

## Biodegradable composites of poly(butylene succinate-co-butylene adipate) reinforced by poly(lactic acid) fibers

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**ABSTRACT:** Biodegradable composites of poly(butylene succinate-co-butylene adipate) (PBSA) reinforced by poly(lactic acid) (PLA) fibers were developed by hot compression and characterized by Scanning electron microscopy (SEM), differential scanning calorimetry (DSC), dynamic mechanical analyzer, and tensile testing. The results show that PBSA and PLA are immiscible, but their interface can be improved by processing conditions. In particular, their interface and the resulting mechanical properties strongly depend on processing temperature. When the temperature is below 120 °C, the bound between PBSA and PLA fiber is weak, which results in lower tensile modulus and strength. When the processing temperature is higher (greater than 160 °C), the relaxation of polymer chain destroyed the molecular orientation microstructure of the PLA fiber, which results in weakening mechanical properties of the fiber then weakening reinforcement function. Both tensile modulus and strength of the composites increased significantly, in particular for the materials reinforced by long fiber. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43530.

**KEYWORDS:** biomaterials; composites; fibers; mechanical properties

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### INTRODUCTION

The development and application of biodegradable polymers have attracted much attention recently. Various biodegradable polymers have been developed and are now commercially available in the market. However, many characteristics of the most biodegradable polymers, such as their thermal and mechanical properties, are still not as good as conventional polymers. Poly(butylene succinate-co-butylene adipate) (PBSA), an aliphatic thermoplastic polyester, is one of the few commercial biocompostable polymers with reasonable balance between thermal and mechanical properties.<sup>1</sup> For example, it has better toughness than poly(lactic acid) (PLA), and higher modulus than polycaprolactone and has the ability to be reprocessed without a diminution in properties.<sup>2</sup> The polymer is semicrystalline and is designed to have processability and physical properties that are similar to those of polyethylene.<sup>1,3</sup>

The drive to improve mechanical properties is an ongoing aim for all materials. In particular, for PBSA-based materials, increasing modulus and tensile strength is the priority since these values do not meet many applications currently. In the last three years, there have been many publications about improving the mechanical properties of PBSA, such as by: crosslinking,<sup>4</sup> blending,<sup>5–12</sup> and reinforcing them with nanoparticles<sup>13–15</sup> and fibres.<sup>16–25</sup> It is well known that reinforcement with fiber is one of the most efficient ways to improve modulus

and strength. Various fibers, such as bamboo,<sup>16</sup> hemp,<sup>17</sup> cotton,<sup>18</sup> kenaf,<sup>19,20</sup> jute,<sup>21</sup> basalt,<sup>22</sup> sisal,<sup>23,24</sup> coconut,<sup>24</sup> sugarcane<sup>24</sup> bagasse,<sup>24</sup> curaua,<sup>24</sup> and carbon nanotubes<sup>23,24</sup> have been used to reinforce PBSA.

Natural fibers have been widely investigated as reinforcements for biodegradable composites because of their natural biodegradability. Currently, the development of biocomposites that are based on a combination of biodegradable polymers and natural fibers is developing rapidly.<sup>26</sup> However, natural fibers composites have some drawbacks such as incompatibility with polyesters including PBSA, the dark color of the most composites, and reduced toughness.<sup>27</sup> In this work, the biodegradable PBSA reinforced by biodegradable poly(lactic acid) (PLA) fibers were developed. The composites were fabricated via compression molding, characterized by microscopy, differential scanning calorimetry, dynamic mechanical analysis, and tensile testing. Both long and short fibers were used in this work to understand the influence of this factor on properties. The advantages of this synthetic biodegradable fiber include its light color, low density, and controllable properties such as length, diameter, which result in repeatable properties of the resultant composites.

