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► **To cite this version:**

Jingjing Liao, Nicolas Brosse, Antonio Pizzi, Sandrine Hoppe, Xiaojian Zhou, et al.. Characterization and 3D printability of poly (lactic acid)/acetylated tannin. *Industrial Crops and Products*, 2020, 149, pp.112320. 10.1016/j.indcrop.2020.112320 . hal-02508080

HAL Id: hal-02508080

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1 Characterization and 3D printability of poly (lactic acid)/acetylated tannin 2 composites

3 Jingjing LIAO^{a,b,c}, Nicolas BROSSE^{b*}, Antonio PIZZI^b, Sandrine HOPPE^c, Xiaojian ZHOU^{a*}, and Guanben
4 DU^a

5 ^a Key Laboratory for Forest Resources Conservation and Utilisation in the Southwest Mountains of China
6 (Southwest Forestry University), Ministry of Education, Kunming, 650224, PR China

7 ^b LERMAB, University of Lorraine, Boulevard des Aiguillettes BP 70239, 54506 Vandœuvre-lès-Nancy, France

8 ^c LRGP, University of Lorraine, 1, Rue Grandville, BP 451, 54001 Nancy Cedex, France

9 * Correspondence: nicolas.brosse@univ-lorraine.fr; xiaojianzhou@hotmail.com

10
11 **Abstract:** In this study, a three-dimensional (3D) printing filament prepared from
12 poly (lactic acid) (PLA) and acetylated tannin via a twin-screw extruder was reported.
13 The impact of acetylated tannin loading content on the final properties of the
14 resulting composite materials and their 3D printability were investigated. The
15 experimental results indicate that PLA can be compounded with up to 20 wt%
16 acetylated tannin without any obvious deterioration in the tensile property. The
17 resulting composites acquired better degradation rate in aquatic system compared
18 with neat PLA, especially in alkaline medium. Moreover, all composites are printable
19 and showed generally good printing quality with brown color, however, this is
20 limited to temperatures reasonably below 220°C to avoid printing defects, especially
21 at high loadings of acetylated tannin.

22
23 **Keywords:** poly (lactic acid), acetylated tannin, composite, degradation, 3D
24 printability

25 26 1. Introduction

27 Additive manufacturing, commonly known as three-dimensional (3D) printing, is a
28 promising manufacturing technology whose related numerous applications have been
29 explored in the fields like construction, manufacturing, healthcare and medicine, art and
30 fashion, food industry (Lee et al., 2017; Liu et al., 2019). With this technique, customized
31 complex and high-resolution three-dimensional parts can be rapidly built through

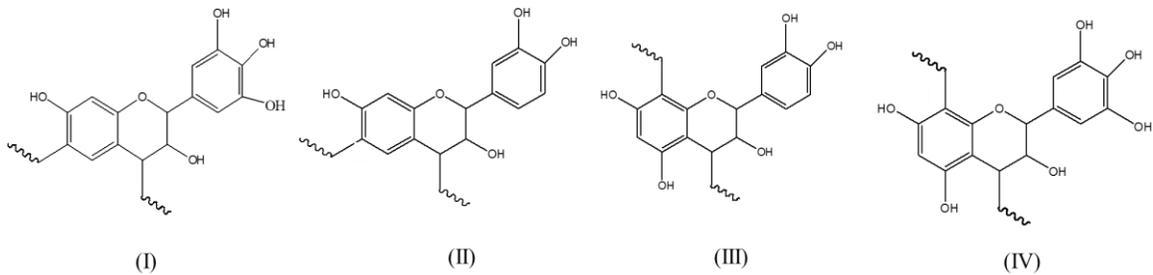
32 successive layer-by-layer deposition of materials like plastic, metal, ceramics, or living
33 cells (Tappa and Jammalamadaka, 2018). For producing thermoplastics prototype parts,
34 fused deposition modeling (FDM) or melt-extrusion 3D printing is the most widely used
35 additive manufacturing technique.

