Thermal and Mechanical Properties of Bleached Pulp-filled Poly(Lactic Acid) Composites Fabricated with an Internal Mixing Process

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Bioderived poly(lactic acid) (PLA) is a promising alternative for fossil-based polymers, but its poor hydrophilicity, high brittleness, and low heat-resistance are problems for its utilization. In this work, bleached softwood kraft pulp (BSKP) fiber was adopted to modify PLA with MAPP as the coupling agent, with BSKP accounting for 10 wt% to 50 wt%. Internal mixing (IM) was applied to mix the PLA/fiber blend instead of screw grinding. The thermal and mechanical properties of the composites were assessed. The IM process was proven qualified for its effective dispersion of BSKP fibers in the PLA matrix. At a fiber loading of 50 wt%, IM-processed composites acquired satisfactory tensile strength (50.49 MPa, slightly higher than PLA) and Young's modulus (2.56 GPa, 45.8% higher than PLA). The pulp fillers matched PLA matrix well for the characteristic temperatures in thermal decomposition. The BSKP/PLA composites were thermally strengthened by pulp fibers characterized by higher content of residues. The fibers improved the interfacial crystallinity of PLA in the composites (*i.e.*, from 5.22% to 11.86%). The increased crystallinity resulted in enhanced stiffness or weaker damping performance of the composites. In conclusion, natural plant fibers are a feasible option to modify PLA for extended applications.

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Keywords: Poly(lactic acid); Biocomposite; Pulp fiber; Internal mixing

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INTRODUCTION

Biodegradable substitutes from renewable natural sources are strongly encouraged to replace plastics derived from fossil fuels (Hopewell *et al.* 2009; Brems *et al.* 2012; Nechyporchuk *et al.* 2016; Benítez and Walther 2017). Polylactic acid (PLA) is a promising alternative for plastics (Muthuraj *et al.* 2017).

Bioderived PLA from plant sources such as corn has the advantages of easy processibility, good compatibility, and competitive properties with petroleum-based polymers. Its most attractive properties are biosafety and biodegradability, which ensures its vast market future in food packaging, biomedicine, automobiles, electronics, and other fields (Yang *et al.* 2016).

PLA is a linear polymer having a high quantity of ester bonds. The polymeric material shows high brittleness, low heat-resistance in processing, and slow crystallization rate. In addition, PLA is somewhat expensive compared with some general plastics. These problems limit the industrial production and commercial promotion of PLA. It is crucial to modify PLA to improve its performance and cost so that it might gain broader market applications.

Natural plants fibers can be used to enhance the properties of PLA. Micro- or nano-size units from plants improve the technical and thermal properties of PLA (Suryanegara *et al.* 2009; Nair *et al*. 2018; Qian *et al*. 2018; Shojaeiarani and Hartman 2019). However, the micro/nano-size plant fillers may not be cost-competitive for large-scale production of PLA composites. Bleached pulp fibers are more cost-effective and have been chosen by some researchers for PLA enhancement (Du *et al.* 2013; Espinach *et al*. 2018). The added pulp fibers are stable when they are melt-processed together with PLA. To acquire better interfacial interactions, chemical compatibilizers, *e.g.*, maleic anhydride modified polypropylene (MAPP) or polyethylene oxide (PEO) can be applied (Huda *et al.* 2006; Singh *et al.* 2020a). The fiber surface can be chemically modified as well (Sato *et al.* 2016; Espinach *et al.* 2018).

Most related studies have been centered on PLA-based biomaterials with low fiber loadings, and large-scale production and green applications are a big challenge. This requires developing feasible methods from the laboratory to the industry (Suzuki *et al.* 2013; Oksman *et al.* 2016). This study investigated the feasibility of modifying PLA polymeric materials by pulp fibers at elevated loading levels. The mechanical and thermal properties of the composites were evaluated.

