

# Crystalline, Rheological and Mechanical Enhancement in PBAT/PPC/Silica Nanocomposites with Double Percolation Network

You-Mei Ma<sup>a</sup>, Feng-Xiang Gao<sup>b</sup>, and Shu-Ling Zhang<sup>a\*</sup>

<sup>a</sup> College of Chemistry, Jilin University, Changchun 130012, China

<sup>b</sup> Key Laboratory of Polymer Ecomaterials, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

 Electronic supplementary information

**Abstract** Nanocomposites of blends of biodegradable poly(butylene adipate-co-terephthalate) (PBAT) and sustainable poly(propylene carbonate) (PPC) with nanosilica were prepared by melt compounding method. PBAT/PPC blend was partially miscible system with sea-island structure, and nanosilica particles were selectively dispersed in the continuous phase PBAT matrix to form the double percolation network. The introduction of nanosilica into PBAT/PPC blend reduced the size of dispersed PPC phase, promoted the crystallization of PBAT in the nanocomposites, and increased the storage modulus of the nanocomposites. The study of rheological behaviors indicated that the double percolation network was formed at the nanosilica loading of 5 wt%, as a result, the nanocomposites exhibited the solid-like viscoelastic behavior and their relaxation time was extended. With the increase of the nanosilica content, the PBAT/PPC/silica nanocomposites displayed increased Young's modulus and yield strength.

**Keywords** Nanocomposites; Selective dispersion; Double percolation; Enhanced properties

**Citation:** Ma, Y. M.; Gao, F. X.; Zhang, S. L. Crystalline, rheological and mechanical enhancement in PBAT/PPC/silica nanocomposites with double percolation network. *Chinese J. Polym. Sci.* 2022, 40, 1482–1492.

## INTRODUCTION

Recently, environmentally friendly polymers achieve a great deal of interest in materials science due to the increasing waste and pollution originated from non-biodegradable plastic and growing shortage of oil resources.<sup>[1,2]</sup> Biodegradable polymers have been widely studied in biomedical and industrial applications<sup>[3]</sup> because of their combination of biodegradability and biocompatibility.<sup>[4]</sup> Poly(butylene adipate-co-terephthalate) (PBAT), an aliphatic aromatic copolyester, is one of the promising biodegradable copolyesters,<sup>[5]</sup> which is manufactured from the condensation reaction between 1,4-butanediol, dimethyl terephthalate and adipic acid. PBAT shows low modulus and high elongation at break due to its flexible butylene adipate section (BA).<sup>[6]</sup> In addition, PBAT has moderate water vapor permeability.<sup>[7]</sup> Therefore, it can be used as breathable and packing films. Nonetheless, the low modulus and strength of PBAT have become a bottleneck for the further wide application of PBAT in many fields.<sup>[8]</sup> Consequently, some research efforts such as physical blending<sup>[9,10]</sup> and incorporation of fillers have been extensively studied.<sup>[11,12]</sup>

Usually, PBAT is used as the dispersed phase to toughening other biodegradable polymers, especially to toughening

poly(lactic acid) (PLA). Many properties of PLA/PBAT blends have been found to be greatly improved, including the elongation at break, melt elasticity and viscosity, and crystallization rate.<sup>[13,14]</sup> In addition, some properties of PLA/PBAT blends, such as the melting peak temperature and degree of crystallinity reduced with increasing PBAT contents.<sup>[15]</sup> Kumar *et al.*<sup>[16]</sup> prepared PLA/PBAT blends with glycidyl methacrylate (GMA) as a reactive compatibilizer and found an improvement in the impact strength and tensile modulus. Al-Itry *et al.*<sup>[17]</sup> studied the thermal degradation of PLA/PBAT blends by using the reactive extrusion with functionalized epoxy and found that the thermal stability of blends increased. Blends based on PBAT, such as PBAT/stereocomplex polylactide (SC-PLA) blends were prepared by melt blending and showed an enhancement in the rheological and mechanical properties compared with PBAT components.<sup>[18]</sup> Blown films of PBAT/PLA blends by twin-screw extruder exhibited the enhanced tensile strength and modulus.<sup>[19]</sup> It can be seen that there are few reports on the blends of PBAT and other polymers.

Poly(propylene carbonate) (PPC) is a sustainable and environmentally benign polymer,<sup>[20]</sup> which is synthesized by copolymerization of carbon dioxide (CO<sub>2</sub>) and oxirane in the presence of catalyst.<sup>[21]</sup> PPC has excellent processability so that it can be molded by various thermoplastic processing methods,<sup>[22]</sup> including solvent casting, blown film, compression molding, spin casting, injection molding, blow molding

\* Corresponding author, E-mail: zsl@jlu.edu.cn

Received February 28, 2022; Accepted April 5, 2022; Published online June 24, 2022

and extrusion casting.<sup>[23,24]</sup> Moreover, PPC shows high modulus and tensile strength compared with PBAT. Thus, in this study, sustainable PPC was selected to as minor phase to be blended with PBAT to prepare a binary blend with good processability.

Besides, composites with nanofillers is also an effective method for fabricating polymer materials with good property.<sup>[25]</sup> In recent years, there have been many reports on nanofillers improving the properties of PBAT. For example, montmorillonite (MMT) was found to decrease the biodegradation rate and water vapor transmission rate of PBAT/MMT nanocomposites.<sup>[26]</sup> The antibacterial and anti-static properties of PBAT were enhanced by the introduction of multi-walled carbon nanotubes (MWCNTs).<sup>[27]</sup> In addition, graphene oxide nanosheets (GONS),<sup>[28]</sup> nanoclay,<sup>[29]</sup> TiO<sub>2</sub> nanoparticles,<sup>[30]</sup> etc., have all been found to improve certain properties of PBAT. Fumed silica, a kind of nanoparticle, is considered a good nanofiller due to its high strength and modulus, low price, light mass, and rich resource. However, there have been few reports on the study of silica nanoparticles modified PBAT polymer and its blends. Therefore, in the present study, on the basis of PBAT/PPC blend, silica nanoparticles was selected as nanofiller to prepare the PBAT/PPC/silica nanocomposites by melt blending method. The effect of silica nanoparticles content on the phase morphology, thermal behaviors, and rheological and mechanical properties of PBAT/PPC/silica nanocomposites was investigated.

## EXPERIMENTAL

### Materials

PBAT with weight-average molecular weight ( $M_w$ ) of  $1.50 \times 10^5$  g/mol and polydispersity of 1.45 was purchased from Xinjiang Blue Ridge Tunhe Chemical Industry Joint Stock Co., LTD. PPC with  $M_w$  of  $1.3 \times 10^5$  g/mol and polydispersity of 2.60 was supplied free from Changchun Institute of Applied Chemistry, CAS. The nanosilica with SiO<sub>2</sub> content greater than 99.8% (AEROSIL 200) was provided by Degussa AG (Hanau, Germany). The diameter and specific surface area were 12 nm and 220 m<sup>2</sup>/g, respectively.

### Sample Preparation

Prior to blending, PBAT, PPC and nanosilica were dried in a vacuum oven of 50 °C for 24 h. Melt mixing of PBAT, PPC and nanosilica was conducted on a Haake batch intensive mixer (Haake Rheomix 600, Karlsruhe, Germany). The chamber temperature, residence time, and screw speed were 170 °C, 4 min, and 60 r/min, respectively. Then, all samples were compression molded at 150 °C for 5 min and cold pressed to form sheet with thickness of 1 mm. Neat PBAT underwent the same thermal processing in order to obtain the same thermal history. In the PBAT/PPC/silica nanocomposites, the mass ratio of PBAT to PPC was set to 70:30 (see the electronic supplementary information, ESI, for other mass ratio of PBAT to PPC), and the mass percentages of nanosilica were 0 wt%, 2 wt%, 5 wt% and 10 wt%. For convenience, PBAT/PPC/silica nanocomposites were designated as PBAT/PPC-*X*, where *X* represented the weight percentage of nanosilica in the nanocomposites.

## Characterization

### Scanning electronic microscopy (SEM)

The phase morphology of PBAT/PPC blend and PBAT/PPC/silica nanocomposites was observed on a SEM (FEI Co., Eindhoven, Netherlands) with an accelerating voltage of 10 kV. All specimens were cooled in liquid nitrogen for about 10 min, and then they were fractured. Before SEM observation, the fracture surfaces of the samples were sputtered with a layer of gold.

### Dynamic mechanical analysis (DMA)

DMA tests of neat PBAT, PPC and PBAT/PPC/silica nanocomposites were carried out on a dynamic mechanical analyzer of TA instruments (Q800, USA) in tensile mode. Rectangular specimens (20 mm × 10 mm × 1 mm) were used in this work. The test frequency, temperature range and heating rate were 1 Hz, −60–80 °C, and 3 °C/min, respectively.

