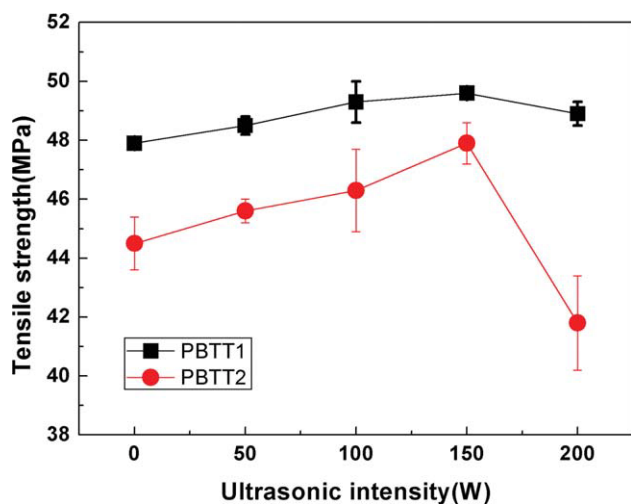
### Morphology and mechanical properties

SEM images of the PBTT composites were taken to investigate the effects of ultrasound and its intensity on the dispersion of talc in PBT. In general, the size of the aggregates of the fillers decreased, and its distribution became even in inorganic-filler-filled polymer composites after the surface treatment of the fillers with a coupling agent. A similar change can be seen in Figure 6, where large and aggregated talc particles can be observed on the fractured surface; however, the talc particles became small, and the aggregation of the talc particles disappeared in the presence of 150 W of ultrasonic irradiation. This confirmed that by the application of ultrasound, the compatibility of PBT and talc was improved with a relatively homogeneous dispersion of talc particles into the PBT matrix.

The tensile strength of the PBTT composites, untreated or treated by ultrasound, is shown in

Figure 7. The tensile strength of neat PBT was 44 MPa. It could be found that the tensile strength increased with 2 wt % talc added to the PBT matrix. However, with the introduction of 20 wt % talc, it was hard to increase the tensile strength because of the larger aggregates of talc. The tensile strength of PBTT1 was higher than that of PBTT2 because of the increasing aggregation of a higher content of talc in PBT. However, as stated previously, ultrasonic treatment could decrease the size of talc aggregates. It could be seen that the tensile strength of PBTT composites increased gradually when the ultrasonic intensity increased from 0 to 150 W. The maximum increasing amplitude for PBTT1 and PBTT2 amounted to 1.7 and 3.4 MPa, respectively.

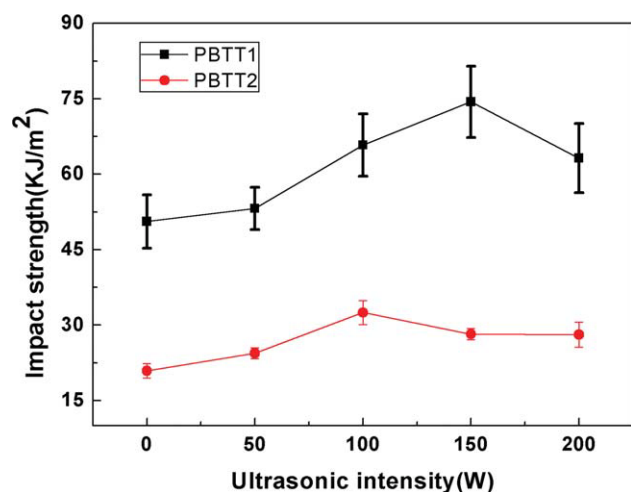
Figure 8 shows the dependence of the impact strength on the ultrasonic intensity. The impact strength of neat PBT was 53 KJ/m<sup>2</sup>. It could be found that the impact strength decreased with the introduction and increase of talc. However, the ultrasonic treatment could reduce this negative impact. The impact strength of PBTT1 increased with increasing ultrasonic intensity from 0 to 150 W, and PBTT2 owned the highest impact strength when the



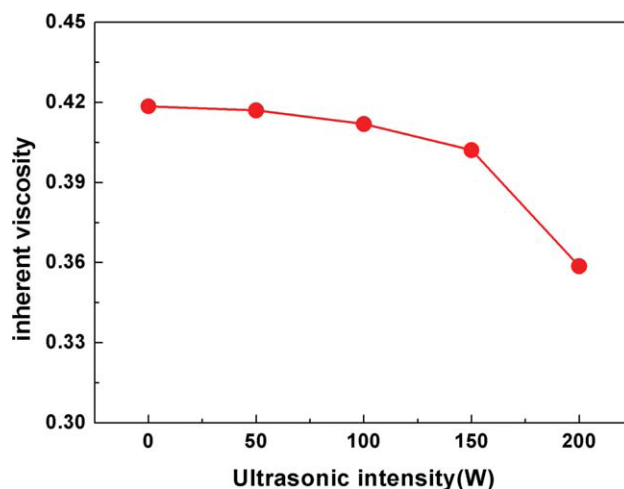
**Figure 7** Tensile strengths for the PBTT composites untreated and treated at different ultrasonic intensities. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

ultrasonic intensity was 100 W. The maximum increasing amplitudes of impact strength for PBTT1 and PBTT2 were 23.8 and 11.6 KJ/m<sup>2</sup>. The more significant improvement of impact strength for PBTT1 was attributed to its smaller size of aggregates and more even dispersion of talc particles, as revealed in Figure 6.