EXPERIMENTAL

Materials

Bleached softwood kraft pulp (BSKP), dried to a moisture content of 5 wt%, was supplied by Yang Run Trading Co., Ltd (Dalian, China). Poly(lactic acid) (PLA, Nature Works TM 3251D, L-lactic content 95wt%, specific weight 1.24) was purchased from Dongguan Suyun Plastic Co., Ltd (China). Its melt flow rate is nominally 35 g/10 min at 190 °C/2.16 kg (ASTM D1238 2013). Maleic anhydride-grafted polypropylene (MAPP, PMA-H1000P), as the coupling agent, was provided by the TOYOBO Co., Ltd (Osaka, Japan) with molecular weight of 7.2×10^4 g/mol and maleic anhydride content of 5.74 wt%.

Composites Fabrication

The composites were fabricated following the internal mixing process (IM process, Fig. 1), using a rheology processing system (HAAKE Polylab OS, Thermo-Fisher Scientific Inc., Waltham, MA, USA), instead of the screw-extruding method. Bleached softwood kraft pulps were pre-broken into disperse fibers by high-speed shearing treatment. The MAPP coupling agent was fully pre-blended into the PLA materials. Subsequently, BSKP fibers and PLA material were mixed at 170 °C with rotation rate of 70 rpm. The mixing time was controlled as 5 to 20 min along with increasing fiber loadings. The BSKP fibers accounted for 10 wt% to 50 wt% of the total weight. Four percent of MAPP were added. The mixture was hot-pressed or injected into specimens as required by characterization procedures. The samples were conditioned at 60 °C for 48 h to constant weight before testing.

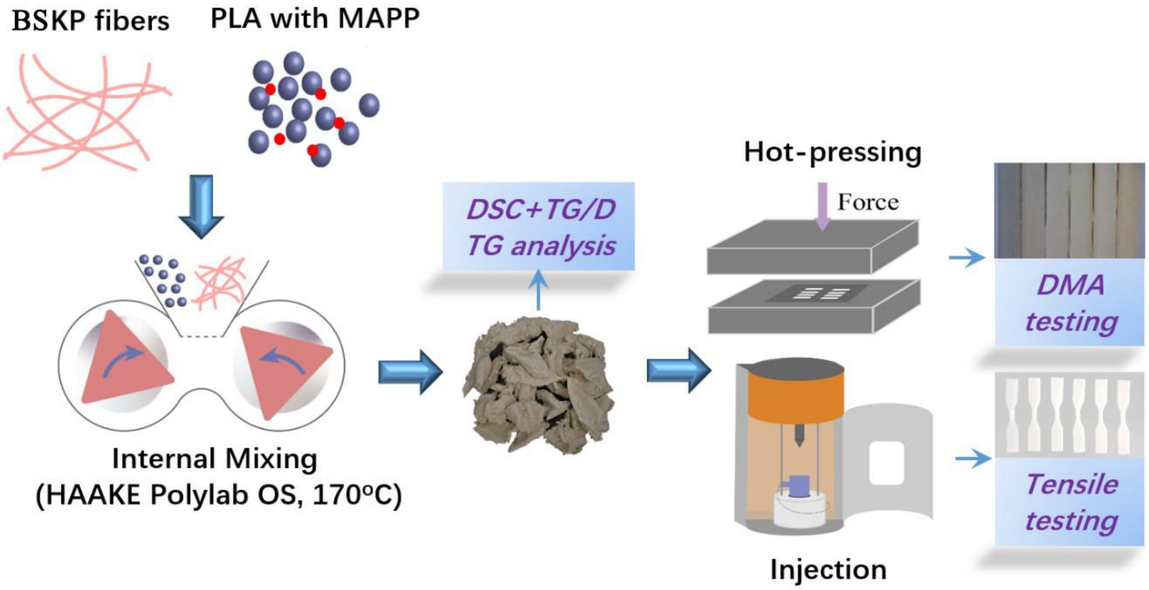


Fig. 1. Schematic representation for melt compounding processes of BSKP/PLA composites

Tensile Testing and Fracture Analysis

Dumb-bell shaped specimens for tensile loading were prepared directly by injection molding (WZS 10D, Xinshuo Equipment Co., Ltd., Shanghai, China). The dimensions followed the requirements in ASTM D638 standard (2014) for V-type tensile specimens, *i.e.*, overall length and width were 63.5 mm and 9.53 mm, and length and width of the center narrow section were 9.53 mm and 3.18 mm, respectively. The thickness was 3.5 mm. Five replications of each group were tested using a universal machine (CMT4202, Sans Testing Co., Ltd., Shenzhen, China). The speed of the moving head was set as 10 mm/min.