### Differential scanning calorimetry (DSC)

The thermal behaviors of neat PBAT and PBAT/PPC/silica nanocomposites were studied by using a TA Instruments DSC Q20 (USA) at nitrogen atmosphere. All samples weighing 5–8 mg were heated from −70 °C to 160 °C, at a heating rate of 10 °C/min (first heating), isothermal for 3 min, then cooled to −70 °C at a rate of 10 °C/min (first cooling), and finally heated to 160 °C at a rate of 10 °C/min again (second heating).

### Rheological measurements

The rheological properties of PBAT/PPC/silica nanocomposites were investigated using a rotational rheometer (TA Series AR2000ex, USA) equipped with a 25 mm parallel plate. The sheet samples with thickness of 1.0 mm were heated to 150 °C for frequency scanning. The frequency sweep range and amplitude were 0.05–100 rad/s and 1.25%, respectively. The test process was carried out in a nitrogen atmosphere.

### Tensile tests

Tensile tests were carried out by using a tensile testing machine (Instron-1121, USA) based on the ISO 527-1:2012 standard. The crosshead speed and test temperature were 20 mm/min and 25 °C, respectively.

### Contact angle

The contact angles were measured on a DSA100S static contact angle measurement instrument at ambient temperature. Double distilled water (H<sub>2</sub>O) and diiodomethane (CH<sub>2</sub>I<sub>2</sub>) were used as probe liquids.

## RESULTS AND DISCUSSION

### Formation of Percolation Network

It is well known that the rheological properties are much sensitive to phase morphology and microstructure in multiphase polymeric composites.<sup>[31,32]</sup> The oscillatory shear rheological test was performed at 150 °C in order to investigate the effect of nanosilica particles and dispersed PPC phase on the rheological properties of PBAT matrix. Figs. 1(a), 1(c), 1(e) and 1(f) illustrate the changes of the storage modulus ( $G'$ ), loss modulus ( $G''$ ), complex viscosity ( $|\eta^*|$ ) and  $\tan\delta$  as a function of frequency for neat PBAT and PPC, PBAT/PPC blend and PBAT/PPC/silica nanocomposites.

It is seen that the storage modulus ( $G'$ ) of PPC increases slightly with the addition of nanosilica at low angular frequency when the amount of nano silica reached 2 wt%. At

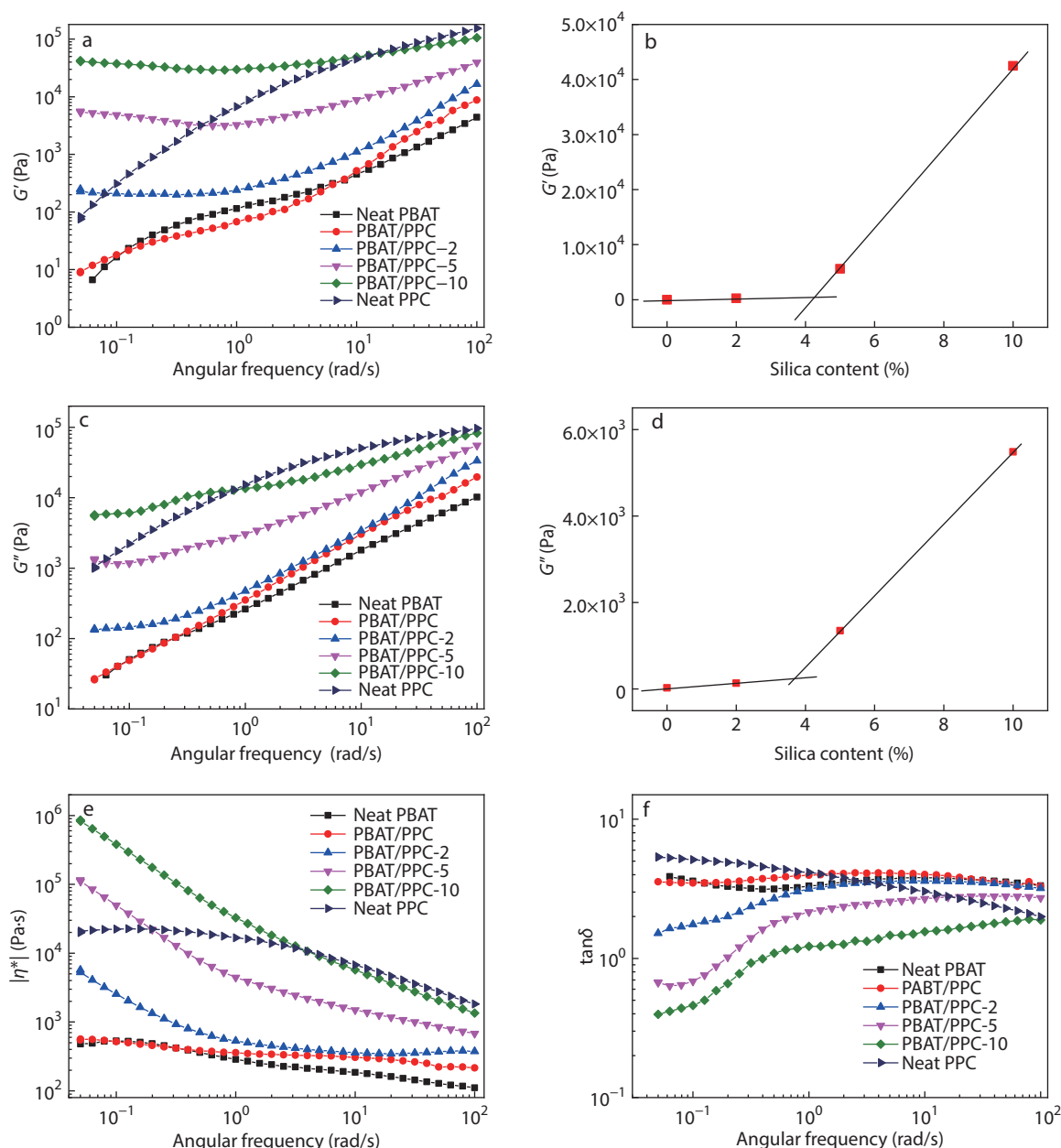


**Fig. 1** Change of (a) storage modulus ( $G'$ ), (c) loss modulus ( $G''$ ), (e) complex viscosity ( $|\eta^*|$ ) and (f)  $\tan\delta$  as a function of angular frequency for neat PBAT and PPC, PBAT/PPC blend and PBAT/PPC/silica nanocomposites; (b)  $G'$  and (d)  $G''$  values at the frequency of 0.05 rad/s as a function of silica content in the nanocomposites.

nanosilica content over 5 wt%, the elastic modulus ( $G'$ ) exhibits a platform in the low frequency region. Especially below 1 rad/s, it is interesting to see that the plateau modulus of PBAT/PPC/silica nanocomposites increases significantly from 0.15 kPa to 40 kPa with increasing the silica content.

According to Figs. 1(a) and 1(c), the plots of  $G'$  and  $G''$  for neat PBAT and PPC exhibit a smooth linear relationship in the low frequency zone, illustrating their liquid-like behaviors. Since  $G'$  and  $G''$  of neat PPC are higher than those of neat PBAT, especially in the high frequency region, the PBAT/PPC binary blend shows a higher  $G'$  and  $G''$  than neat PBAT in the high frequency region. For the PBAT/PPC/silica nanocomposites, the gradual increase in the nanosilica content signifi-

cantly increased the  $G'$  and  $G''$  of the resulting nanocomposites. The viscoelastic response of PBAT/PPC/silica nanocomposites is altered at low frequency regions, where  $G'$  and  $G''$  exhibit almost no dependence on frequency. This result implied that a characteristic gel-like of solid structure, that is, network structure composed of spherical fillers was formed in the nanocomposite system.<sup>[33]</sup> Generally speaking, the minimum content of the fillers forming the network structure is called the percolation threshold. Figs. 1(b) and 1(d) show the plots of the  $G'$  and  $G''$  at a frequency of 0.05 rad/s versus nanosilica content, respectively. The inflection point of these curves could be considered as the percolation threshold of this system.<sup>[34]</sup> As can be seen that the percolation threshold

of PBAT/PPC/silica nanocomposites was approximately 4 wt%, which was lower than that of poly( $\epsilon$ -caprolactone) (PCL)/silica nanocomposites (5 wt%–7 wt%)<sup>[35]</sup> and poly(L-lactide) (PLLA)/silica (6.4 wt%).<sup>[36]</sup> This was because the nanosilica particles were selectively dispersed in the PBAT matrix.

