Preparation and Characterization of Poly(butylene succinate)/Polylactide Blends for Fused Deposition Modeling 3D Printing

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ABSTRACT: To obtain a new type of biodegradable material with high toughness and strength used for fused deposition modeling (FDM) printing, a series of poly(butylene succinate) (PBS)-based polymer materials was prepared via blending with polylactide (PLA). The rheological, thermal, and mechanical properties as well as FDM printing performances of the blends, such as distortion, cross section, and the interlayer bond strength, were characterized. The results show that with increasing PLA content, the blends possess higher melt viscosity, larger tensile strength, and modulus, which are more suitable for FDM printing. Especially, when the content of PLA is more than 40%, distortion due to residual stress caused by volume shrinkage disappears during the printing process and thus products with good dimensional accuracy and pearl-like gloss are obtained. The results demonstrate that the blend compositions with moderate viscosity, low degree of crystallinity, and high modulus are more suitable for FDM printing. Compared with the low elongation upon breaking of commercially FDM-printed material, the PBS/PLA blend materials exhibit a typical ductile behavior with elongation of 90–300%. Therefore, besides biodegradability, the PBS/PLA blends present excellent mechanical properties and suitability as materials for FDM printing. In addition, our study is expected to provide methods for valuating the suitability of whether a thermoplastic polymer material is suitable for FDM printing or not.

INTRODUCTION

Three-dimensional (3D) printing, also known as additive manufacturing, is a rapid prototyping technology that directly produces three-dimensional entities under the control of computer-aided design software. 1,2 Compared with the traditional processing methods such as injection molding, 3D printing demonstrates some unique advantages, such as individual customization, lack of need of molds, and much shorter time from design to production. 1,2 Therefore, it has been widely applied in automotive, construction, clothing, health care, and other industries, especially where there are requirements for individual customization. 3,4 Among the various types of 3D printing, fused deposition modeling (FDM) has been recognized as the cheapest and the most widely adopted prototyping technology, where a thermoplastic filament is heated to melt, then extruded from the nozzle and deposited layer by layer on a support platform. 3,4 According to the above-mentioned principles, there are several requirements for a matrix material that could be used in FDM. First, its melt should have proper viscosity and strength so that it can be consistently extruded out of the nozzle without breakage or buckling. Once the melt-breaking happens, not only will the time-consuming processes be interrupted but also the already started printing process cannot be continued, which will cause trouble in commercial applications. Second, when the surface of one layer touches another, the consolidation and thermal shrinkage happen simultaneously, which may lead to unfavorable distortion. 4 Considering the filaments would shrink after extruding from the nozzle, the volume shrinkage rate of materials would determine the dimensional accuracy of printing. It has been shown that the crystallization of material is the main factor that affects molding shrinkage. Finally, mechanical properties of the finished parts largely depend on the interfacial adhesion between two neighboring layers. 5,6

In the past few decades, researchers have been devoted to develop new polymer materials to obtain FDM products with both good mechanical properties and high dimensional accuracy. Polylactide (PLA), a bio-based and biodegradable aliphatic polyester, has attracted much attention and been widely used in the FDM printing. 7–11 With monomers obtained from the fermentation of starch, PLA can be completely degraded into carbon dioxide and water under natural conditions. Moreover, during printing, compared with acrylonitrile-butadiene-styrene (ABS) copolymers and polyamides, the PLA filaments can be melted at lower temperature with little awful smell and the support platform can be set at room temperature. 5 However, although having a relatively high tensile strength, PLA is a typical brittle material with extremely

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low elongation at break (≤3%), which has limited its applications. Considering most 3D printing filaments are brittle, it is necessary to develop new ductile materials for different application requirements.

Poly(butylene succinate) (PBS), a semicrystalline aliphatic polyester, has demonstrated excellent processability, thermal stability, and biodegradability. Due to its excellent ductility and relatively low melting point (less than 120 °C), it is considered to be a candidate for use as FDM filament. However, there are few published studies on 3D printing with PBS. One reason is that its low melt strength makes it difficult to continually form monofilament when extruded, which makes printing fail halfway. Moreover, the distortion caused by the relatively large volume shrinkage during cooling probably happens after crystallization, thus resulting in defective products. Therefore, modification of PBS is quite necessary to solve the drawbacks mentioned above and make the material suitable for FDM printing.

Blending can combine the advantages of the two components, which is thus one of the most commonly used modification methods for polymer materials. PBS has been blended with starches, wood flours, and other biodegradable polymers. Chieng at al. blended PBS with poly(butylene adipate-co-terephthalate) and organomodified montmorillonite to improve the strength and modulus. Similarly, Okamoto et al. reported that PBS/layered-silicate nanocomposites had significantly improved the modulus but with decreased tensile strength. In addition, Qiu et al. prepared PLA/PBS blends with the aim of improving the ductility of PLA and the results showed that the crystallinity of PLA/PBS blends increased with the addition of PBS content. The ductility of PLA can be improved but with a compromise of stiffness and strength. Notably, Zhang et al. found that the tensile properties of PLA/PBS blends were higher than the anticipated values and a synergistic effect was proposed to explain this phenomena. Although there have been a few reports on PBS blends, there is still little research done on the application of PBS blends in FDM 3D printing.