### EXPERIMENTAL

#### Materials and Specimen Preparation

Commercially available poly(butylene succinate-co-butylene adipate) (PBSA, commercial name Bionolle<sup>TM</sup>, Grade 3001) was

**Table I.** Effect of Compressing Temperature on the Mechanical Properties of PBSA Reinforced by Long PLA Fiber

Temperature (°C)	Modulus (GPa)	Tensile strength (MPa)	Elongation (%)
Pure PBSA film	1.01 ± 0.34	16.78 ± 2.59	86.57 ± 4.30
110	1.93 ± 0.71	39.33 ± 2.59	10.74 ± 1.77
120	2.32 ± 0.88	40.87 ± 4.36	9.24 ± 0.90
130	3.01 ± 0.54	45.21 ± 3.74	9.48 ± 0.89
140	3.25 ± 0.91	44.22 ± 4.29	9.89 ± 1.00
150	3.63 ± 0.64	48.75 ± 5.68	8.28 ± 1.46
160	4.85 ± 0.57	54.54 ± 4.81	6.70 ± 0.05
170	3.76 ± 0.65	22.85 ± 3.07	9.08 ± 6.11
Pure PLA fiber	7.24 ± 0.48	124.62 ± 7.48	27.21 ± 8.18

supplied by Showa Polymers (Japan). Poly(L-lactide) (PLA) was supplied in pellet form by NatureWorks (grade PLA 4302). The materials were dried at 65 °C for 24 h in a vacuum oven before processing.

Melt spinning of the PLA fiber was carried out on a Busschaert bicomponent system that contains a single screw extruder connected by a spin block.<sup>28</sup> The multifilament bundle produced by melt extrusion was passed through a vertical air quenching system. The cooling of the filaments was optimized by passing the multi filament bundle through a distance of 5–6 m, at take up speeds of 500 m/min. The diameter of the PLA fiber is about 30–40 μm. The PBSA films (about 0.05 mm thickness) was fabricated via extrusion using a Haake single-screw extruder (Ø = 30) connected with a sheet die (with 60 mm width).

The composites of PBSA-PLA long fibers were prepared by firstly twining the fiber on a fragment in one direction, then put the twined fibers between two PBSA films, and then pressed under 2 tons at various temperatures (110–170 °C) for 10 min in a plate hot-presser (Wabash Vantage Series Hydraulic Pesses-200). The ratio of PBSA/PLA fiber is 50/50 (w/w). The thickness of the films is about 0.15 mm. Pure PBSA sample was also prepared by pressing two pure PBSA films under same conditions, in order to be used as a reference.

The composites reinforced by short fibers were prepared by three steps: (1) to homogeneously distribute the short PLA fiber into PBSA matrix, the long PLA fiber was fixed in between two PBSA films (fiber content was 90% by weight) followed by pressing at 120 °C for 5 min, with these sandwiched fibers cut into lengths of 5–8 mm; (2) PBSA pellet and the flack (containing PLA short fiber) were mixed in a Haake mixer at 120 °C at 20 rpm for 3 min in different weight ratios; and (3) the materials from Haake mixer were pressed between hot platens under 2 tons, to prepare film at various temperatures (120–170 °C) for 10 min. The thickness of the films produced was ca. 0.2 mm. Pure PBSA sample was also prepared by mixing, then hot pressing under same conditions used as a reference.

### Microstructure Characterization

Scanning electron microscopy (SEM, JOEL 7001F) was used to examine the tensile fracture surface of the PBSA-PLA composites. The samples used for SEM were coated with iridium and viewed at a scanning mode with 5 kV.

### Thermal Properties

A Perkin-Elmer DSC 8500 was used in the work to study the thermal properties of the composites. The samples (~5 mg) were weighed and sealed in an aluminum pan. The samples were heated from 20 °C to 180 °C at 20 °C/min. Three distinct measurements were performed for each sample type and the average of the results, with standard deviations calculated, were reported.