36 Polylactic acid (PLA) is one of the most popular 3D printing thermoplastic materials
37 due to its printability, favorable mechanical properties, and biocompatibility. It is an
38 renewable and biodegradable polyester that can be synthesized directly through
39 polycondensation of lactic acids or ring-opening polymerization of lactides (Ren, 2011).
40 PLA can be also incorporated with sustainable materials or biopolymers (e.g. wood
41 powder, plant fiber, cellulose, lignin, hemicellulose) for the purpose of reinforcing
42 and/or specific functions, and/or reducing cost. However, studies of these PLA-based
43 bio-composites as 3D printing materials are still limited (Bajpai et al., 2014; Basu et al.,
44 2017; Murariu and Dubois, 2016). Sustainable materials or biopolymers applied as 3D
45 printing feedstock are promising substitutes for fossil-based fillers due to their
46 sustainability, biodegradability, and cost-efficient characteristics. For instance, the
47 presence of wood powder in 3D printing, PLA filaments displays higher stiffness and less
48 abrasive properties compared to other composite filaments, such as carbon-fiber filled
49 PLA filaments and metal-filled PLA filaments (Guo et al., 2018). Fibers derived from
50 wood, bamboo, and cellulose were also investigated as feedstock for PLA-based
51 filaments because of their positive effects on the mechanical properties and heat
52 resistance of PLA matrix (LI et al., 2016; Long et al., 2019). Hemicellulose has been
53 investigated to partially replace PLA as feedstock material in 3D printing (Xu et al.,
54 2018). This combination makes use of the characteristics of hemicelluloses such as
55 biocompatibility, biodegradability, and presence of versatile active sites for biomedical
56 applications. PLA combined with lignin has attracting characteristics such as antioxidant,
57 antifungal and antimicrobial capacities, resistance to UV-radiation, and fire-retardant
58 properties (Kai et al., 2016). One example was reported to study PLA/lignin composites
59 for 3D printing (Gkartzou et al., 2017). However, the lignin aggregation and its low
60 compatibility with PLA matrix caused imperfect printed objects and surface roughness,

61 even at low loading content (5 wt%). According to the published literature as yet, it
62 appears that the dispersion and distribution of fillers are key factors for processing 3D
63 printing materials (Nguyen et al., 2018).

64 Condensed tannins are interesting abundant and sustainable biopolymers for 3D
65 printing, however, there is no related research work about their applications in the field
66 of 3D printing to date. Condensed tannins are mainly composed of flavonoid units in
67 varying degrees of condensation (**Erreur ! Source du renvoi introuvable.**) and they can
68 be easily extracted from soft tissues of woody plants like leaves, needles, and bark using
69 water or organic solvent (Pizzi, 1980). They display great potential as component of PLA
70 bio-composites due to some interesting characteristics like antioxidant (Koleckar et al.,
71 2008), antimicrobial (Ge et al., 2003) and stabilizing properties (Liao et al., 2019; Olejar
72 et al., 2016; Tomak et al., 2018). Over the past few years, tannins have been
73 investigated as functional additives or at least a component of polymeric composites.
74 For instance, tannins have been reported as stabilizing additive with antioxidant and UV-
75 protective properties on polypropylene (Ambrogi et al., 2011; Samper et al., 2013),
76 polyethylene (Bridson et al., 2015), poly(vinylchloride) (PVC) (Shnawa et al., 2015), and
77 polyvinyl alcohol (Zhai et al., 2018). Anwer reported a native tannin as a filling
78 component of PLA composite material (Anwer et al., 2015), where poor adhesion
79 between tannin and PLA matrix as well as dispersion of tannin in PLA were found,
80 thereby, poor tensile strength was noticed even at higher filler content (15%).
81 Modifications of tannins, like esterification and hydroxypropylation, have been proved
82 to enhance the compatibility and dispersion capacity to various plastics (D. E. García et
83 al., 2015; Gaugler et al., 2007; Grigsby et al., 2014, 2015, 2013; Grigsby and Kadla, 2014).
84 Grigsby and co-workers (Grigsby et al., 2015) modified tannin with ester-bearing long
85 chain, which lowered the melting temperature and claimed this could significantly
86 reduce the incompatibility with PLA matrix, leading meanwhile to easier processability.
87 However, the substitution of higher chain length on tannin flavonoid units becomes
88 progressively more difficult due to the elevated steric hindrance. In another extended
89 study, Grigsby carried out a high loading content of esterified tannin (50%) as