The cross-section microscopic morphology of fractured tensile specimens was analyzed with field emission scanning electron microscope (FE-SEM; JSM-7600F, JEOL Ltd., Tokyo, Japan). The surface morphology of dumb-bell shaped samples was pictured by light microscope (Swift-duo, Vision Engineering Ltd, Woking, UK).

Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA) was conducted using strip-shaped samples of BSKP/PLA composites (*i.e.*, 50 mm by 5 mm by 1 mm) prepared by hot pressing with pressure of 7 MPa at 170 °C (QLB-D, Shanghai No.1 Rubber Machine Factory, Shanghai, China). A dynamic mechanical analyzer (DMA 242E, NETZSCH, Selb, Germany) was applied under the tensile mode and nitrogen protection, from 30 to 100 °C (heating rate: 3 °C/min) and with a frequency of 1 Hz.

Crystallization Behavior Analysis

Differential scanning calorimetry (DSC 214 Polyma, NETZSCH) was used to study the crystallization behavior of BSKP/PLA composites. Each sample of 6 to 10 mg was heated from 30 to 200 °C at a rate of 10 °C/min and cooled at the same rate after 2 min heat preservation to eliminate thermal history. Similarly, the second heating scan was conducted to directly obtain the glass transition temperature (T_g), crystallization temperature (T_c), and melting temperature (T_m).

The NETZSCH Proteus® software was used to acquire the crystallinity of PLA in the composites as follows,

$$X_c=(\Delta H_m-\Delta H_c)/\ \Delta H_0*100 \tag{1}$$

where X_c is crystallinity (%), ΔH_m is the heat of melting enthalpy of PLA in the BSKP/PLA composites (J/g), ΔH_c is the cold crystallization enthalpy of PLA in the composites (J/g), and ΔH_0 is the melting enthalpy of neat crystalline PLA (93.6 J/g) (Mohapatra *et al.* 2014).

Thermal Stability Analysis

The thermal decomposition and stability of BSKP/PLA composites and PLA polymer were investigated by thermogravimetric analysis (TGA; STA 2500 Regulus, NETZSCH) from 30 to 600 °C at a heating rate of 10 °C/min and under a constant nitrogen flow rate (20 mL/min). The related parameters were acquired, *i.e.*, the maximum degradation temperature (T_{max}), onset degradation temperature (T_{onset}), and endset degradation temperature (T_{endset}). All samples were tested in triplicate.

RESULTS AND DISCUSSION

Tensile Properties and Fracture Analysis

The mechanical properties of fiber reinforced polymeric composites are highly reliant on the interfacial interactions between phases. Normal screw grinding and extruding method tends to cause self-agglomeration of fibers in the PLA matrix (Li *et al.* 2014; Herrera *et al.* 2015). With an internal mixing process in which PLA is fully melted as a fluid, however, the fibers became evenly dispersed in the PLA matrix. Figure 2 (panels b through f) shows no interfacial separations of pulp fibers from PLA matrix even under 500× magnification. The MAPP helped to build closer fiber-PLA collections, resulting in good BSKP/PLA interfacial interaction.