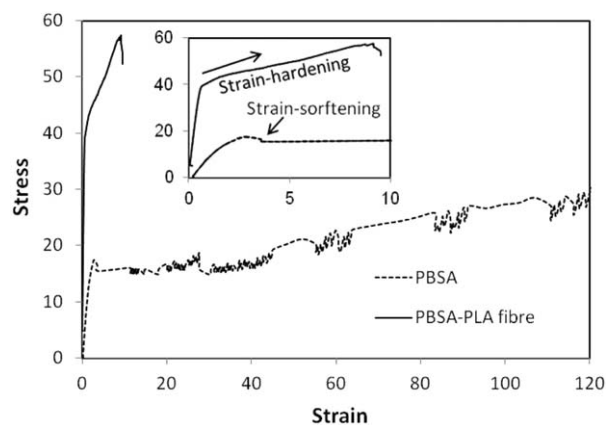
A Perkin-Elmer Pyris Diamond dynamic thermomechanical analysis (DMA) was used to study the dynamic mechanical properties of the composites. Specimens with 8 mm width, 20 mm long, and 0.15 mm thickness were used. The system was run in a rectangular tension mode at 1 Hz, with a temperature range of between –80 °C and 90 °C, and a heating rate of 2 °C/min.

### Tensile Properties

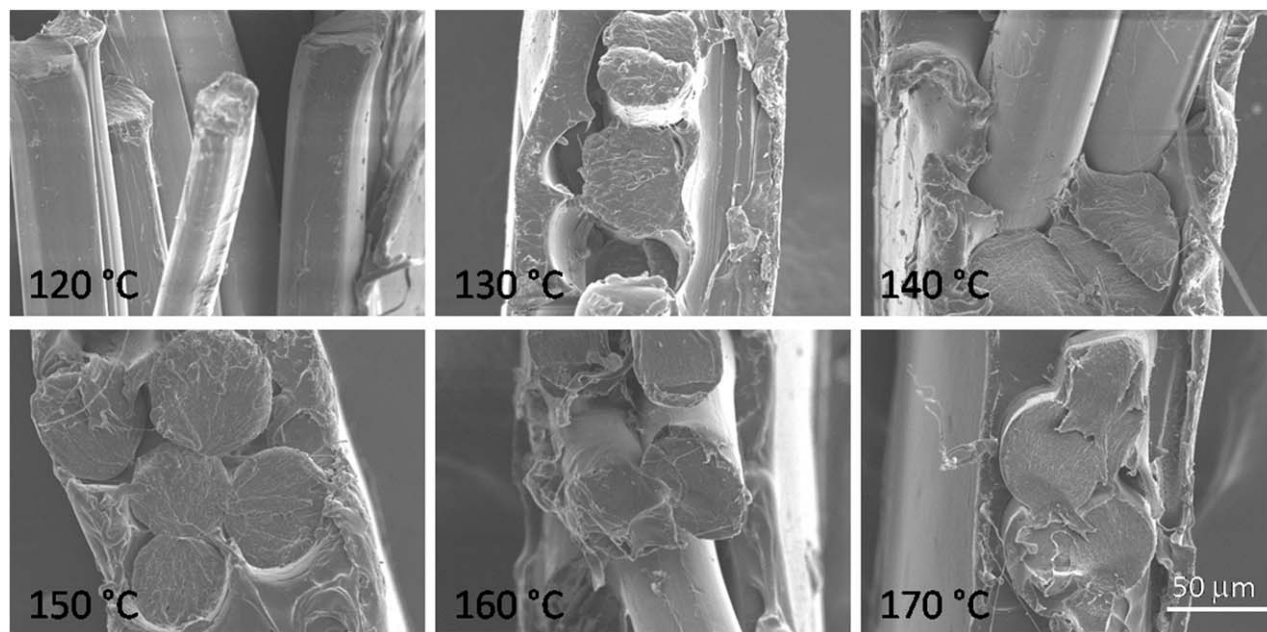
Tensile properties were evaluated in accordance with ASTM D638 on a United tensile tester with a load cell of 100 kg. The test speed is 10 mm/min. The dumb-bell shaped specimens were cut from compression-molded films according to ASTM D638. The specimens of the composites reinforced by long PLA fiber were cut parallel fiber direction. Seven specimens were tested for each sample and the average and standard deviation of different properties reported.