The complex viscosity ( $|\eta^*|$ ) can also be used to reveal the influence of the nanosilica particles on the melt rheological behaviors. It can be seen from Fig. 1(e) that the typical liquid behaviors can be observed for neat PBAT and PPC and PBAT/PPC blend. Since the melt viscosity of PPC is larger than that of neat PBAT, the reinforcement of PPC phase caused the PBAT/PPC blend to exhibit a higher  $|\eta^*|$  than PBAT. Furthermore, the melt viscosity of PBAT/PPC/silica nanocomposites increased significantly with an increase in the nanosilica content. Moreover, the enhancement of melt viscosity of nanocomposites with nanosilica loading was more pronounced as the frequency was decreased. In fact, the incorporation of 5 wt% nanosilica into PBAT/PPC blend almost disappeared the Newtonian plateau of PBAT so that a stable shear thinning behavior was observed with frequency, once again proving the formation of the network structure of nanosilica dispersed in the PBAT phase.

The loss factor ( $\tan\delta$ ) is an important parameter that can characterize the relaxation of viscoelastic materials and is considered to be more sensitive to changes in relaxation than modulus.<sup>[37]</sup> Fig. 1(f) depicts the dependence of  $\tan\delta$  on the frequency of all samples. As can be seen that  $\tan\delta$  of neat PBAT and PBAT/PPC blend were much higher than those of PBAT/PPC/silica nanocomposites. Moreover,  $\tan\delta$  of nanocomposites decreased clearly with increasing nanosilica loading. This phenomenon suggested that nanocomposites melt gradually showed elastic response on account of the interaction between nanosilica particles,<sup>[38,39]</sup> especially after the nanosilica particles formed the percolation network structure.

### Double Percolation Network

Formation of the nanosilica network has been illustrated by linear viscoelasticity in the above section. However, linear

viscoelasticity can only give reasonable information on the structures with greatest mechanical contribution. More direct evidences are needed to justify the morphology of PBAT/PPC/silica nanocomposites and distribution of nanosilica.<sup>[40]</sup>

SEM micrographs of fractured surfaces of PBAT/PPC blend and PBAT/PPC/silica nanocomposites are displayed in Fig. 2. As observed from Fig. 2(a), PBAT/PPC blend shows a sea-island structure, and the nanosilica particles are selectively dispersed in the continuous phase PBAT matrix. For the PBAT/PPC/silica nanocomposites, as shown in Figs. 2(b), 2(c) and 2(d), phase-separated morphology can also be observed and the size of the dispersed PPC phase particles become smaller as the nanosilica content increases. It is worth noting that nanosilica particles detected as white dots were located in the continuous PBAT matrix, following by the formation of double percolation network. This observation suggested that the thermodynamic equilibrium localization of nanosilica particles was in the PBAT phase instead of the PPC phase because of the higher interfacial tension of PPC/silica compared to PBAT/silica.<sup>[41,42]</sup> In other words, nanosilica particles used in this work were selectively dispersed in the PBAT phase, which might be because PBAT could be better wetted by the silica.<sup>[43]</sup>

Fig. 3 illustrates the distribution and particles size of the dispersed PPC phase obtained from Fig. 2. It can be found that the average particle size ( $D$ ) of PPC phases in the PBAT/PPC blends is about 2.91  $\mu\text{m}$ , while  $D$  values for PBAT/PPC/silica nanocomposites containing nanosilica of 2 wt%, 5 wt% and 10 wt% decrease to 2.18, 1.56 and 1.44  $\mu\text{m}$ , respectively. Furthermore, a rather narrow distribution of the PPC dispersed particles can be observed with increasing nanosilica loading. It was widely accepted that the balance between the coalescence and breakup of polymer droplets was the primary mechanism that controlled the morphology development of whole or partially miscible polymer-polymer blend systems.<sup>[44]</sup> The decrease in the size of dispersed phase

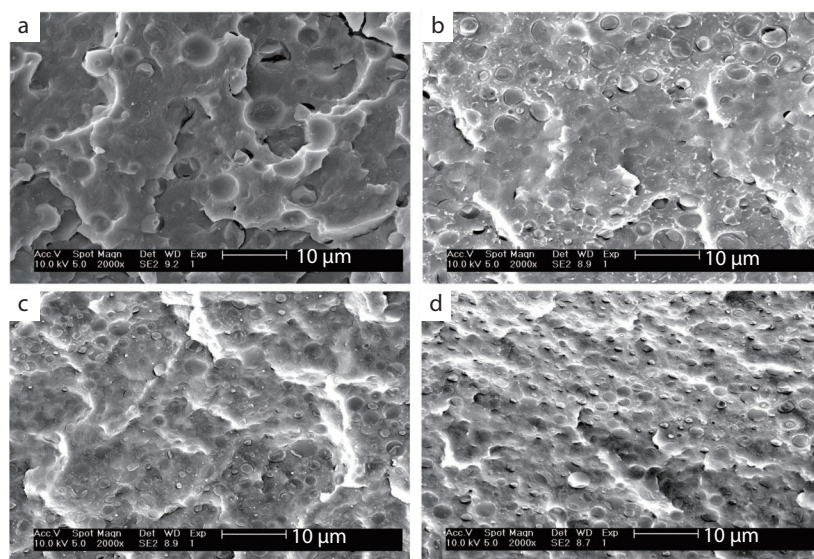


**Fig. 2** SEM micrographs of PBAT/PPC blend and PBAT/PPC/silica nanocomposites with different silica content: (a) PBAT/PPC blend, (b) PBAT/PPC-2, (c) PBAT/PPC-5, (d) PBAT/PPC-10.

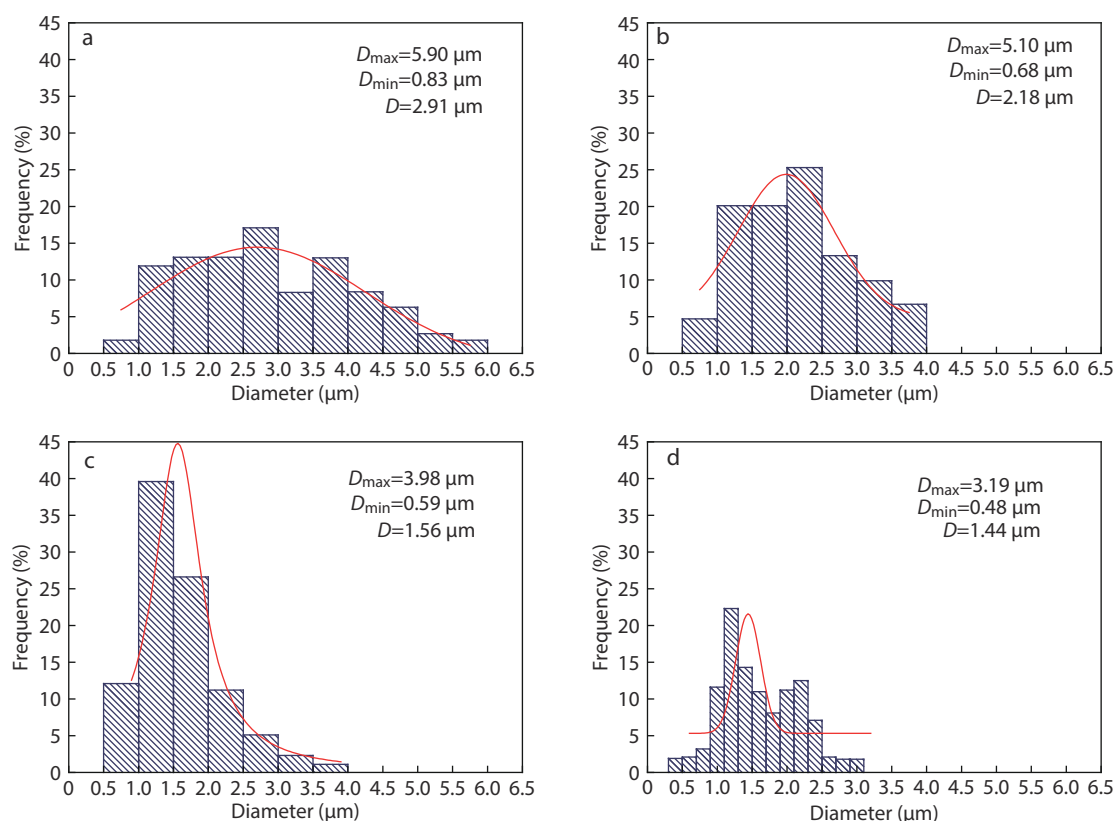


**Fig. 3** Quantitative analyses of distribution of PPC dispersed phase based on the Fig. 2: (a) PBAT/PPC blend; (b) PBAT/PPC-2; (c) PBAT/PPC-5; (d) PBAT/PPC-10.  $D_{\max}$ ,  $D_{\min}$  and  $D$  are the maximum, minimum and average particle diameter, respectively.

by the introduction of nanoparticles was due to a decrease in the coalescence of polymer droplets.<sup>[45]</sup> In the present work, the present of silica nanoparticles resulted in the reduced interfacial tension between continuous PBAT phase and dispersed PPC phase attributed to a lower level of interactions between PBAT and PPC than between PBAT/silica and PPC/silica.<sup>[46]</sup> The same results were consistent with the contact angle, DSC and rheological properties in the other discussion of this work.