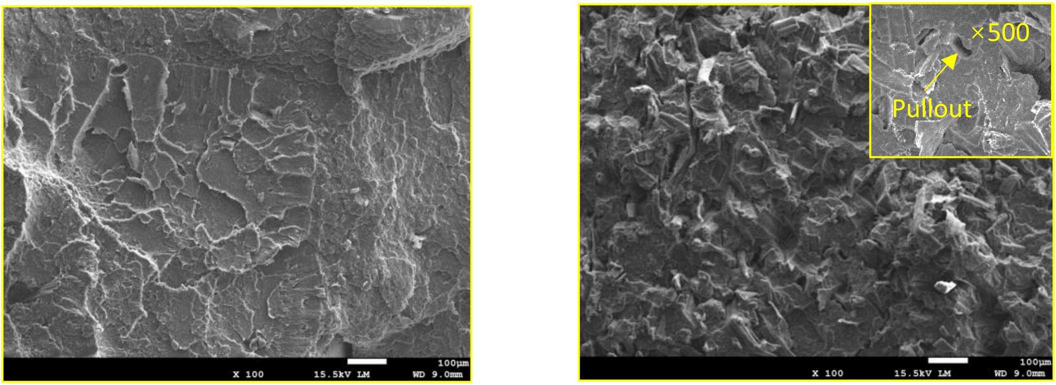
Table 1 presents the tensile performance of BSKP/PLA composites and neat PLA. The fiber-modified PLA showed stiffer characteristics with higher tensile moduli and lower elongation rates. The pulp fiber as a relatively unstretchable filler evidently restricted the free flow and intermolecular slippage of PLA polymer (Zhao *et al.* 2019). Compared with neat PLA polymer, all composites showed satisfactory tensile strength, although there were slight decreases for those at 10 wt% to 40 wt% fiber loadings. Because PLA and pulp fibers have higher tensile strength than the tested results of BSKP/PLA composites, the decreased values may be attributed to the fiber-PLA and fiber-MAPP-PLA bonding interface interactions. In fact, fiber pull-out can be found in the fractured cross-section of tested specimens (*e.g.*, Fig.2 b-f, 500×). As an exception, composites with 50 wt% fibers achieved both the highest strength (50.49 MPa) and Young's modulus (2.56 GPa), which may be due to the distribution of pulp fibers and the highest MAPP-to-PLA ratio.

The FE-SEM images show the gradually changed facture morphology of tensile specimens. Neat PLA polymer showed a smooth surface left by a brittle fracture behavior (Fig. 2a), which implies that the specimens were broken instantly. However, rougher breakage cross-sectional surfaces were produced with fiber fillers, which impeded the rapid flow of PLA macromolecular chains, demonstrating a stepwise failure mode (Fig. 2b-f). This load-bearing characteristics were mostly embodied for the composites with 50 wt% fibers. Thus, the addition of plant fibers was beneficial to improve the creep resistance and overcome the brittleness of the PLA polymer.

Table 1. Tensile Properties of Neat PLA and BSKP/PLA Composites*

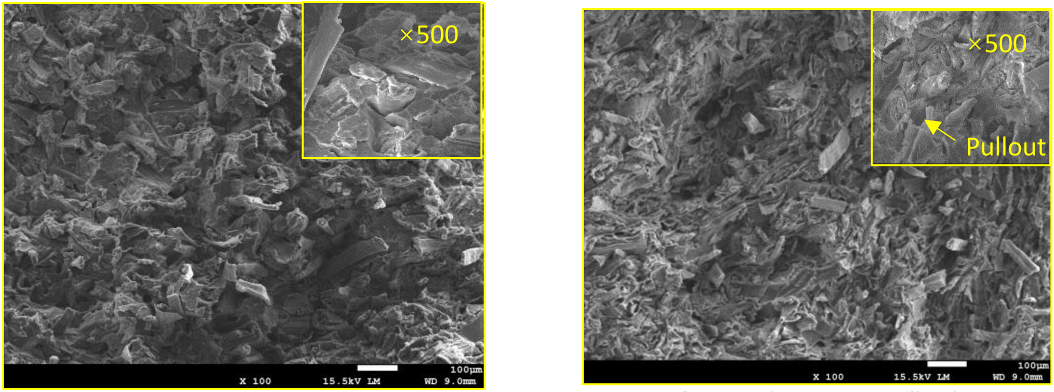
Sample No.	Tensile Strength (MPa)	Elongation at Break (%)	Young's Modulus (MPa)
IM-0(PLA)	49.94 (2.76)	7.40 (1.52)	1758.30 (46.44)
IM-1	42.22 (2.13)	6.90 (1.45)	1827.75(144.07)
IM-2	42.78 (0.77)	6.34 (0.17)	2010.46 (78.37)
IM-3	43.34 (1.72)	5.69 (0.31)	2202.52 (11.12)
IM-4	41.80 (0.35)	5.57 (0.40)	2394.29 (67.82)
IM-5	50.49 (0.83)	6.69 (0.88)	2563.22 (96.57)

* Data in parentheses are standard deviation values for five replications.