90 reinforcing material for PLA fine fiber processed via melt spinning in the presence of
91 transesterification catalyst (Grigsby and Kadla, 2014). This successful incorporation of
92 esterified tannin onto PLA indicated the possibility to process esterified tannin filled PLA
93 filaments for 3D printing. Esterification can reduce the hydrophilicity of tannin, reducing
94 the clogging at the printing nozzle and discontinuous layer deposition during printing
95 process due to good dispersion and distribution of tannin onto the polymer matrix.



96

97

Figure 1. Structure of four main flavonoid units of condensed tannins

98 The present study will focus on developing a new approach to utilize condensed
99 tannin obtained from mimosa wood barks for partial replacement of PLA in 3D printing
100 parts and investigate the feasibility of melt-extrusion 3D printing. For this purpose,
101 mimosa tannin was acetylated to decrease its initial hydrophilicity. Such treatment has
102 been proven to enhance the compatibility of tannin and thermoplastic polymeric
103 matrixes without severe agglomeration (Gaugler et al., 2007; Grigsby et al., 2013). The
104 composite was processed in a twin-screw extruder and the impact of the loading level of
105 acetylated tannin (AT) on the final properties of the resulting composite materials was
106 evaluated in terms of the tensile property, the changes in crystallization, thermal
107 degradation, changes in color, and degradation rate in aquatic system. Besides, the
108 feasibility of melt-extrusion 3D printing of PLA/AT composite was also investigated.

109 2. Materials and Methods

110 2.1. Materials

111 PLA trademarked under the name Ingeo™ Biopolymer (Grade 3D850) with a melt
112 flow index of 7-9 g/10min was obtained from Nature works LLC (Minnesota, USA).
113 Mimosa tannins were purchased from Silva Chimica, Mondovi, Italy. Acetic anhydride

114 used to acetylate tannin and pyridine, a catalyst for tannin acetylation, were supplied
115 from Sigma-Aldrich and Acros-Organics, respectively. Three buffers purchased from
116 Sigma-Aldrich were used for degradation tests, including phosphate buffer (pH=4.0),
117 sodium carbonate buffer (pH=10.0), and phosphate Buffered Saline (PBS, pH=7.4).

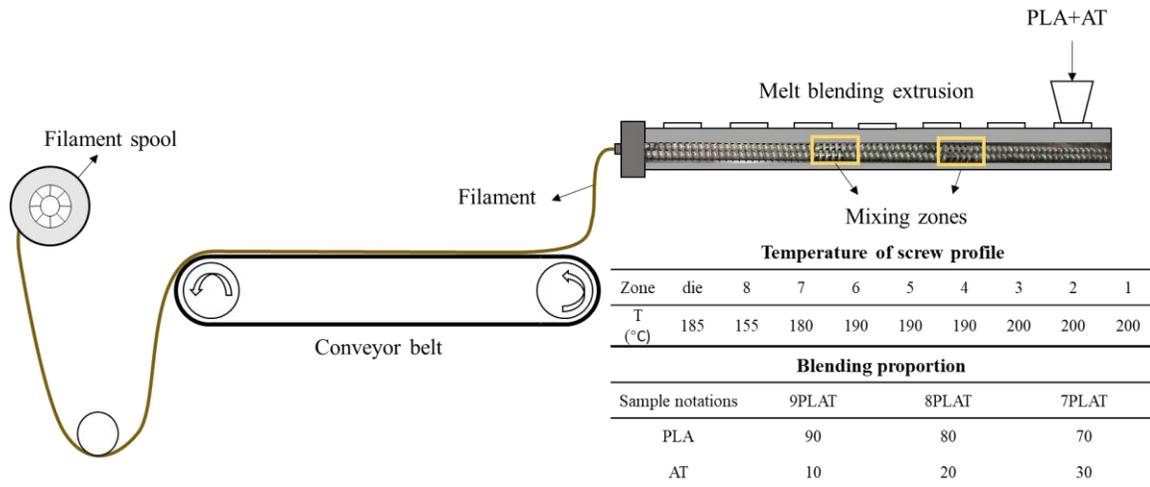
118 **2.2. Preparation of PLA/AT Composites**