### Selective Dispersion of SiO<sub>2</sub> in PBAT Phase

The contact angles of the PPC and PBAT are shown in Table S1 (in ESI), the surface free energies are shown in Table 1. From the data of contact angle test, the contact angle of H<sub>2</sub>O and CH<sub>2</sub>I<sub>2</sub> on the surfaces of PPC and PBAT are 73.0° and 43.1°, respectively, for H<sub>2</sub>O, and 23.1° and 22.0°, respectively, for CH<sub>2</sub>I<sub>2</sub>. According to Eqs. (S1) and (S2) (in ESI), the calculated surface free energies  $\gamma$  are shown in Table 1. For SiO<sub>2</sub>, the corresponding surface energy data is suggested to be 73.8 mJ·m<sup>-2</sup> for  $\gamma$ , 31.2 mJ·m<sup>-2</sup> for  $\gamma^d$  and 38.6 mJ·m<sup>-2</sup> for  $\gamma^p$ . The interfacial tensions between components were then calculated according to Eqs. (S3) and (S4) (in ESI), and the results are shown in Table 2, the interfacial tension between PPC and SiO<sub>2</sub> was calculated to be much higher than that between PBAT and SiO<sub>2</sub>. Finally, the wetting coefficient  $\omega_a$  for SiO<sub>2</sub> in PPC and PBAT blend could be calculated according to Eq. (S5) (in ESI), it is clearly seen from Table 3 that both the harmonic- and geometric-mean predicted the SiO<sub>2</sub> would be in the PBAT phase. The selective location of SiO<sub>2</sub> results were consistent with

**Table 1** Surface free energies  $\gamma$  of the samples.<sup>a</sup>

| Samples          | $\gamma$ (mJ·m <sup>-2</sup> ) | $\gamma^d$ (mJ·m <sup>-2</sup> ) | $\gamma^p$ (mJ·m <sup>-2</sup> ) |
|------------------|--------------------------------|----------------------------------|----------------------------------|
| PPC              | 47.5                           | 42.1                             | 5.5                              |
| PBAT             | 59.7                           | 35.5                             | 24.2                             |
| SiO <sub>2</sub> | 73.8                           | 31.2                             | 38.6                             |

<sup>a</sup>  $\gamma = \gamma^d + \gamma^p$ ;  $\gamma^d$ : dispersive component of  $\gamma$ ;  $\gamma^p$ : polar component of  $\gamma$ .

**Table 2** Interfacial tensions  $\gamma_{12}$  calculated using harmonic- and geometric-mean equation.<sup>a</sup>

| Materials pair        | $\gamma_{12}^h$ (mJ·m <sup>-2</sup> ) | $\gamma_{12}^g$ (mJ·m <sup>-2</sup> ) |
|-----------------------|---------------------------------------|---------------------------------------|
| PPC/SiO <sub>2</sub>  | 25.52                                 | 15.31                                 |
| PBAT/SiO <sub>2</sub> | 3.24                                  | 1.64                                  |
| PBAT/PPC              | 12.50                                 | 7.01                                  |

<sup>a</sup> The superscripts h and g represent the values calculated using harmonic- and geometric-mean equation, respectively.

**Table 3** Wetting coefficient  $\omega_a$  and predicted localization of SiO<sub>2</sub> in the PBAT/PPC blends.<sup>a</sup>

| System                    | $\omega_a^h$ | $\omega_a^g$ | Predicted localization |
|---------------------------|--------------|--------------|------------------------|
| PBAT/PPC/SiO <sub>2</sub> | 1.78         | 1.95         | PBAT phase             |

<sup>a</sup> The superscripts h and g represent the values calculated using harmonic- and geometric-mean equation, respectively.

the SEM characterization.

### Dynamic Mechanical Analysis

Fig. 4(a) displays the variations of loss factor ( $\tan\delta$ ) as a function of temperature for neat PBAT and PPC, PBAT/PPC blend and

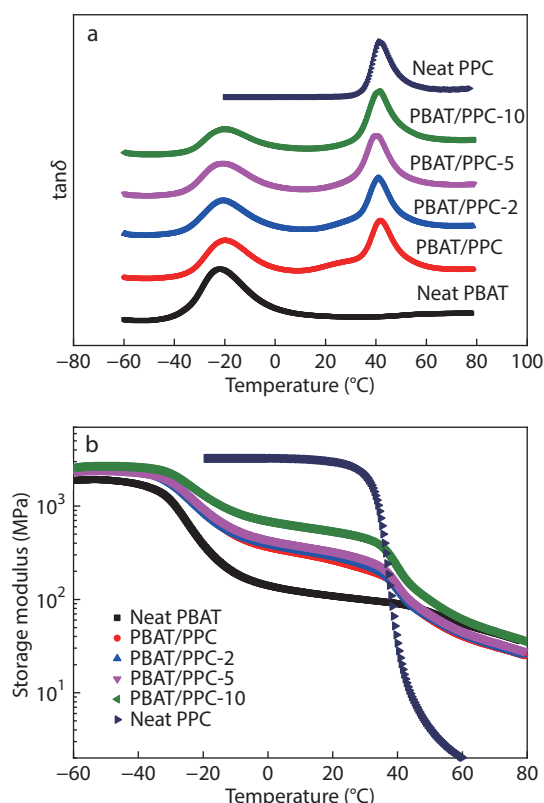


**Fig. 4** DMA traces of neat PBAT and PPC, PBAT/PPC blend and PBAT/PPC/silica nanocomposites: (a)  $\tan\delta$  and (b) storage modulus ( $E'$ ) against temperature curves.

PBAT/PPC/silica nanocomposites, respectively. The glass transition temperatures ( $T_g$ ) obtained from  $\tan\delta$  peaks are summarized in Table S3 (in ESI). Neat PBAT and PPC shows  $T_g$  at about  $-22.1$  and  $42.9$  °C, respectively. In case of PBAT/PPC blend, two  $T_g$ s can be found on the  $\tan\delta$  curve, the lower one corresponding to the PBAT phase and the higher one corresponding to the PPC phase, which suggested that PBAT/PPC blend was not thermodynamically miscible. Furthermore, compared with neat PBAT and PPC, the two  $T_g$ s in the PBAT/PPC blend shift to each other, indicating the partially miscible of the two phases. Besides, it can be found that the  $T_g$ s of PBAT and PPC components in the PBAT/PPC/silica nanocomposites show little change with varying nanosilica loading (see Table S3 in ESI). This result suggested that the introduction of nanosilica into PBAT/PPC blend did not improve the compatibility of the two phases, nor did it affect the segments and chains mobility of the two polymer components.

The changes of storage modulus ( $E'$ ) of all samples as a function of temperature are illustrated in Fig. 4(b). For comparison, the  $E'$  values of  $-50$ ,  $0$  and  $60$  °C for all samples were measured and listed in Table 4. As can be seen that  $E'$  of neat PBAT decreases sharply at temperature range of  $-30$  °C to  $-10$  °C and  $E'$  of neat PPC drops dramatically at about  $43$  °C, due to their glass transitions. When the temperature was lower than the  $T_g$  of PPC phase, which was about  $43$  °C, the  $E'$  of PBAT/PPC blend is higher than that of neat PBAT, because the glassy PPC with high  $E'$  (3335 MPa) could enhance the PBAT matrix. Furthermore, the  $E'$  of PBAT/PPC/silica nanocom-

**Table 4** Storage modulus ( $E'$ ) of neat PBAT and PPC, PBAT/PPC blend and PBAT/PPC/silica nanocomposites at different temperatures.

| Sample      | Storage modulus at $-50$ °C (MPa) | Storage modulus at $0$ °C (MPa) | Storage modulus at $60$ °C (MPa) |
|-------------|-----------------------------------|---------------------------------|----------------------------------|
| PBAT        | 1903                              | 141                             | 55                               |
| PPC         | 3335                              | 3335                            | 3.5                              |
| PBAT/PPC    | 2384                              | 358                             | 40                               |
| PBAT/PPC-2  | 2406                              | 387                             | 42                               |
| PBAT/PPC-5  | 2412                              | 434                             | 45                               |
| PBAT/PPC-10 | 2671                              | 678                             | 60                               |

posites is higher than that of PBAT/PPC blend and increases with nanosilica loading. This was due to the further strengthening effect of high-hardness nanosilica particles on the PBAT matrix. Especially at temperature above  $T_g$  of PBAT and below  $T_g$  of PPC, the PBAT matrix became soft, then the dual reinforcement of PPC phase and nanosilica particles was more prominent. For example, the PBAT/PPC blend and the nanocomposite constituting 10 wt% nanosilica loading were found to obtain an enhancement of  $E'$  up to 358 MPa and 678 MPa at  $0$  °C, showing an increase of 153% and 381%, respectively, compared with neat PBAT. However, when the temperature continued to rise above the  $T_g$  of PPC, the  $E'$  of PPC dropped sharply to about only 3.5 MPa. The reinforcement from PPC phase disappeared, resulting in a decrease in  $E'$  of blend and nanocomposites.