## RESULTS AND DISCUSSION

Table I gives the mechanical properties of PBSA-PLA long fiber composites processed (compression molded) at different temperatures. It can be seen that both the modulus and tensile strength of PBSA are increased significantly after the addition of PLA fiber. Figure 1 shows the typical stress–strain curves of pure PBSA and PBSA-PLA fiber composites, respectively. It has been observed that a stress softening of pure PBSA occurred after yielding, followed by stable neck growth and a slight stress



**Figure 1.** Typical curves of stress–strain of pure PBSA and PBSA reinforced by long PLA fiber compressed at 140 °C.



**Figure 2.** Effect of compressing temperature on the interface between PBSA and long PLA fibers observed under SEM.

hardening prior to failure. In comparison, the PBSA-PLA fiber composites showed no stress softening but a remarkable stress hardening. The specimens of PBSA-PLA fiber composites have higher tensile modulus and strength but lower elongation at break.

It has been noted from Table I that both modulus and strength are increased with increasing processing temperature up to 160 °C. Figure 2 shows the effect of compressing temperature on the interface of the PBSA matrix and PLA fibers observed under SEM. It can be seen that the interface between PBSA matrix and PLA fiber has been slightly improved with increasing processing temperature. Some gaps at the interface between the PBSA matrix and PLA fibers were observed when the compression temperature was low, but the poor interfacial adhesion was not apparent for processing temperatures higher than 150 °C. The improvement of the interface by the increasing process temperature can be used to explain the improvement in mechanical properties. On the other hand, previous studies<sup>28</sup> has showed that both modulus and tensile properties of PLA fiber will decrease if thermal treatment at above its  $T_g$ , and that this decrease continues monotonically with increasing processing temperature. When the processing temperature is higher (>160 °C) in this work, both the modulus and tensile strength of the composites are decreased, due to the reduced properties of PLA. The optimized processing temperature thus occurs at about 150–160 °C, at which the effect of the interface properties and the strength of the PLA fiber are both optimal.

Table II provides the mechanical properties of PBSA reinforced by the short PLA fiber (4 wt %) processed at different temperatures. Similarly, as for reinforcement by long fiber, both modulus and strength are increased with increasing processing temperature. Figure 3 shows the interface between PBSA matrix and the PLA fiber prepared by firstly being mixed in the Haake