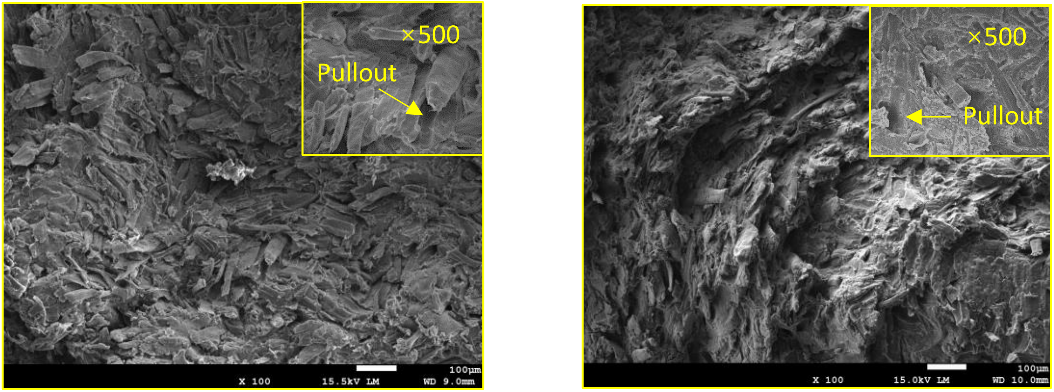
a. IM-0 (×100, neat PLA)

b. IM-1 (×100, 10%fiber)



c. IM-2 (×100, 20%fiber)

d. IM-3 (×100, 30%fiber)



e. IM-4 (×100, 40%fiber)

f. IM-5 (×100, 50%fiber)

Fig. 2. Micro morphology of BSKP fibers, MAPP coupling agent, and fractured surface morphology of PLA polymer and BSKP/PLA composites

Dynamic Mechanical Analysis

The viscoelastic behaviors of PLA polymer and BSKP/PLA composites were evaluated following programmed heating procedures (Fig. 3). The storage modulus (*E'*) of neat PLA decreased sharply from 58.5 to 81.5 °C with elevated temperature, which is attributed to the activated segment mobility of PLA close to the glass transition temperature T_g (Espinach *et al.* 2018; Singh *et al.* 2020a, b). Afterwards, *E'* recovered due to the cold crystallization of PLA polymer (Sharma *et al.* 2020). At the glass transition point, Tanδ reached a peak value of 0.34. Before the glass transition region, neat PLA showed a higher storage modulus than those with pulp fibers. With the increasing of heating temperature, composites with fiber added showed superior ability to maintain the storage modulus at a high level than pure PLA did. This indicates an important advantage of fiber fillers in helping to slow down the decreased storage modulus of composites during the heating process. Moreover, fiber-filled PLA composites showed earlier recovery behavior. Notably, the composites at higher fiber loadings had lower peak loss factor values, *i.e.*, fiber fillers weaken the damping performance of PLA polymer. This finding is in accordance with the enhanced tensile moduli or decreased elongation rates presented in Table 1. Therefore, other additives may be considered if PLA damping performance is required.