#### Thermal Properties

The DSC cooling and heating curves of neat PBAT, PBAT/PPC blend and PBAT/PPC/silica nanocomposites are enumerated in Fig. 5, and the relevant thermal properties data are listed in Table S4 (in ESI). As can be seen from Fig. 5(a) of first cooling scan, neat PBAT shows an exothermic crystallization peak ( $T_c$ ) at  $79.0$  °C. In case of PBAT/PPC blend,  $T_c$  increases to  $81.2$  °C. The incorporation of PPC into PBAT matrix increases the crystallization temperature, indicating that the PPC could promote the crystallization of PBAT in the blend. This was because the crystallization of the matrix polymer would be affected by the dispersed phase for the partially miscible blend systems.<sup>[47,48]</sup> In this work, it could be seen from the results of SEM and DMA that PBAT/PPC blend was partially miscible, and PBAT could be inferred to crystallize at the interface of the two phases during cooling process. The dispersed PPC phase might act as the nucleation sites of PBAT. As a result, the enhancement in crystallization of PBAT might be ascribed to the positive effect of PPC dispersion on the nucleation of PBAT.

For PBAT/PPC/silica nanocomposites,  $T_c$  is higher than that in neat PBAT. The  $T_c$  increases first and then decreases with increasing nanosilica loading and shows the maximum value in PBAT/PPC-5 sample. The reasons for the influence of nanosilica and its loading on PBAT crystallization were as follows. The crystallization process of polymers consists of two parts: nucleation and growth. On the one hand, the nanosilica particles act as nucleating agent and were conducive to the crystallization of PBAT in the nanocomposites.<sup>[49,50]</sup> On the other hand, with the increase of nanosilica content, the percolation network of nanosilica particles formed and the melt viscosity of the nanocomposite increased, which limited the regular arrangement of PBAT segments and was not conducive to the crystallization of PBAT.<sup>[25]</sup> When the nanosilica content was less than or equal to 5 wt%, the nucleation effect

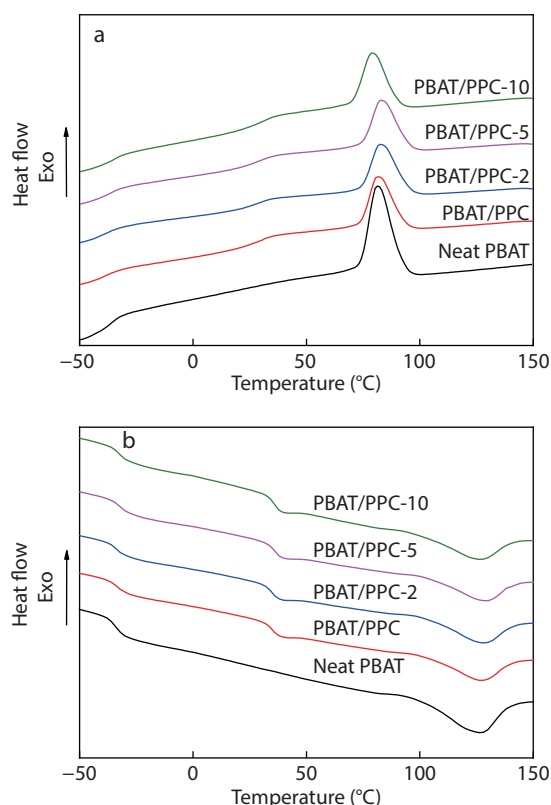


**Fig. 5** DSC thermograms of neat PBAT, PBAT/PPC blend and PBAT/PPC/silica nanocomposites: (a) first cooling scan and (b) second heating scan.

of nanosilica was predominant. When the nanosilica content increased to 10 wt%, the restricted effect of nanosilica was predominant. As a result, with the increase of nanosilica loading,  $T_c$  shows a trend of increasing first and then decreasing. Similar results were also found in other silica nanocomposites.<sup>[51]</sup> On the second heating curves in Fig. 5(b), two  $T_g$ s are observed on the curves of blend and nanocomposites, indicating the partial miscibility of PBAT and PPC, which was consistent with the results of DMA. The melting enthalpy ( $\Delta H_m$ ) and degree of crystallinity ( $X_c$ ) of PBAT/PPC/silica increased with increasing the silica content and illustrated that the addition of  $\text{SiO}_2$  could improve crystallinity of PBAT. This might be ascribed that nanosilica particles provides crystallization sites for PBAT.

### Rheological Properties

The Han curves for neat PBAT and PPC, PBAT/PPC blend and PBAT/PPC/silica nanocomposites at 150 °C obtained by plotting  $G'$  against  $G''$  are shown in Fig. 6(a).<sup>[52]</sup> Firstly, the slope of Han plot for the PBAT/PPC blend changes compared with neat PPC and PBAT in the low frequency region, indicating the partial miscibility of the blend. Secondly, the slopes of Han curves for nanocomposites that decrease with increasing silica content indicated that the PBAT/PPC/silica nanocomposites were more heterogeneous. Furthermore, as nanosilica content increases, the inflection point at which the slope of the Han curve changed toward the direction of high modulus, indicative of more energy was needed to alter the degree of heterogeneity of the nanocomposites. This was due to the fact that the

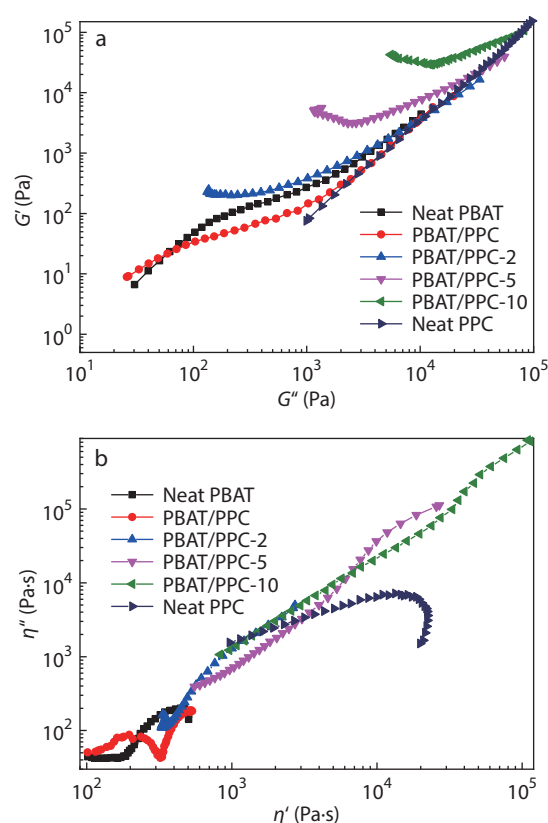


**Fig. 6** (a) Han plots and (b) Cole-Cole plots of neat PBAT and PPC, PBAT/PPC blend and PBAT/PPC/silica nanocomposites

interactions between nanosilica particles were enhanced with the increase of nanosilica loading.

Once the nanosilica particles formed the network structure, the large scale relaxation of PBAT chains might be highly arrested by the network of nanosilica. The relaxation time ( $\lambda$ ) of polymer composites could be calculated by using Eq. (1):<sup>[18]</sup>

$$\lambda = \frac{G'}{|\eta^*| \times \omega^2} \quad (1)$$

where  $\omega$  is angular frequency. At a frequency of 0.05 rad/s, the ratios of the relaxation time of PBAT/PPC blend and PBAT/PPC/silica nanocomposites to that of neat PBAT ( $\Delta\lambda$ ) are 1 for neat PBAT, 1.9 for PBAT/PPC blend, 2.7 for PBAT/PPC-2, 5.6 for PBAT/PPC-5 and 5.7 for PBAT/PPC-10. Clearly,  $\Delta\lambda$  of nanocomposites increased gradually with nanosilica loadings, indicating that the higher the nanosilica content, the more obvious its influence on the relaxation behaviors of the PBAT chains. In other words, the introduction of nanosilica did greatly restrict the mobility of PBAT chains, especially after the percolation network of nanosilica particles was formed.