The main goal of this research is to prepare PBS/PLA blends with different compositions and validate their suitability as filaments for FDM printing. The rheological, thermal, and mechanical properties of the blends were investigated, and different specimens were printed with these filaments to evaluate their suitability for FDM system. Interlayer bond strength in the printed products was also measured. Furthermore, we expect to find a relationship between the properties of materials and the performance of FDM printing so as to give a reference for judging whether a thermoplastic polymer material, not limited to polymer blends, is suitable for FDM printing or not.

### RESULTS AND DISCUSSION

**Characterization of PBS/PLA Blends. Rheological Properties of Different Blends.** Since viscosity is an important parameter for both filament extrusion and FDM printing, we first measured the shear viscosity of the polymer blend melt in
a rotary rheometer, with the results shown in Figure 1. In general, the complex viscosity of the PBS/PLA blends increases with the addition of PLA, since PLA melt has a much higher zero-shear viscosity than that of PBS at the measured temperature. In the low-frequency range, both the virgin PBS and its blends exhibit a Newtonian plateau, whereas they demonstrate shear thinning in the high-frequency range. Moreover, with the increasing content of PLA, the shear thinning behavior becomes more significant, representing a typical characteristic of the pseudoplastic fluid behavior. On one hand, the proper increase of complex viscosity is expected to be favorable for the FDM printing process based on extrusion. As reported in the literature, the modulus/viscosity ratio of FDM-printed filaments before heating zones should be in a range of $(3-5) \times 10^5$ s$^{-1}$ to ensure the continuous convey of polymer filament without buckling. On the other hand, a very high viscosity of the polymer melt would result in swelling of the extruded rod and poor adhesion of the neighboring layers, which can directly cause the failure of printing. Therefore, the shear viscosity of the melt should be in a proper range. The dynamic shear storage modulus ($G^\prime$) and loss modulus ($G^\prime\prime$) of the polymer blends with changed frequencies were measured, as presented in Figure 1b,c. Obviously, it can be seen that all polymer blends exhibit a typical viscoelastic behavior ($G^\prime > G^\prime\prime$) in the whole frequency range. The storage modulus of PBS/PLA blends is higher than that of the virgin PBS, which mainly attributes to the incorporation of PLA hindering the motion of molecules. Power law model of the viscosity is described by eq 1

$$\eta^* = K \gamma^{n-1}$$

where $K$ is a constant prefactor, $n$ is the power law exponent, and $\gamma$ is the shear rate. The parameters calculated by the power law model are summarized in Table 1. With addition of PLA, the $n$ value of the blends drops compared with the virgin PBS, indicating a stronger trend of shear thinning. Meanwhile, the melt viscosity has been improved, which is consistent with the analysis of complex viscosity mentioned above.

We have estimated the shear rates in filament extrusion and FDM printing according to eq 2

$$\dot{\gamma} = \frac{8\bar{v}}{D}$$

where $\bar{v}$ and $D$ represent the average extrusion rate of the melt and the inner diameter of the rod die, respectively. For filament extrusion, the extrusion rate was around $1.8$ m min$^{-1}$, namely, $0.03$ m s$^{-1}$. The inner diameter of the extrusion die was $0.003$ m. The estimated shear rate for filament extrusion was approximately $40$ s$^{-1}$. For FDM printing, the material was extruded at a rate of $0.04$ m s$^{-1}$ through a nozzle with inner diameter of $0.0004$ m so the shear rate was around $400$ s$^{-1}$. The shear rate during preparation of the filaments is in the range of oscillatory rheology measurements and that in the later FDM printing using the filaments is out of the range and can be measured by a capillary rheometer.

**Differential Scanning Calorimetry (DSC) Analysis of the Polymer Blend Filaments.** Thermal properties such as the glass transition temperatures of the blends were measured via DSC. The thermograms during the first heating scan are plotted in Figure 2. The PLA used in this work is an amorphous polymer with a glass transition temperature ($T_g$) of $54 ^\circ\text{C}$. The used PBS is a semicrystalline polymer with $T_g$ around $-35 ^\circ\text{C}$ and melting point about $114 ^\circ\text{C}$. The melt temperature ($T_m$) of PBS in the blends is lower, but the crystallization temperature ($T_c$) during cooling is slightly higher than that of pure PBS, which indicates that PLA or the interface of the two components may show a nucleation effect on the crystallization of PBS. Moreover, all blends demonstrate only one endothermal melting peak, which belongs to PBS crystalline phase. The degree of crystallinity of the PBS phase ($X_{C,PBS}$) is determined by eq 3