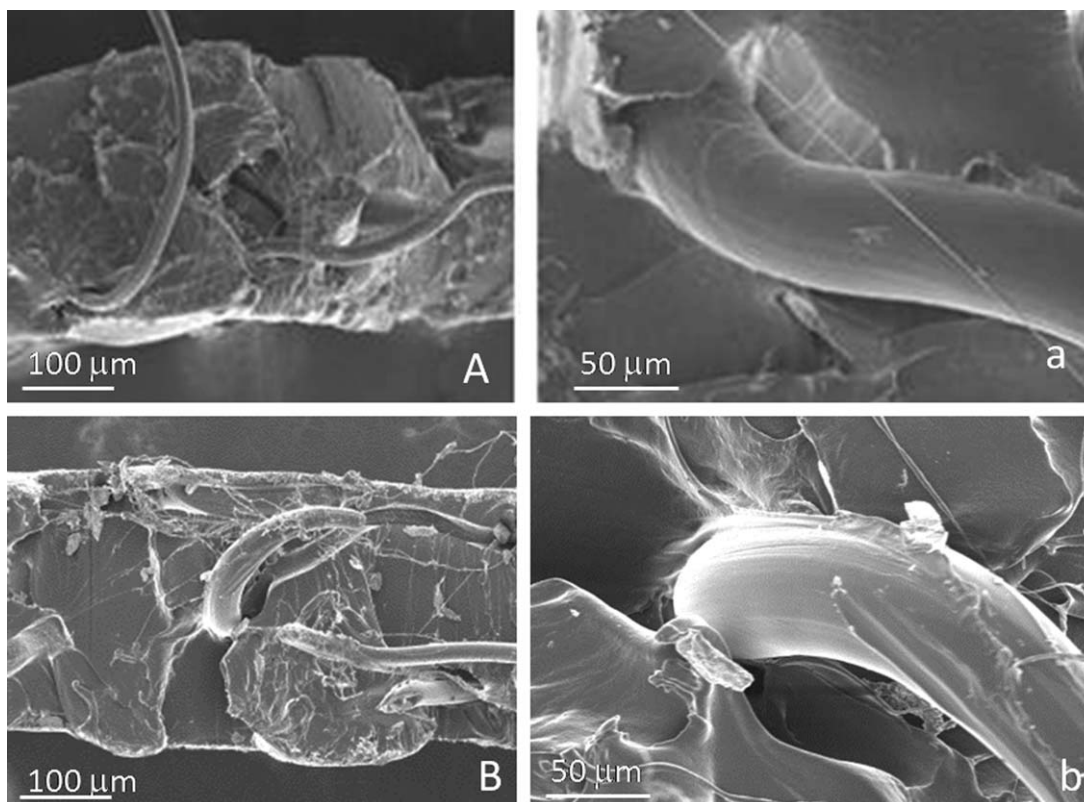
mixer at 120 °C (A and a) and then by compressed under 2 tons (B and b) at 140 °C. It can be seen that the bond between PBSA and PLA fiber is weak for the samples prepared only by mixing since the surface of PLA fibers were smooth after being pulled out during mechanical testing. The interface has been improved after the hot compression and the boundary interface between PBSA matrix and the PLA fiber can be clearly observed under SEM. Table III lists the mechanical properties of PBSA-PLA short fiber composites with different fiber content and both modulus and tensile strength are increased with increasing PLA fiber content.

Figure 4 shows the differential scanning calorimetry (DSC) thermograms of PBSA reinforced by (a) long PLA fiber prepared at different temperatures and (b) short PLA fiber with different fiber content. The thermal properties of both PBSA and PLA have been extensively studied and widely reported.<sup>28–30</sup> The peaks in the temperature ranges 80–100 °C are the melting peaks for PBSA,<sup>29</sup> while the peaks in the temperature ranges

**Table II.** Effect of Compressing Temperature on the Mechanical Properties of PBSA Reinforced by Short PLA Fiber (4%)

Temperature (°C)	Modulus (GPa)	Tensile strength (MPa)	Elongation (%)
110	1.20 ± 0.03	15.78 ± 1.17	52.06 ± 5.75
120	1.34 ± 0.29	17.47 ± 1.22	52.08 ± 9.38
130	1.44 ± 0.28	16.94 ± 2.46	48.03 ± 6.57
140	1.56 ± 0.41	17.68 ± 3.35	49.72 ± 7.52
150	1.53 ± 0.52	18.80 ± 1.61	53.76 ± 9.29
160	1.42 ± 0.67	16.43 ± 2.76	49.42 ± 5.49
170	1.33 ± 0.62	15.83 ± 2.37	41.42 ± 5.11





**Figure 3.** SEM of the interface between PBSA and short PLA fibers prepared by mixing using Haake mixer at 120 C (A,a) and then compressed under 2 tons at 140 C (B,b).