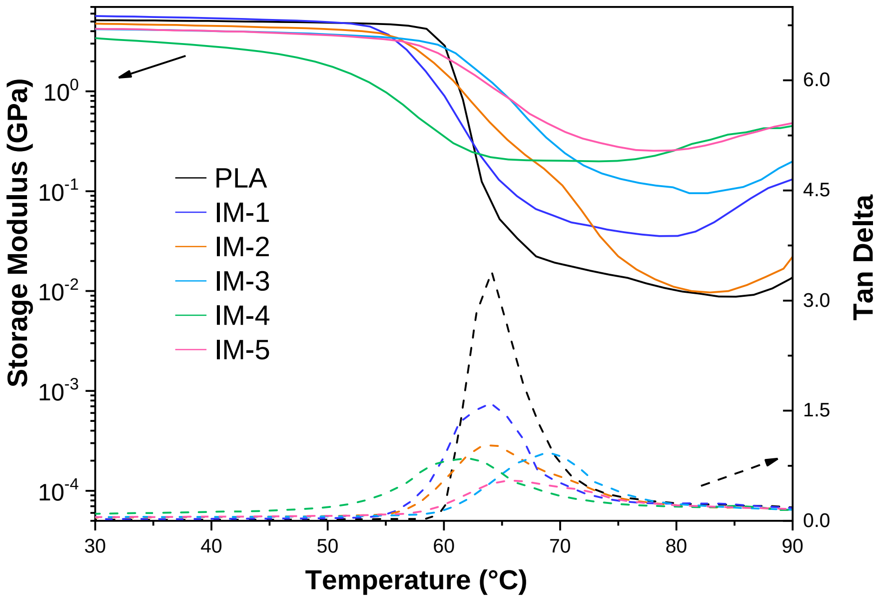


Fig. 3. Storage modulus and loss factor of BSKP/PLA composites at 1Hz

Crystallization Behavior Analysis

The DSC analysis characterizes the exothermic and endothermic behaviors of PLA and its composites during thermal transition process. Figure 4 shows typical characteristics of PLA polymer. Its calculated T_g, T_c, and T_m values were 58.2 °C, 102.6 °C, and 167.1 °C, respectively, which can be referred to in processing of PLA and its composites (Singh *et al.* 2020a,b). The T_g and T_m values of BSKP/PLA composites slightly changed compared with pure PLA, while their T_c values were visibly lower, indicating easy crystallization (Table 2). Similar heterogeneous nucleation behavior in other composites has been reported (Shojaeiarani and Hartman 2019; Zhao *et al.* 2019; Sharma *et al.* 2020). Interestingly, the cold crystallization enthalpy (ΔH_c) and melting enthalpy (ΔH_m) were clearly reduced when the content of BSKP was higher than 30 wt% in composites, demonstrating chain movement restriction and effects of fiber rigidly filling in PLA.

The BSKP content was positively correlated to crystallinity of composites regardless of melting processes. The uniform distribution of BSKP fillers is also conducive to the improvement of the crystallinity (Liu *et al.* 2014). Comprehensively, BSKP plays an important role in enhancing the stiffness of PLA. This effect can be attributed to the following reasons. BSKP limits the polymer segment mobility, and BSKP of excellent dispersion in PLA provides nucleating sites, improving the crystallinity of composites. Consistently, IM-5 sample had the highest crystallinity and reasonably the highest modulus.

Table 2. DSC Thermal Parameters of Neat PLA and BSKP/PLA Composites Derived from the Second Heating Scan

Sample	T_g (°C)	T_c (°C)	T_m (°C)	△H_c (J/g)	△H_m (J/g)	Crystallinity (%)
IM-0(PLA)	58.6	102.4	167.0	27.19	32.07	5.22
IM-1	58.3	97.9	166.7	22.86	28.95	6.50
IM-2	58.3	97.3	169.0	17.38	24.85	7.98
IM-3	60.1	95.8	166.7	17.88	26.23	8.92
IM-4	57.6	94.6	166.5	12.27	22.08	10.47
IM-5	59.2	90.1	167.1	5.23	16.33	11.86