$$X_C = \frac{\Delta H_{m} - \Delta H_{f}}{\Delta H_{100}} \times 100\%$$

where $\Delta H_{m}$ is the enthalpy of melting and $\Delta H_{f}$ is the enthalpy of cold crystallization. $\Delta H_{100}$ is the enthalpy of fusion for a 100% crystalline polymer, which is $110.3$ J g$^{-1}$ for PBS. The thermal properties of PBS/PLA blends and their FDM-printed parts are summarized in Table 2. Since PLA used here is nearly amorphous, the apparent crystallinity in the blends decreases with the addition of PLA. Recrystallization of PBS crystals during heating is clearly observed in the blends with PBS content larger than 60%, which agrees with our previous DSC results. To present the difference of crystallinity in the polymer blends, the Y-axis of all thermograms in Figure 2a is in the same scale of W g$^{-1}$ and the curves are vertically offset to separate and show them clearly. Figure 2b shows the enlarged view of the thermograms at around the glass transition temperature of PLA. The endotherm peak accompanying the glass transition in PBS40/PLA60 and PBS20/PLA80 blends probably results from enthalpic relaxation of the aged PLA component in the blends after storage.

**Mechanical Properties of the Injection-Molded Bars of the Blends.** The pellets of polymer blends were injection-molded in a microinjection machine to prepare dumbbell-shaped and cuboid bars for tensile and impact tests, respectively. The mechanical properties of these bars are presented in Table 3. The tensile modulus of the materials increases with introduction of PLA. Significantly, the tensile modulus has been improved by 2.88 times when the PLA content reaches 80%. With the increasing content of PLA from 0 to 80 wt %, the tensile strength of PBS increases from 41.5 to 55.6 MPa and the elongation at break decreases. It is of particular interest that the PBS80/PLA20 blend exhibits the maximum elongation at break. This phenomenon can be attributed to the effect of rigid filler toughening. When a small amount of brittle polymer (e.g. PLA) is dispersed in a ductile polymer matrix (PBS), the dispersed phase acting as a point of stress concentration can absorb energy by mechanical deformation. Other possible mechanisms of toughening may result from more microvoids and larger shear yielding in the matrix in presence of the dispersed phase. The tensile properties of the commercially available filaments produced by the company Stratasys are listed in Table 4 for comparison.

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**Table 1. Power Law Fitting Parameters of the Melt Shear Viscosity at 160 °C**

| sample codes | $K$ (Pa s$^n$) | $n$ |
|--------------|---------------|-----|
| PBS100       | 607.2         | 0.88|
| PBS80/PLA20  | 1154.8        | 0.84|
| PBS60/PLA40  | 1494.0        | 0.83|
| PBS40/PLA60  | 2941.0        | 0.77|
| PBS20/PLA80  | 3489.0        | 0.74|

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**Table 2. Mechanical Properties of the Injection-Molded Bars of the Blends**

| sample codes | tensile modulus (MPa) | tensile strength (MPa) | elongation at break (%) |
|--------------|-----------------------|------------------------|-------------------------|
| PBS100       | 60.7                  | 41.5                   | 143.5                   |
| PBS80/PLA20  | 17.3                  | 49.1                   | 122.5                   |
| PBS60/PLA40  | 21.0                  | 52.1                   | 114.0                   |
| PBS40/PLA60  | 25.8                  | 55.1                   | 100.0                   |
| PBS20/PLA80  | 29.6                  | 55.6                   | 80.0                    |

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**Table 3. Mechanical Properties of the Injection-Molded Bars of the Blends**

| sample codes | tensile modulus (MPa) | tensile strength (MPa) | elongation at break (%) |
|--------------|-----------------------|------------------------|-------------------------|
| PBS100       | 60.7                  | 41.5                   | 143.5                   |
| PBS80/PLA20  | 12.8                  | 45.2                   | 128.5                   |
| PBS60/PLA40  | 15.8                  | 48.1                   | 118.0                   |
| PBS40/PLA60  | 21.8                  | 52.1                   | 108.0                   |
| PBS20/PLA80  | 26.8                  | 55.1                   | 90.0                    |
Obviously, the elongation at break of PBS/PLA blends prepared in this work is much higher than that of commercially available filaments listed in Table 4. At the same time, the polymer blends exhibit acceptable tensile strength and modulus, with tensile strength higher than that of most of the commercially adopted materials listed in Table 4. More specifically, the impact strength of PBS/PLA blends is significantly improved when the weight percent of PLA reaches 20%, which means that the blend PBS80/PLA20 is toughened and strengthened simultaneously due to the above-mentioned synergistic effect. Notably, the Izod impact strength values of the studied blends are all higher than that of the pure PBS. Compared with pure PLA, the studied polymer blends, especially PBS20/PLA80, PBS40/PLA60, and PBS60/PLA40, possess high impact strength and elongation at break as well as not much decreased tensile strength and modulus so they are good candidate materials for FDM printing.