Cole-Cole curve, a plot of imaginary viscosity versus real viscosity, can be used to characterize the strong restriction of the formed percolation network structure on the chains of the matrix polymer.<sup>[53]</sup> Fig. 6(b) presents the Cole-Cole curves of neat PBAT and PPC, PBAT/PPC blend and PBAT/PPC/silica nanocomposites. Neat PPC shows a single arc, corresponding to monomodal molecular weight distributions, which illustrated its local dynamic relaxation. Neat PBAT shows a single arc and a rigid tail, corresponding to its local dynamic relaxa-

tion and long-term relaxation with time distribution. For PBAT/PPC blend, the Cole-Cole plots exhibits the contributions of the two phases coexisting in the blend. The two relaxation peaks in the Cole-Cole curves corresponded to the relaxation of the PBAT matrix and the dispersed PPC phase, respectively. Similar results had been reported in other immiscible blend systems.<sup>[54,55]</sup> However, for the PBAT/PPC/silica nanocomposites, the presence of nanosilica resulted in a remarkable increase in relaxation time. The rigid tail at the high viscosity region representing the long-term relaxation of constrained molecular chains of PBAT became longer with the increase of silica content. When the silica content was increased to 5 wt%, the arc related to local relaxation of PBAT chains almost disappeared, demonstrating that the long-range relaxation of restricted PBAT molecular chains dominated the entire relaxation process. This phenomenon was also an evidence for the formation of the silica percolation network structure at the present silica loading.

### Tensile Mechanical Properties

The typical stress-strain curves of neat PBAT, PBAT/PPC blend and PBAT/PPC/silica nanocomposites are depicted in Fig. 7. The main mechanical properties are listed in Table 5. Neat PBAT exhibits a rubbery-like behavior with significantly higher tensile strain (1264%) and much lower modulus (85 MPa) and yield strength (9.0 MPa). Clearly, the PBAT/PPC blend also fractured in ductile mode. The elongation at break of blends only dropped to 1032%, the modulus and yield strength increased to 129 MPa

**Table 5** Tensile properties of neat PBAT, PBAT/PPC blend and PBAT/PPC/silica nanocomposites.

| Sample      | Young's modulus (MPa) | Yield strength (MPa) | Elongation at break (%) |
|-------------|-----------------------|----------------------|-------------------------|
| PBAT        | 85 ± 13               | 9.0 ± 0.7            | 1264 ± 123              |
| PBAT/PPC    | 129 ± 24              | 9.2 ± 0.3            | 1032 ± 92               |
| PBAT/PPC-2  | 149 ± 34              | 9.5 ± 0.2            | 608 ± 84                |
| PBAT/PPC-5  | 170 ± 21              | 10.3 ± 0.4           | 454 ± 31                |
| PBAT/PPC-10 | 260 ± 39              | 12.2 ± 0.9           | 26 ± 3                  |

and 9.2 MPa, respectively. This was attributed to the enhancement of PPC, which had a high modulus compare with PBAT matrix at room temperature. In the case of PBAT/PPC/silica nanocomposites, it can be seen from Fig. 7 that the distinct yielding and neck growth during cold drawing can be observed, except for nanocomposites with a nanosilica content of 10 wt%. The modulus and yield strength of PBAT/PPC/silica nanocomposites are higher than those of neat PBAT and PBAT/PPC blend, and increased with nanosilica loading. The previous discussion proved that nanosilica particles were selectively filled in the PBAT matrix. Therefore, the enhanced modulus and yield strength of the nanocomposites might be due to the fact that the nanosilica with high modulus serve as carriers of stress and load, which were transferred from the PBAT matrix to the silica particles, thereby giving rise to a uniform and effective stress distribution, leading to an increase in the tensile modulus and yield strength of the nanocomposites.<sup>[56,57]</sup> On the other hand, the percolated nanosilica particles network structure<sup>[58]</sup> and the increase of crystallinity inhibited the movement of PBAT segments, leading to the enhancement of the tensile modulus and yield strength.<sup>[59]</sup>

Additionally, the elongation at break of PBAT/PPC/silica nanocomposites was obviously decreased with increasing nanosilica loading. This observation could be explained as following. Since nanosilica particles had different elastic properties compared to PBAT matrix, PBAT deformed, but silica did not deform under tensile stress. Nanosilica particles would debond from the PBAT matrix at the interface when the tensile stress was greater than the bonding strength between the PBAT matrix and nanosilica particles at the interface.<sup>[60]</sup> As the nanosilica content increases, the interface area between PBAT matrix and silica increases, and debonding occurs earlier and more easily, resulting in a decrease in elongation at break of nanocomposites with nanosilica loading. Most importantly, PBAT/PPC/silica nanocomposites exhibit a certain degree of ductility and enhanced modulus and yield strength. The elongation at break of the nanocomposite with 5 wt% nanosilica still maintains at 454%. The combination of enhancement of modulus and yield strength and good ductility made the performance of PBAT/PPC/silica nanocomposites easier to meet the requirements of commodity plastics.

### CONCLUSIONS

A novel PBAT/PPC/silica composite with enhanced performances was fabricated by melt blending, in which PPC and silica nanoparticles served as the first and second reinforcing components of PBAT, respectively. Moreover, silica was selectively located in PBAT continuous phase rather than PPC dispersed phase, due to the smaller interface

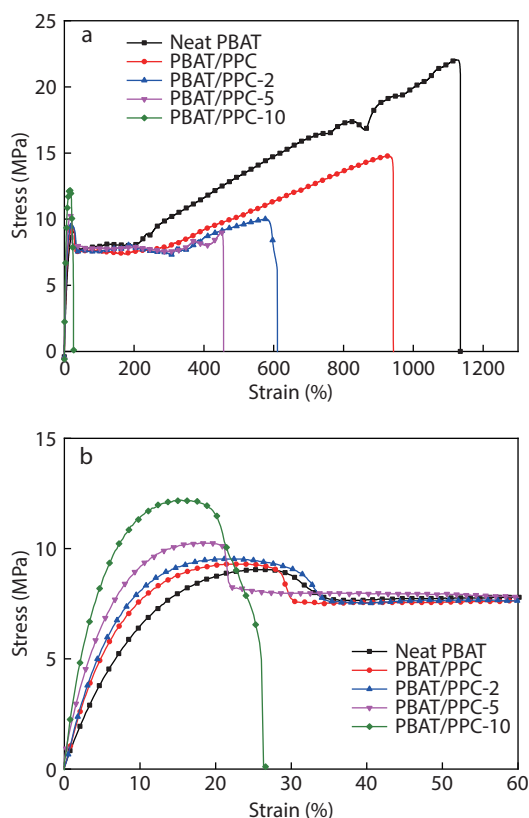


**Fig. 7** (a) Tensile stress-strain curves of neat PBAT, PBAT/PPC blend and PBAT/PPC/silica nanocomposites; (b) details of stress-strain curves of (a).

tension between silica and PBAT compared to silica and PPC. For partially miscible PBAT/PPC(70/30) blend with sea-island structure, the percolation threshold of silica was reduced to as low as 5 wt%, which should attributed to the formation of double percolation structure. Furthermore, the introduction of silica reduced the size of PPC dispersed phase due to the decrease in the coalescence of polymer droplets. It is worth mentioning that the PBAT/PPC(70/30) blend and the composite constituting 10 wt% nanosilica loading were found to obtain an enhancement of storage modulus up to 358 MPa and 678 MPa at 0 °C, respectively, showing an increase of 153% and 381%, respectively, compare with neat PBAT. Additionally, the PBAT/PPC(70/30) blend and the composite containing 10 wt% nanosilica content could increase the Young's modulus by 52% and 205%, respectively, compared to pure PBAT. The improvement in mechanical properties of PBAT should be attributed to the intrinsic properties of PPC and nanosilica, as well as the fabrication of nanosilica percolation network and the increase of crystallinity.

In summary, a novel PBAT/PPC/silica composite with enhanced performances was obtained by the introduction of PPC and nanosilica, which could better meet the requirements of commodity plastics.

## NOTES

The authors declare no competing financial interest.

## Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-022-2753-x>.