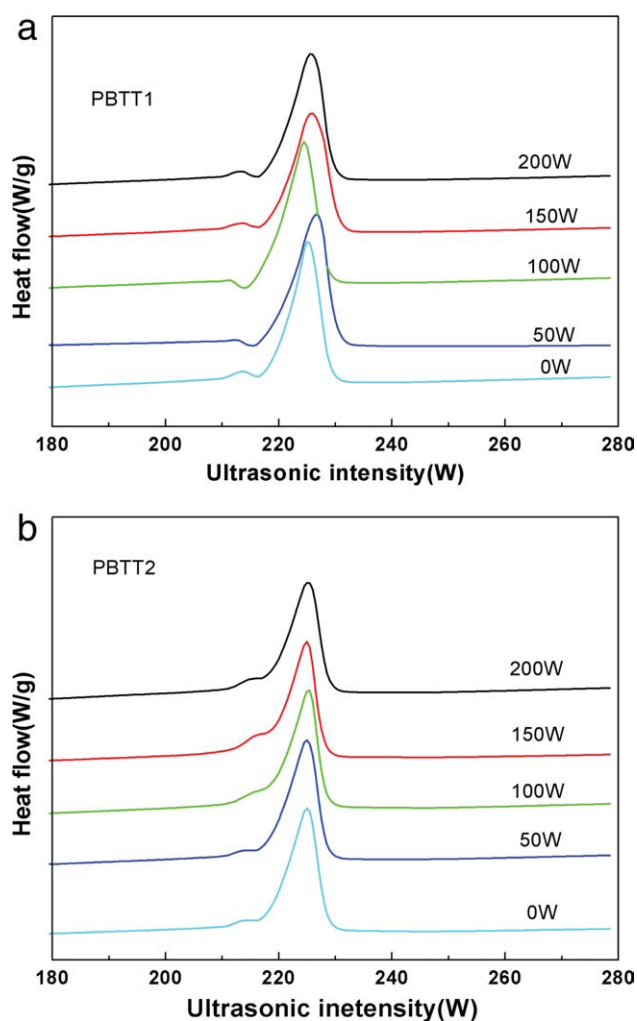
In Figures 7 and 8, we can find that the tensile strength and impact strength of the PBTT composites decreased seriously at an ultrasonic intensity of 200 W (in the case of the impact strength of PBTT2, the inflexion point appeared at 150 W). This decrease in the mechanical properties was connected to the change of the molecular weight of PBT in the presence of ultrasonic irradiation. The molecular



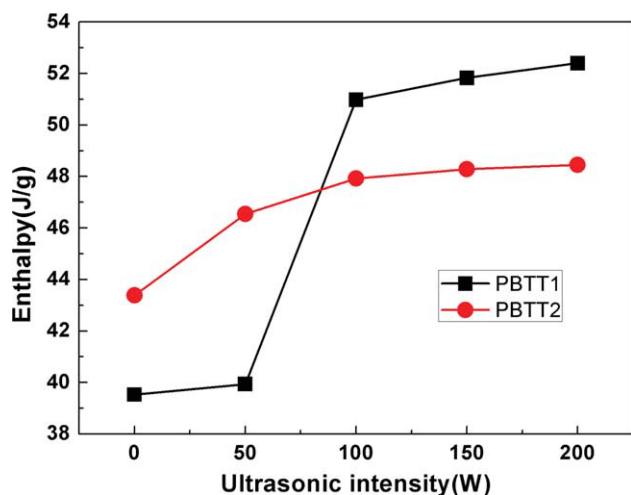
**Figure 8** Impact strengths of the PBTT composites untreated and treated at different ultrasonic intensities. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 9** Inherent viscosities of PBT untreated and treated at different ultrasonic intensities. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 10** DSC melt curves for the PBTT composites untreated and treated at different ultrasonic intensities. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 11** Enthalpy of PBT of the PBTT composites untreated and treated at different ultrasonic intensities. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

weight could be expressed by the inherent viscosity of PBT, which is shown in Figure 9. It could be seen that the inherent viscosity remained almost invariable from 0 to 150 W but decreased once the ultrasonic intensity was higher than 150 W. This decrease in the molecular weight finally led to the deterioration of the mechanical properties of the PBTT composites.

### Differential scanning calorimetry (DSC) results

Figure 10 shows the first DSC heating thermograms for the PBTT composites. The melting enthalpy, which characterized the crystallinity of PBT, could be measured according to Figure 10. It could be found that the effect of ultrasonic irradiation on the melting point was negligible. However, the introduction of ultrasound led to an obvious change of the melting enthalpy, as shown in Figure 11. Compared with net PBT with a melt enthalpy of 33.4 J/g, the introduction of talc led to an increase of the melt enthalpy. It was ascribed to the heterogeneous nucleation of talc. The melting enthalpy of PBTT1 increased from 39.5 to 52.4 J/g when the ultrasonic intensity increased from 0 to 200 W. In the same range of ultrasonic intensity, the increasing amplitude of melting enthalpy of PBTT2 was 5.2 J/g. The higher increasing amplitude of the melting enthalpy of PBTT1 compared to that of PBTT2 was mainly due to the smaller size and better dispersion of talc particles in PBTT1, which increased the nucleating efficiency. Furthermore, the increase of crystallinity was in favor of the mechanical properties.

### CONCLUSIONS

In summary, the ultrasonic irradiation with high frequency and low amplitude obviously improved the processability and morphology of the PBTT composites. With the introduction of ultrasound and its increasing intensity, the apparent quality improved, and the melt pressure and diameter of the extrudates decreased. The ultrasonic oscillations could also break up the aggregation of talc particles in PBT. Therefore, the compatibility of the composites and nucleating efficiency of talc increased; this led to the improvement of the mechanical properties. However, when the ultrasonic intensity was higher than 200 (or 150) W, the serious ultrasonic degradation of PBT occurred, and then, the mechanical properties deteriorated.

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