**FDM Printing Using PBS/PLA Blend Filaments.**

Figure 2. (a) DSC thermograms of PBS/PLA blend filaments during first heating. (b) Partial enlargement of DSC thermograms around the glass transition temperature of PLA component in (a). The number after PBS indicates the weight percentage of PBS in its blends with PLA.

### Table 2. Thermal Properties of PBS/PLA Blends

| materials       | $T_g$ (°C) | $T_c$ (°C) | $T_m$ (°C) | $\Delta H$ (J g$^{-1}$) | $X_{C,PBS}$ (%) |
|-----------------|------------|------------|------------|--------------------------|-----------------|
| PBS100          | 65.7       | 114.8      | 52.74      | 52.74                    | 47.82           |
| PBS80/PLA20     | 51.2       | 75.6       | 112.9      | 41.08                    | 37.24           |
| PBS60/PLA40     | 51.0       | 77.9       | 112.7      | 31.32                    | 28.40           |
| PBS40/PLA60     | 52.3       | 80.0       | 112.4      | 26.03                    | 23.60           |
| PBS20/PLA80     | 52.3       | 111.6      | 11.15      | 11.15                    | 10.11           |

### Table 3. Mechanical Properties of the PBS/PLA Blend Bars Produced by Injection Molding

| blend compositions | tensile strength (MPa) | tensile modulus (MPa) | elongation at break (%) | impact strength (kJ m$^{-2}$) |
|--------------------|------------------------|-----------------------|-------------------------|-------------------------------|
| PBS100             | 41.5 ± 2.6             | 554 ± 45              | 324 ± 36                | 7.2 ± 0.6                    |
| PBS80/PLA20        | 46.8 ± 3.8             | 794 ± 114             | 356 ± 36                | 20.9 ± 0.7                   |
| PBS60/PLA40        | 45.6 ± 1.6             | 1546 ± 35             | 297 ± 19                | 14.7 ± 0.5                   |
| PBS40/PLA60        | 51.2 ± 0.9             | 2045 ± 101            | 159 ± 44                | 13.9 ± 0.6                   |
| PBS20/PLA80        | 55.6 ± 2.2             | 2150 ± 177            | 93 ± 27                 | 12.9 ± 0.3                   |

### Table 4. Tensile Properties of PBS/PLA Blends Studied Here and the Commercially Available Filaments Used for FDM

| no. | material          | tensile strength (MPa) | tensile modulus (MPa) | elongation at break (%) |
|-----|-------------------|------------------------|-----------------------|-------------------------|
| 1   | PBS20/PLA80       | 55.6                   | 2150                  | 93                      |
| 2   | PBS40/PLA60       | 51.2                   | 2045                  | 159                     |
| 3   | PBS60/PLA40       | 45.6                   | 1546                  | 297                     |
| 4   | ASA$^a$           | 33                     | 2010                  | 9                       |
| 5   | FDM Nylon 12      | 48                     | 1310                  | 6.5                     |
| 6   | ABS-ESD7          | 36                     | 2400                  | 3                       |
| 7   | ABSi              | 37                     | 1920                  | 4.4                     |
| 8   | ABSplus-P430      | 33                     | 2200                  | 6                       |
| 9   | PC$^b$            | 68                     | 2300                  | 5                       |
| 10  | PC-ABS            | 34                     | 1720                  | 5                       |
| 11  | PPSF$^c$          | 55                     | 2100                  | 3                       |

$^a$Acrylonitrile-styrene-acrylate copolymer. $^b$Polycarbonate. $^c$Polyphe- nylsulfone.

Figure 3. Appearance of the PBS/PLA blend bars prepared by FDM printing.
weight ratio of PBS is more than 80%, serious distortion can be observed. The distortion may be attributed to the thermal stress caused by volume shrinkage during cooling. The blends with more PBS have a higher degree of apparent crystallinity (Table 2) and lower modulus (Table 3), thus leading to higher distortion. Printing with pure PBS fails due to the serious warping and distortion, proving that the modification of PBS is necessary for its application in FDM printing.

After being quenched in liquid nitrogen, the FDM-printed PBS/PLA bars were fractured and the cross sections were observed in scanning electron microscope (SEM) after being sputtered with gold, as shown in Figure 4. The layer structure is quite obvious when the PBS content is less than 60%. Due to lower melt viscosity (Figure 1a), the PBS80/PLA20 and pure PBS bars exhibit better interlayer bonding, as demonstrated in Figure 4d,e.