## ACKNOWLEDGMENTS

This work was financially supported by Jilin Province Industrial Technology Research and Development Project (No. 2021C036-1), and Jilin Province Science and Technology Development Program of China (No. 20200501004GX). The authors will thank Changchun Institute of Applied Chemistry, CAS for great help in experiments.

## REFERENCES

- Mohanty, A. K.; Vivekanandhan, S.; Pin, J. M.; Misra, M. Composites from renewable and sustainable resources: challenges and innovations. *Science* **2018**, 362, 536–542.
- Wu, F.; Misra, M.; Mohanty, A. K. Challenges and new opportunities on barrier performance of biodegradable polymers for sustainable packaging. *Prog. Polym. Sci.* **2021**, 117, 101395.
- Tian, H. L.; Wang, Z. P.; Jia, S. L.; Pan, H. W.; Han, L. J.; Bian, J. J.; Li, Y.; Yang, H. L.; Zhang, H. L. Biodegradable foaming material of poly(butylene adipate-co-terephthalate) (PBAT)/poly(propylene carbonate) (PPC). *Chinese J. Polym. Sci.* **2022**, 40, 208–219.
- Li, Y.; Han, C. Y.; Yu, Y. C.; Xiao, L. G. Effect of loadings of nanocellulose on the significantly improved crystallization and mechanical properties of biodegradable poly( $\epsilon$ -caprolactone). *Int. J. Biol. Macromol.* **2020**, 147, 34–45.
- Lule, Z. C.; Kim, J. Properties of economical and eco-friendly polybutylene adipate terephthalate composites loaded with surface treated coffee husk. *Compos. Part A-Appl. Sci. Manuf.* **2021**, 140, 106154.
- Pawar, S. P.; Misra, A.; Bose, S.; Chatterjee, K.; Mittal, V. Enzymatically degradable and flexible bio-nanocomposites derived from PHBV and PBAT blend: assessing thermal, morphological, mechanical, and biodegradation properties. *Colloid Polym. Sci.* **2015**, 293, 2921–2930.
- Lai, L.; Li, J. X.; Liu, P. W.; Wu, L. B.; Severtson, S. J.; Wang, W. J. Mechanically reinforced biodegradable poly(butylene adipate-co-terephthalate) with interactive nanoinclusions. *Polymer* **2020**, 197, 122518.
- Liu, W. Y.; Liu, S. G.; Wang, Z. J.; Liu, J. H.; Dai, B. F.; Chen, Y.; Zeng, G. S. Preparation and characterization of compatibilized composites of poly(butylene adipate-co-terephthalate) and thermoplastic starch by two-stage extrusion. *Eur. Polym. J.* **2020**, 122, 109369.
- Bai, J.; Pei, H. J.; Zhou, X. P.; Xie, X. L. Reactive compatibilization and properties of low-cost and high-performance PBAT/thermoplastic starch blends. *Eur. Polym. J.* **2021**, 143, 110198.
- Li, C. Q.; Chen, F. P.; Lin, B. W.; Zhang, C. H.; Liu, C. S. High content corn starch/poly(butylene adipate-co-terephthalate) composites with high-performance by physical-chemical dual compatibilization. *Eur. Polym. J.* **2021**, 159, 110737.
- Hoffmann, R.; Morais, D. D. S.; Braz, C. J. F.; Haag, K.; Wellen, R. M. R.; Canedo, E. L.; de Carvalho, L. H.; Koschek, K. Impact of the natural filler babassu on the processing and properties of PBAT/PHB films. *Compos. Part A-Appl. Sci. Manuf.* **2019**, 124, 105472.
- Morelli, C. L.; Belgacem, M. N.; Branciforti, M. C.; Bretas, R. E. S.; Crisci, A.; Bras, J. Supramolecular aromatic interactions to enhance biodegradable film properties through incorporation of functionalized cellulose nanocrystals. *Compos. Part A-Appl. Sci. Manuf.* **2016**, 83, 80–88.
- Arruda, L. C.; Magaton, M.; Bretas, R. E. S.; Ueki, M. M. Influence of chain extender on mechanical, thermal and morphological properties of blown films of PLA/PBAT blends. *Polym. Test* **2015**, 43, 27–37.
- Jiang, L.; Wolcott, M. P.; Zhang, J. W. Study of biodegradable polylactide/poly(butylene adipate-co-terephthalate) blends. *Biomacromolecules* **2006**, 7, 199–207.
- Yeh, J. T.; Tsou, C. H.; Huang, C. Y.; Chen, K. N.; Wu, C. S.; Chai, W. L. Compatible and crystallization properties of poly(lactic acid)/poly(butylene adipate-co-terephthalate) blends. *J. Appl. Polym. Sci.* **2010**, 116, 680–687.
- Kumar, M.; Mohanty, S.; Nayak, S. K.; Parvaiz, M. R. Effect of glycidyl methacrylate (GMA) on the thermal, mechanical and morphological property of biodegradable PLA/PBAT blend and its nanocomposites. *Biores. Technol.* **2010**, 101, 8406–8415.
- Al-Itry, R.; Lamnawar, K.; Maazouz, A. Improvement of thermal stability, rheological and mechanical properties of PLA, PBAT and their blends by reactive extrusion with functionalized epoxy. *Polym. Degrad. Stabil.* **2012**, 97, 1898–1914.
- Zhao, H. W.; Liu, H.; Liu, Y. Q.; Yang, Y. Blends of poly(butylene adipate-co-terephthalate) (PBAT) and stereocomplex polylactide with improved rheological and mechanical properties. *RSC Adv.* **2020**, 10, 10482–10490.
- Sirisinha, K.; Somboon, W. Melt characteristics, mechanical, and thermal properties of blown film from modified blends of poly(butylene adipate-co-terephthalate) and poly(lactide). *J. Appl. Polym. Sci.* **2012**, 124, 4986–4992.
- Muthuraj, R.; Mekonnen, T. Recent progress in carbon dioxide (CO<sub>2</sub>) as feedstock for sustainable materials development: co-