160–180°C are the melting peaks for PLA.<sup>28,30</sup> Since the composites containing long PLA fiber have a higher PLA content (50% w), the composites with short fiber contains mainly PBSA (98–90% w) and the two figures well represent the thermal properties of the composites with different ratios of the two components. It is seen that both melting temperatures of PBSA and PLA are clearly identified, and both PBSA and PLA did not influence the thermal behavior of the others. That means the PBSA and PLA are immiscible, which is the same as previously reported.<sup>31,32</sup>

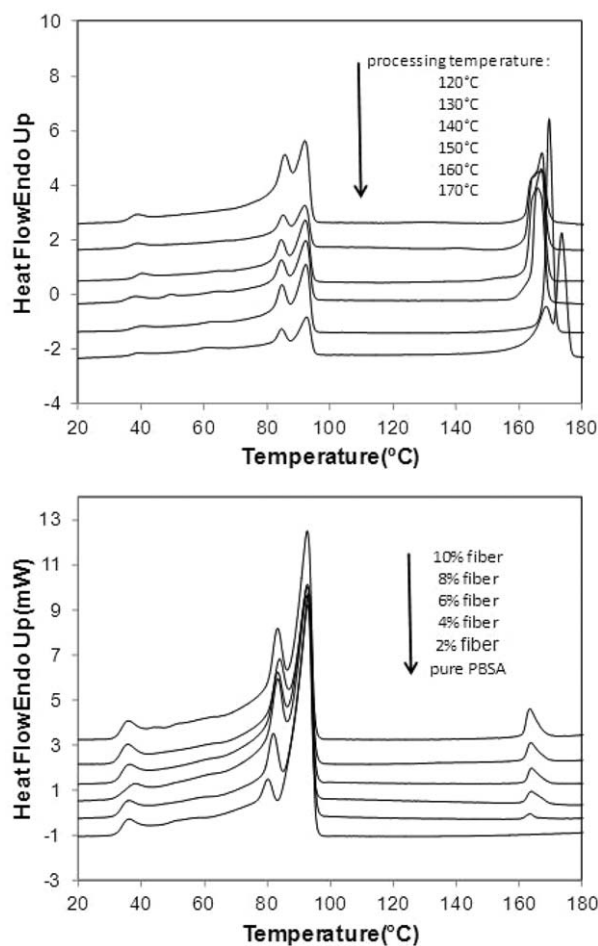
Figure 5 shows the storage modulus ( $E'$ ) and mechanical loss ( $\tan \delta$ ) of PBSA-PLA short fiber composites with different content. It can be seen that the modulus increased slightly with increasing PLA fiber content, as observed in tensile testing. There is no change in the temperature location of  $\tan \delta$  of PBSA after adding PLA fibers, which also indicates that the two polymers are immiscible.

It is well known that fully miscible blends are relatively rare, because the Gibb's free energy of mixing is positive due to the negligible change in entropy as a consequence of high molecular weight of polymers, with enthalpy term itself often being positive. However, the compatibility between polymers can be improved by various methods, such as introducing compatibilizer or coupling agents.<sup>26,27</sup> Based on above results, it is seen as for other unmelted fibers, such as glass, cellulose, and carbon, the PLA fiber can soften or partially-melt at certain temperatures, which provides a unique opportunity to improve the

interface between polymer matrix (PBSA) and the fiber. However, the higher temperature could decrease the mechanical properties of polymer fiber itself, which results in a reduced reinforcement function, or may even melt the fiber, which leads to properties of a polymer blend (as opposed to a composite). The key issue presented by polymer-based fibers is to find and control the processing window of temperature to counterbalance the two opposite effects, quite similar as self-reinforced polymeric composites.<sup>33</sup> Some of the processing conditions, such as compression pressure, may also have an influence of properties such as the degree of enhancement of the boundary between the polymer matrix and polymer fibers during processing.