Differential Scanning Calorimetry (DSC) Analysis of FDM-Printed Parts. During FDM printing, the previously printed layer is reheated by the new printing layer on top, which leads to recrystallization in the former. Thus, the different parts of printed articles probably possess different degrees of crystallinity. Moreover, the printing parameters, such as the temperature of the printing nozzle and the support platform, were reported to have a considerable effect on the crystallinity of printed specimens.79 To investigate the effect of FDM printing process on the crystallization behavior of the PBS/PLA blends, thermal analysis of the printed bars was performed on a DSC. Samples used for DSC analysis were all obtained from their bottom almost at the same position, since the crystallization behavior might not be the same at the different heights of FDM-printed parts.7 The thermograms of the specimens from the printed bars during the first heating run could indicate the initial crystallization information during

| material sample   | $T_g$ (°C) | $T_m$ (°C) | $T_c$ (°C) | $\Delta H$ (J g$^{-1}$) | $X_{C,PBS}$ (%) |
|-------------------|------------|------------|------------|--------------------------|-----------------|
| PBS100 filament   | 65.7       | 114.8      |            | 52.74                    | 47.82           |
| FDM               | 78.0       | 113.2      |            | 58.07                    | 52.65           |
| PBS80/PLA20 filament | 51.2   | 75.6       | 112.9      | 41.08                    | 37.24           |
| FDM               | 78.0       | 112.0      |            | 49.9                     | 45.24           |
| PBS60/PLA40 filament | 51.0   | 77.9       | 112.7      | 31.32                    | 28.40           |
| FDM               | 75.0       | 112.2      |            | 35.22                    | 31.93           |
| PBS40/PLA60 filament | 52.3   | 80.0       | 112.4      | 26.03                    | 23.60           |
| FDM               | 72.2       | 112.7      |            | 25.24                    | 22.88           |
| PBS20/PLA80 filament | 52.3   | 111.6      | 11.15      | 10.11                    |                 |
| FDM               | 111.7      | 11.68      |            | 10.59                    |                 |

Table 5. Comparison of the Degrees of Crystallinity of PBS in the PBS/PLA Filaments Extruded by a Single-Screw Extruder and Those in the Bars Printed by FDM.
processing, which are compared with the thermograms of the raw filaments, as summarized in Table 5. The degree of crystallinity in the FDM-printed parts of PBS100, PBS80/PLA20, and PBS60/PLA40 is higher than that in the raw filaments. Considering that all printing was conducted with a support platform at room temperature and its effect on crystallization was negligible, this phenomenon might be attributed to the fact that cooling of the printed bars was slow and recrystallization probably happened when the new printing layer on top reheated the bottom layer in contact.

**Optimal Composition and Nozzle Temperature for PBS/PLA Blends Used in FDM Printing.** From the above results, PBS40/PLA60 blend with moderate melt viscosity, a high modulus, and a low degree of crystallinity (thus low volume shrinkage) is more suitable as filaments for FDM printing in terms of the final product performance of good interlayer bonding and low distortion. Since the interlayer bonding during FDM printing occurs almost quiescently, the zero-shear viscosity of melt is an important factor. To find a suitable printing temperature range for the blend, the zero-shear viscosity of PBS40/PLA60 under different temperatures was tested and the results are shown in Figure 5. The zero-shear viscosity increases sharply when the melt temperature drops from 190 to 160 °C. Referring to the size accuracy and smoothness of the printed parts, the optimal nozzle temperature for PBS40/PLA60 should be set above 190 °C, for example, at a temperature range of 200–230 °C.

**Interlayer Bond Strength of the FDM-Printed Specimens.** In a typical FDM system, specimens are usually prepared track by track and layer by layer. Such a printing process generates a large amount of voids and gaps inevitably, resulting in worse mechanical performances when compared with those made by the traditional processing method. To characterize the bond strength in the vertical direction between two neighboring layers of FDM-printed parts, we printed the specimens according to the type V in ASTM D638 standard and two rectangular thin sections on the bottom of each specimen were designed to assure firm attachment on the platform, as shown in Figure 6. The specimens were printed with different blend filaments without a preheated support platform or any adhesive. Then, the tensile strength of these specimens was measured. We chose PBS40/PLA60 with both good mechanical properties and printing performance, as a reference material to evaluate the effect of printing temperature on the interlayer bond strength. The results are summarized in Table 6. With the increasing content of PLA, the tensile strength of the printed parts decreases, which can be attributed to weaker interlayer bonding due to higher zero-shear viscosity of the melt (as shown in Figure 1a). For the fixed blend composition, when the nozzle temperature becomes higher, the interlayer bond strength decreases in the studied temperature range, which is out of expectation. Usually, the materials extruded at higher temperature should show lower melt viscosity and thus better interlayer adhesion so as to improve the bond strength. However, this expectation contradicts the experimental results here. We propose that the decreased bond strength at higher printing temperature may arise from thermal degradation of PLA when the nozzle temperature is higher than 190 °C. The considerable thermal degradation of PLA 2002D after thermal processing at 170–200 °C was previously reported.27