- polymers and polymer blends. *Polymer* **2018**, *145*, 348–373.
- 21 Xu, J. W.; Feng, E.; Song, J. Renaissance of aliphatic polycarbonates: new techniques and biomedical applications. *J. Appl. Polym. Sci.* **2014**, *131*, 16.
  - 22 Li, Y.; Yu, Y. C.; Han, C. Y.; Wang, X. H.; Huang, D. X. Sustainable blends of poly(propylene carbonate) and stereocomplex polylactide with enhanced rheological properties and heat resistance. *Chinese J. Polym. Sci.* **2020**, *38*, 1267–1275.
  - 23 Liu, Z. H.; Huang, J. Q.; Sun, L. J.; Lei, D.; Cao, J.; Chen, S.; Shih, W. C.; Qing, F. L.; You, Z. W. PPC-based reactive hot melt polyurethane adhesive (RHMPA)-efficient glues for multiple types of substrates. *Chinese J. Polym. Sci.* **2018**, *36*, 58–64.
  - 24 Spencer, T. J.; Kohl, P. A. Decomposition of poly(propylene carbonate) with UV sensitive iodonium salts. *Polym. Degrad. Stabil.* **2011**, *96*, 686–702.
  - 25 Pan, H.; Yu, J.; Qiu, Z. B. Crystallization and morphology studies of biodegradable poly( $\epsilon$ -caprolactone)/polyhedral oligomeric silsesquioxanes nanocomposites. *Polym. Eng. Sci.* **2011**, *51*, 2159–2165.
  - 26 Mondal, D.; Bhowmick, B.; Mollick, M. M. R.; Maity, D.; Saha, N. R.; Rangarajan, V.; Rana, D.; Sen, R.; Chattopadhyay, D. Antimicrobial activity and biodegradation behavior of poly(butylene adipate-co-terephthalate)/clay nanocomposites. *J. Appl. Polym. Sci.* **2014**, *131*, 40079.
  - 27 Wu, C. S. Antibacterial and static dissipating composites of poly(butylene adipate-co-terephthalate) and multi-walled carbon nanotubes. *Carbon* **2009**, *47*, 3091–3098.
  - 28 Ren, P. G.; Liu, X. H.; Ren, F.; Zhong, G. J.; Ji, X.; Xu, L. Biodegradable graphene oxide nanosheets/poly-(butylene adipate-co-terephthalate) nanocomposite film with enhanced gas and water vapor barrier properties. *Polym. Test* **2017**, *58*, 173–180.
  - 29 Bittmann, B.; Bouza, R.; Barral, L.; Gonzalez-Rodriguez, M. V.; Abad, M. J. Nanoclay-reinforced poly(butylene adipate-co-terephthalate) biocomposites for packaging applications. *Polym. Compos.* **2012**, *33*, 2022–2028.
  - 30 Venkatesan, R.; Rajeswari, N. TiO<sub>2</sub> nanoparticles/poly(butylene adipate-co-terephthalate) bionanocomposite films for packaging applications. *Polym. Adv. Technol.* **2017**, *28*, 1699–1706.
  - 31 Van Hemelrijck, E.; Van Puyvelde, P.; Velankar, S.; Macosko, C. W.; Moldenaers, P. Interfacial elasticity and coalescence suppression in compatibilized polymer blends. *J. Rheol.* **2004**, *48*, 143–158.
  - 32 Van Hemelrijck, E.; Van Puyvelde, P.; Macosko, C. W.; Moldenaers, P. The effect of block copolymer architecture on the coalescence and interfacial elasticity in compatibilized polymer blends. *J. Rheol.* **2005**, *49*, 783–798.
  - 33 Zhao, H. W.; Bian, Y. J.; Li, Y.; Dong, Q. L.; Han, C. Y.; Dong, L. S. Bioresource-based blends of poly(3-hydroxybutyrate-co-4-hydroxybutyrate) and stereocomplex polylactide with improved rheological and mechanical properties and enzymatic hydrolysis. *J. Mater. Chem. A* **2014**, *2*, 8881–8892.
  - 34 Wu, D. F.; Wu, L.; Zhang, M.; Zhao, Y. L. Viscoelasticity and thermal stability of polylactide composites with various functionalized carbon nanotubes. *Polym. Degrad. Stabil.* **2008**, *93*, 1577–1584.
  - 35 Li, Y.; Han, C. Y.; Zhang, X.; Bian, J. J.; Han, L. J. Rheology, mechanical properties, and biodegradation of poly( $\epsilon$ -caprolactone)/silica nanocomposites. *Polym. Compos.* **2013**, *34*, 1620–1628.
  - 36 Li, Y.; Han, C. Y.; Bian, J. J.; Han, L. J.; Dong, L. S.; Gao, G. Rheology and biodegradation of polylactide/silica nanocomposites. *Polym. Compos.* **2012**, *33*, 1719–1727.
  - 37 Xu, Z. H.; Niu, Y. H.; Yang, L.; Xie, W. Y.; Li, H.; Gan, Z. H.; Wang, Z. G. Morphology, rheology and crystallization behavior of polylactide composites prepared through addition of five-armed star polylactide grafted multiwalled carbon nanotubes. *Polymer* **2010**, *51*, 730–737.
  - 38 Ma, Y. M.; Zhang, S. L. Transparent nanocomposites with enhanced performances from poly(propylene carbonate) and silica. *J. Appl. Polym. Sci.* **2022**, 139e51513.
  - 39 Dil, E. J.; Favis, B. D. Localization of micro- and nano-silica particles in heterophase poly(lactic acid)/poly(butylene adipate-co-terephthalate) blends. *Polymer* **2015**, *76*, 295–306.
  - 40 Lin, S. S.; Li, B. K.; Chen, T. T.; Yu, W.; Wang, X. H. Mechanical reinforcement in poly(propylene carbonate) nanocomposites using double percolation networks by dual volume exclusions. *Compos. Sci. Technol.* **2018**, *167*, 364–370.
  - 41 Zhao, X. D.; Zhao, J.; Cao, J. P.; Wang, D. R.; Hu, G. H.; Chen, F. H.; Dang, Z. M. Effect of the selective localization of carbon nanotubes in polystyrene/poly(vinylidene fluoride) blends on their dielectric, thermal, and mechanical properties. *Mater. Des.* **2014**, *56*, 807–815.
  - 42 Dil, E. J.; Carreau, P. J.; Favis, B. D. Morphology, miscibility and continuity development in poly(lactic acid)/poly(butylene adipate-co-terephthalate) blends. *Polymer* **2015**, *68*, 202–212.
  - 43 Amoabeng, D.; Roell, D.; Clouse, K. M.; Young, B. A.; Velankar, S. S. A composition-morphology map for particle-filled blends of immiscible thermoplastic polymers. *Polymer* **2017**, *119*, 212–223.
  - 44 Thomas, S.; Groeninckx, G. Reactive compatibilisation of heterogeneous ethylene propylene rubber (EPM)/nylon 6 blends by the addition of compatibiliser precursor EPM-g-MA. *Polymer* **1999**, *40*, 5799–5819.
  - 45 Taguet, A.; Cassagnau, P.; Lopez-Cuesta, J. M. Structuration, selective dispersion and compatibilizing effect of (nano)fillers in polymer blends. *Prog. Polym. Sci.* **2014**, *39*, 1526–1563.
  - 46 Jiang, G.; Wang, F.; Zhang, S. D.; Huang, H. X. Structure and improved properties of PPC/PBAT blends via controlling phase morphology based on melt viscosity. *J. Appl. Polym. Sci.* **2020**, *137*, 48924.
  - 47 Shibata, M.; Teramoto, N.; Inoue, Y. Mechanical properties, morphologies, and crystallization behavior of plasticized poly(*l*-lactide)/poly(butylene succinate-co-*l*-lactate) blends. *Polymer* **2007**, *48*, 2768–2777.
  - 48 Zhang, C. M.; Zhai, T. L.; Turng, L. S.; Dan, Y. Morphological, mechanical, and crystallization behavior of polylactide/polycaprolactone blends compatibilized by *l*-lactide/caprolactone copolymer. *Ind. Eng. Chem. Res.* **2015**, *54*, 9505–9511.
  - 49 Sun, X. Y.; Zhu, Z.; Xie, Z. H.; Liu, J.; Yin, J.; Yang, Y. B.; Jia, C. F.; Liu, F. D.; Yang, J. J. Self-assembly crystal, manipulated polymorphic crystalline structure and elevated thermal degradation temperature of poly(1,4-butylene adipate): effects of an aryl bisamide-based compound. *Compos. Commun.* **2021**, *25*, 100765.
  - 50 Sun, Z. H.; Yan, Z. Q.; Yin, R.; Huang, X. S.; Yue, K. C.; Li, A. R.; Qian, L. Homogeneous poly(vinylidene fluoride)-graphene films with secondary percolation behaviors towards negative permittivity properties. *Compos. Commun.* **2020**, *17*, 18–21.
  - 51 Li, Y.; Han, C. Y.; Bian, J. J.; Zhang, X.; Han, L. J.; Dong, L. S. Crystallization and morphology studies of biodegradable poly( $\epsilon$ -caprolactone)/silica nanocomposites. *Polym. Compos.* **2013**, *34*, 131–140.
  - 52 Han, C. D.; Kim, J. K. On the use of time-temperature superposition in multicomponent multiphase polymer systems. *Polymer* **1993**, *34*, 2533–2539.
  - 53 Cole, K. S.; Cole, R. H. Dispersion and absorption in dielectrics. i. Alternating current characteristics. *J. Chem. Phys.* **1941**, *9*, 341–351.
  - 54 Wu, D.; Wu, L.; Sun, Y.; Zhang, M. Rheological properties and crystallization behavior of multi-walled carbon nanotube/poly( $\epsilon$ -caprolactone) composites. *J. Polym. Sci., Part B: Polym. Phys.* **2007**, *45*, 3137–3147.

- 55 Al-Itry, R.; Lamnawar, K.; Maazouz, A. Rheological, morphological, and interfacial properties of compatibilized PLA/PBAT blends. *Rheol. Acta* **2014**, 53, 501–517.
- 56 Huda, M. S.; Drzal, L. T.; Mohanty, A. K.; Misra, M. Chopped glass and recycled newspaper as reinforcement fibers in injection molded poly(lactic acid) (PLA) composites: a comparative study. *Compos. Sci. Technol.* **2006**, 66, 1813–1824.
- 57 Du, W. H.; Zhang, J. T.; Zhao, Z. X.; Zhang, X. Preparation of novel temperature-responsive double-network hydrogel reinforced with aramid nanofibers. *Compos. Commun.* **2020**, 22, 100438.
- 58 Bai, X.; Zhang, C. X.; Zeng, X. L.; Ren, L. L.; Sun, R.; Xu, J. B. Recent progress in thermally conductive polymer/boron nitride composites by constructing three-dimensional networks. *Compos. Commun.* **2021**, 24, 100650.
- 59 Zheng, Z. B.; Wu, H. Y.; Si, Y.; Jia, Y. T.; Ding, B. Stretchable and resilient fibrous sponges tailored by interlocking double-network for warmth retention. *Compos. Commun.* **2021**, 27, 100788.
- 60 Kim, G. M.; Michler, G. H. Micromechanical deformation processes in toughened and particle filled semicrystalline polymers. Part 2: Model representation for micromechanical deformation processes. *Polymer* **1998**, 39, 5699–5703.