**Table III.** Mechanical Properties of PBSA Reinforced by Short PLA Fiber with Different Fiber Content (Processed at 140 °C)

Fiber content (%)	Modulus (GPa)	Tensile strength (MPa)	Elongation (%)
0	1.01 ± 0.34	16.78 ± 2.59	86.57 ± 4.30
2	1.17 ± 0.39	16.28 ± 2.29	51.98 ± 3.52
4	1.56 ± 0.41	17.68 ± 3.35	49.72 ± 7.52
6	1.46 ± 0.25	17.89 ± 2.45	51.55 ± 2.40
8	1.55 ± 0.34	18.78 ± 3.24	37.90 ± 3.95
10	1.59 ± 0.61	17.90 ± 3.67	34.98 ± 0.00

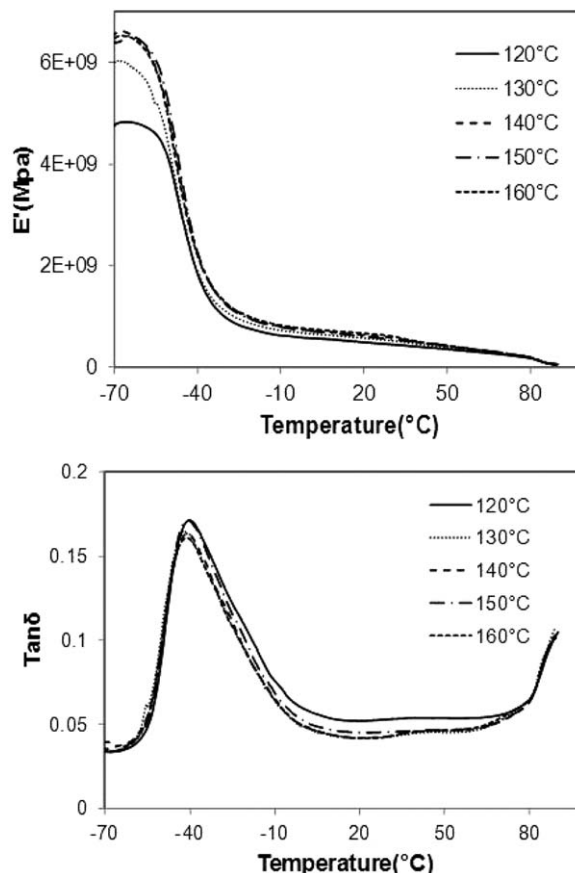


**Figure 4.** DSC thermograms of PBSA reinforced by long PLA fiber (top) prepared at different temperatures and short PLA fiber (bottom) with different content (% w).

## CONCLUSIONS

Biodegradable composites of PBSA-PLA fibers were developed via compression molding, and characterized using SEM, DSC, DMA, and tensile testing. Both long and short PLA fibers were used in this work and it was found that the tensile modulus and strength were increased significantly after the addition of the PLA fibers. Both PBSA and PLA did not influence the thermal behavior of other blend components, which indicates they are immiscible. Similarly, there is no change in location of the  $\tan \delta$  maximum detected by DMA for PBSA, following the addition of the PLA fibers, which confirms the two polymers are immiscible.

Unlike other reinforcing fibers, which do not melt, such as glass, cellulose, and carbon, the PLA fiber is able to soften or become molten at certain temperature, which provides unique opportunity to improve the interface between polymer matrix (PBSA) and the fiber. The interface between PBSA matrix and PLA fiber can be improved by processing conditions and influence the mechanical properties of the composite. When the processing temperature is lower ( $<120^\circ\text{C}$ ) the boundary interfaces between PBSA and PLA fiber are weak, which results in lower tensile modulus and strength. When the processing tem-



**Figure 5.** Storage modulus ( $E'$ ) and  $\tan \delta$  of PBSA reinforced by short PLA fiber prepared at different compression temperature.

perature is greater ( $>160^\circ\text{C}$ ), the orientation microstructure of PLA fiber is destroyed, which results in weakening mechanical properties of the fiber itself, therefore is reinforcing function. The key issue reinforced by polymer-based fiber is to find and control process window of temperature to balance the two opposite effects. Pressure enhances the boundary between PBSA matrix and PLA fibers. Both tensile modulus and strength of the composites are likewise increased with increasing PLA short fiber content.

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