**Models of PBS/PLA Blends Printed by FDM.** Two 3D-printed models, a rabbit printed with PBS60/PLA40 and a tower printed with PBS40/PLA60, are shown in Figure 7a,b. The smooth printing process and the nice appearance of the models indicate that the two blends are suitable as FDM filaments. For each blend, the optimal processing conditions are defined, such as the temperature of nozzle, infill degree, and layer thickness. The prepared PBS/PLA blends can be used to print not only thick-walled but also thin-walled hollow structures without observable distortion and defects. Furthermore, the platform to support the printed models can be set at room temperature during the whole printing process and no other support structure or adhesive is necessary, endowing these blend materials with ease of FDM printing and better mechanical properties.

![Figure 5](image)

*Figure 5. Variation of the zero-shear viscosity of PBS40/PLA60 melt with temperature.*

| Blend compositions | Printing temperature (°C) | Zero-shear viscosity (Pa s) | Tensile strength (MPa) |
|--------------------|---------------------------|---------------------------|-----------------------|
| PBS100             | 210                       | 67                        | 25.0 ± 1.2            |
| PBS80/PLA20        | 210                       | 96                        | 20.5 ± 1.3            |
| PBS60/PLA40        | 210                       | 123                       | 19.6 ± 1.1            |
| PBS40/PLA60        | 190                       | 564                       | 21.4 ± 5.2            |
| PBS40/PLA60        | 200                       | 438                       | 19.5 ± 2.7            |
| PBS40/PLA60        | 210                       | 262                       | 18.4 ± 2.7            |
| PBS40/PLA60        | 230                       | 130                       | 16.5 ± 2.7            |
In this work, PBS/PLA blends used for FDM printing were prepared. All blends exhibit excellent processing properties and can be extruded as monofilaments with a 1.75 mm diameter via a single-screw extruder. With increasing PBS content, the elongation at break and impact strength of the blends increase. However, orientation of the printed bars increases due to larger volume shrinkage resulting from the higher degree of crystallinity in the blends. In addition, the interlayer bond strength improves due to the decreased melt viscosity. When PLA content in the blends is less than 40 wt %, FDM printing can proceed smoothly with neither observable distortion nor detachment from the platform at room temperature. PBS60/PLA40 and PBS40/PLA60 are the optimal blend compositions, considering both material toughness, distortion of printed bars, and interlayer bond strength. Models with porous structure can be successfully printed using PBS60/PLA40 and PBS40/PLA60 filaments, and good dimensional accuracy and gloss appearance of the printed models have been obtained. Compared with the commercial printing materials, the blends are proved to possess both high dimensional accuracy and gloss appearance as well as dimensional accuracy, the bio-based PBS/PLA blends are new promising materials for producing FDM filaments for applications in many fields, especially for architectural design. Furthermore, our study is expected to provide methods for evaluating whether a thermoplastic polymer material is suitable for FDM printing or not.

**EXPERIMENTAL SECTION**

**Materials.** The PLA (2002D, with melt flow rate (MFR) of 6 g/10 min under a 2.16 Kg load at 210 °C) was purchased from Nature Works Co. Ltd. Its number-average molecular weight ($M_n$) and the polydispersity index ($M_w/M_n$) were reported to be 120 000 and 1.75, respectively.27 PBS (TH803S, with MFR of 8 g/10 min under a 2.16 Kg load at 190 °C) was provided by Xinjiang Blue Ridge Tunhe Polyester Co. Ltd. (China). $M_n$ and $M_w/M_n$ of PBS were measured to be 83 000 and 2.68, respectively.

**Sample Preparation.** PBS and PLA pellets were dried at 65 °C for 12 h in a vacuum oven before processing to ensure the removal of any absorbed moisture. Subsequently, PBS and PLA with different feeding ratios were added into a twin-screw extruder (Nanjing Hass Extrusion Equipment Co., Ltd. China). Temperatures at the four heating zones (from hopper to extruder die) were set at 150, 170, 180, and 185 °C, respectively. Then, the extrudate cooled in a water bath was pelletized using a granulator. Dried again in vacuum, the pellets of the blends were homogenized through mixing and finally reextruded into 1.75 ± 0.02 mm monofilaments via a single-screw extruder (Haake Polylab OS, Thermo Fisher). Temperatures of the heating zone 1–3 in the single-screw extruder were 130, 150, and 160 °C, respectively. The die temperature was 150 °C, and the speed of the screw was 10.0–30.0 rpm, which varied with the blending ratio. After being dried again in vacuum, a portion of the monofilament was pelletized again and molded into different specimens with a specified size for various measurements.