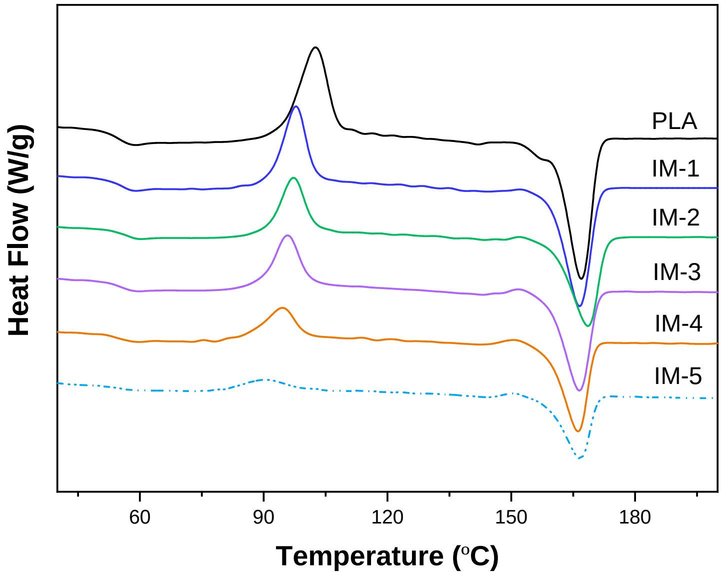


Fig. 4. DSC thermograms of PLA and BSKP/PLA composites

Thermal Decomposition and Thermal Stability

Table 3 and Fig. 5 evaluate the thermal stability of PLA and its BSKP-filled composites. Neat PLA had weight loss from 340 to 380 °C (*i.e.*, T_{onset}=343.5 °C; T_{max}=367.3 °C; and T_{endset}=379.8 °C), due to the thermal decomposition of molecular chains (Tao *et al.* 2017). BSKP/PLA composites presented similar thermal change behaviors, with slightly-decreased onset and peak temperatures. This result indicates that the addition of BSKP fibers did not adversely affect thermal stability of PLA polymers. However, the addition of BSKP fibers increased the content of charcoal residues, which may be sourced from the wrapping protection of fibers by PLA shells (Peng *et al.* 2013). This is crucial because the fibrous "bones" supply mechanical support for the whole composites. From this aspect, the addition of pulp fibers enhances the thermal stability of PLA composites.

Phanthong *et al*. (2016) reported the relationship between crystallinity and thermal stability of nanocellulose, saying that high crystallinity leads to high thermal stability. However, such a rule for unique nanocellulose fails to satisfy the BSKP/PLA composite materials, where multiple factors rather than the mere crystallinity of PLA co-determine the thermal stability, *e.g*., compositions, uneven dispersion of fibers, weak BSKP/PLA interfaces, and differential thermal characteristics of BSKP and PLA materials.

Table 3. Thermal Degradation Temperatures T_{max}, T_{onset}, and T_{endset} of PLA and BSKP/PLA Composites

Sample	T_{max} (ºC)	T_{onset} (ºC)	T_{endset} (ºC)
IM-0(PLA)	367.3	343.5	379.8
IM-1	359.8	339.5	375.9
IM-2	358.0	337.4	373.1
IM-3	357.8	337.0	372.3
IM-4	356.8	334.2	372.8
IM-5	354.1	331.4	369.9

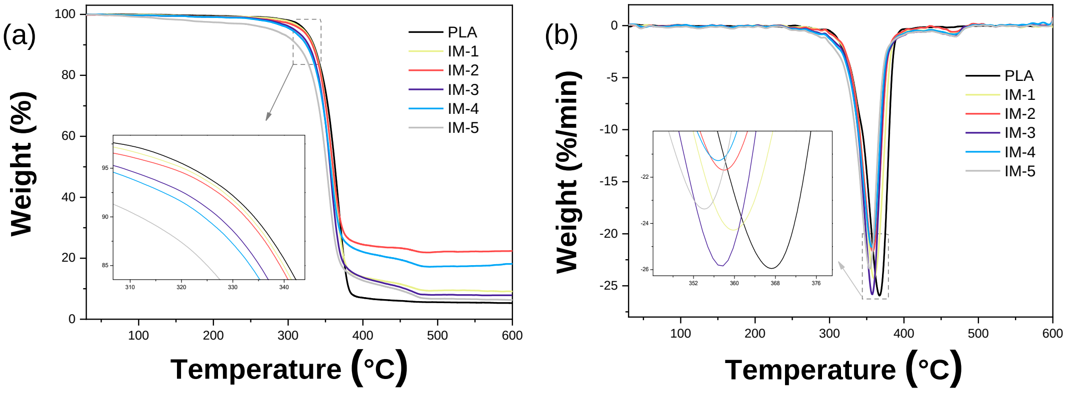


Fig. 5. TG(a) and DTG(b) analysis of PLA and BSKP/PLA composites

CONCLUSIONS

1. This study fabricated bleached softwood kraft pulp/poly(lactic acid) (BSKP/PLA) composites by internal mixing, resulting in good fiber distribution in the PLA matrix. BSKP fibers ensured the stepwise load-bearing mode of the composites, thus overcoming the brittleness of PLA polymer.

2. Fiber fillers stiffen the PLA polymer with improved crystallization and loss factor, thus weakening the damping performance of PLA composites.
3. The addition of pulp fibers enhances the thermal stability of PLA polymeric composites.
4. It is technically feasible and industrially expected to use pulp fibers to modify PLA for extended applications.

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