Monofilaments of different blends were used to print different specimens and models with an FDM printer (AOD Dreamer, Qingdao Autolay 3D printing Co., Ltd. China). A typical FDM printing process is as follows: First, digital models were predesigned in a computer with the software and then exported as standard triangle language (STL) file types. Second, the STL files were modified with the printer software and exported as g-code files. The g-code files were exported into the FDM printer. Third, a 1.75 mm monofilament was fed into the FDM printer via two pinch rollers. The nozzle diameter of the FDM printer was 0.40 mm, and the nozzle temperature was set at 190 °C if not specified. The printer platform was placed at room temperature without heating or using any adhesives. The printing head speed was maintained at 1.5 m min$^{-1}$ for all layers. The layer height was set as 0.1 mm. Then, the specimens were printed layer by layer. The first layer was printed with a deposition orientation of 45°, and the second layer was printed with an orientation of 135°. The other layers were printed with the two orientations alternatively. To obtain the optimal mechanical properties, the infill ratio was set as 100%.

**Characterization.** The thermal transition temperatures of the materials were examined via differential scanning calorimetry (DSC) on a DSC-60 apparatus from Shimadzu, Japan. For each blend, a 2.0–3.5 mg sample was sealed in an aluminum pan and the blank pan was used as the reference. The thermograms during the first heating run were obtained during heating from room temperature to 160 °C at a heating rate of 10 °C min$^{-1}$ under nitrogen flow of 45 mL min$^{-1}$. The DSC curves during the following cooling run from 160 to 50

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**CONCLUSIONS**

Figure 7. Rabbit printed with PBS60/PLA40 (a) and a tower printed with PBS40/PLA60 filaments (b).
°C at a cooling rate of 10 °C min⁻¹ were recorded as well. Rheology of the samples was measured on a rotary rheometer (MCR301, Anton Paar, Austria). The samples were tested in the oscillation mode with small amplitude, using a parallel-plate geometry with a diameter of 25 mm. The gap between plates was set at 2.0 mm. The strain was set at 1.0% and the testing temperature was 160 °C, if not specified. The frequency sweep range was from 628.3 to 0.06283 rad s⁻¹. Testing samples for rheology were compression-molded at 210 °C under a pressure of 8 MPa. Tensile tests were performed with dumbbell-shaped samples with dimensions of 10.0 mm (length) × 4.0 mm (neck width) × 2.0 mm (thickness) by using an UTM-1432 tensile testing machine from Chengde Jinjian Testing Instrument Co., Ltd. at a crosshead speed of 50 mm min⁻¹. The Izod impact strength of the notched samples was set at 25.0 mm. The gap between the clamps was set at 2.0 mm and that between the gauges was set at 210 °C.

The authors declare no competing financial interest.

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**Notes**

The authors declare no competing financial interest.

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**REFERENCES**

(1) Shambley, W. From RP to AM: A Review of Prototyping Methods. *Mod. Cast.* 2010, 100 (7), 30–33.

(2) Wendel, B.; Rietzel, D.; Kühnlein, F.; Feulner, R.; Hülder, G.; Schmachtenberg, E. Additive Processing of Polymers. *Macromol. Mater. Eng.* 2008, 293, 799–809.

(3) Huang, S. H.; Liu, P.; Mokasdar, A.; Hou, L. Additive Manufacturing and its Societal Impact: A literature Review. *Int. J. Adv. Manuf. Technol.* 2013, 67, 1191–1203.

(4) Wang, X.; Jiang, M.; Zhou, Z.; Gou, J.; Hui, D. 3D Printing of Polymer Matrix Composites: A Review and Prospective. *Composites, Part B* 2017, 110, 442–458.

(5) Lebedev, S. M.; Gefle, O. S.; Amitov, E. T.; Zhirulavlev, D. V.; Berchuk, D. Y.; Mikutskiy, E. A. Mechanical Properties of PLA-based Composites for Fused Deposition Modeling Technology. *Int. J. Adv. Manuf. Technol.* 2018, 97, 511–518.

(6) Sun, Q.; Rizvi, G. M.; Bellehemeur, C. T.; Gu, P. Effect of Processing Conditions on the Bonding Quality of FDM Polymer Filaments. *Rapid Prototyping J.* 2008, 14, 72–80.

(7) Drummer, D.; Cifuentes-Cuellar, S.; Rietzel, D. Suitability of PLA/TCP for Fused Deposition Modeling. *Rapid Prototyping J.* 2012, 18, 500–507.

(8) Haq, R. H. A.; Rahman, M. N. A.; Ariffin, A. M. T.; Hassan, M. F.; Yunus, M.Z.; Adzila, S. Characterization and Mechanical Analysis of PCL/PLA Composites for FDM Feedstock Filament. *IOP Conf. Ser.: Mater. Sci. Eng.* 2017, 226, No. 012038.

(9) Wang, L.; Gramlich, W. M.; Gardner, D. J. Improving the Impact Strength of Poly(lactic acid) (PLA) in Fused Layer Modeling (FLM). *Polymer* 2017, 114, 242–248.

(10) Wittbrodt, B.; Pearce, J. M. The Effects of PLA Color on Material Properties of 3D Printed Components. *Addit. Manuf.* 2015, 8, 110–116.

(11) Lanzotti, A.; Grasso, M.; Staiano, G.; Martorelli, M. The Impact of Process Parameters on Mechanical Properties of Parts Fabricated in PLA with an Open-source 3D Printer. *Rapid Prototyping J.* 2015, 21, 604–617.

(12) Guo, R.; Ren, Z.; Bi, H.; Song, Y.; Xu, M. Effect of Toughening Agents on the Properties of Poplar Wood Flour/poly (lactic acid) Composites Fabricated with Fused Deposition Modeling. *Eur. Polym. J.* 2018, 107, 34–45.

(13) Torres, J.; Cole, M.; Owji, A.; DeMaistry, Z.; Gordon, A. P. An Approach for Mechanical Property Optimization of Fused Deposition Modeling with Polyactic Acid via Design of Experiments. *Rapid Prototyping J.* 2016, 22, 387–404.

(14) http://www.stratasys.com/materials/search.

(15) Xu, J.; Guo, B. H. Poly(butylene succinate) and its Copolymers: Research, Development and Industrialization. *Biotechnol. J.* 2010, 5, 1149–1163.

(16) Deng, Y.; Thomas, N. L. Blending Poly(butylene succinate) with Poly(lactic acid): Ductility and Phase Inversion Effects. *Eur. Polym. J.* 2015, 71, 534–546.

(17) Chieng, B. W.; et al. Effect of Organo-modified Montmorillonite on Poly(butylene succinate)/poly(butylene adipate-co-terephthalate) Nanocomposites. *Express Polym. Lett.* 2010, 4, 404–414.

(18) Okamoto, K.; Ray, S. S.; Okamoto, M. New Poly(butylene succinate)/layered Silicate Nanocomposites. II. Effect of Organically Modified Layered Silicates on Structure, Properties, Melt Rheology, and Biodegradability. *J. Polym. Sci., Part B: Polym. Phys.* 2003, 41, 3160–3172.

(19) Qiu, T. Y.; Song, M.; Zhao, L. G. Testing, Characterization and Modelling of Mechanical Behaviour of Poly(l-lactic acid) and Poly(butylene succinate) Blends. *Mech. Adv. Mater. Mod. Process* 2016, 2, 1–11.

(20) Zhang, X.; Liu, Q.; Shi, J.; Ye, H.; Zhou, Q. Distinctive Tensile Properties of the Blends of Poly(l-lactic acid) (PLLA) and Poly(butylene succinate) (PBS). *J. Polym. Environ.* 2018, 26, 1737–1744.
(21) Lv, S.; Gu, J.; Tan, H.; Zhang, Y. The Morphology, Rheological, and Mechanical Properties of Wood Flour/starch/poly(lactic acid) Blends. J. Appl. Polym. Sci. 2017, 134, No. 44743.
(22) Venkataraman, N.; Rangarajan, S.; Matthewson, M. J.; Harper, B.; Safari, A.; Danforth, S. C.; Wu, G.; Langrana, N.; Guceri, S.; Yardimci, A. Feedstock Material Property–Process Relationships in Fused Deposition of Ceramics (FDC). Rapid Prototyping J. 2000, 6, 244–253.
(23) Turner, B. N.; Gold, S. A. A Review of Melt Extrusion Additive Manufacturing Processes: II. Materials, Dimensional Accuracy, and Surface Roughness. Rapid Prototyping J. 2015, 21, 250–261.
(24) Lv, Z. Y.; Zhang, M. C.; Zhang, Y.; Guo, B. H.; Xu, J. Study on melting and recrystallization of poly(butylene succinate) lamellar crystals via step heating differential scanning calorimetry. Chin. J. Polym. Sci. 2017, 35, 1552–1560.
(25) Liang, J. Z. Toughening and Reinforcing in Rigid Inorganic Particulate Filled Poly(propylene): A review. J. Appl. Polym. Sci. 2002, 83, 1547–1555.
(26) Chen, S.; Lu, J.; Feng, J. 3D-printable ABS Blends with Improved Scratch Resistance and Balanced Mechanical Performance. Ind. Eng. Chem. Res. 2018, 57, 3923–3931.
(27) Signori, F.; Coltelli, M. B.; Bronco, S. Thermal Degradation of Poly(lactic acid) (PLA) and Poly(butylene adipate-co-terephthalate) (PBAT) and their Blends upon Melt Processing. Polym. Degrad. Stab. 2009, 94, 74–82.