119 2.2.1. Tannin acetylation

120 Acetylation of mimosa tannin was described elsewhere by using acetic anhydride
121 and pyridine as catalyst (Nicollin et al., 2013). Mimosa tannin was mixed with acetic
122 anhydride in a weight ratio of 1:5 with 1 wt% pyridine (based on tannin) as catalyst in a
123 round bottom flask fitted with a condenser. The mixture was heated to 60°C under
124 stirring for 6 h. After the acetylation is achieved, the suspension was precipitated in iced
125 water and centrifuged to recover the acetylated tannin powder, which was washed 5
126 times with distilled water and finally air-dried at room temperature for several days.

127 2.2.2. Composite filament preparation

128 PLA was ground into powder by a grinder to ensure simplistic mixing with tannin.
129 Then, PLA and acetylated tannin (AT) powder were dried in an oven at 80°C for more
130 than 12 h to remove any absorbed water on the surface. A twin-screw extruder (Thermo
131 Scientific™ Process 11, Villebon-Sur-Yvette, France) was used to blend PLA powder and
132 AT. Two mixing zones of screw profile can guarantee high level of homogeneous
133 dispersion of AT in PLA. The temperature of the heating zones and the die along the
134 extruder barrel ranged are shown in Figure 2. The filaments were extruded through melt
135 blending extrusion with a rotation rate of 80 rpm via a nozzle diameter of 4 mm. A
136 filament with a diameter of 1.75 ± 0.1 mm was obtained by controlling the speed of
137 spool rotation and conveyer belts then the 3D printable filaments were collected by a
138 spool.



139

140

141 *Figure 2. Composite filaments preparation via melt blending extrusion: the tables show the*
 142 *parameters of screw profile and blending components proportions*

143 2.2.3. 3D printing process

144 An open-source 3D printer named Mondrian 3.0 was used to print scaffold (20.1 ×
 145 20.1 × 3 mm) and standard dog bones (ISO 527, type 1A) using PLA/AT filaments at
 146 190°C. Abundant of filament was needed to construct dog bone specimen, thus, we
 147 prepared only one dog bone specimen due to the limited filament amounts. The
 148 scaffolds were printed using PLA and PLA/AT composite filaments under three printing
 149 temperature (180°C, 200°C, 220°C). The used printing parameters are shown in Table 1.
 150 The scaffold and dog bone were designed by using a Slic3r program and printing process
 151 were controlled by Pronterface software.

152

Table 1. 3D printing parameters

Printing temperature	180 - 220°C
Layer height	0.2 mm
Infill density	100%
Infill pattern	linear
Layer angle	45°
Printing speed	12 mm/s

153 2.3. Characterizations

154 The acetylation of tannin was confirmed by NICOLET 6700 FT-IR spectrometer in
155 attenuated total reflection (ATR) mode with a resolution of 4 cm^{-1} and a total of 16
156 scans in the range $400\text{-}4000\text{ cm}^{-1}$.

157 Instron tensile testing machine (model 5569, Norwood, MA, USA) equipped with a
158 50 kN load cell was used for tensile strength tests with a cross-head speed 1 mm/min
159 according to EN ISO 527:1996. The whole testing process was performed at room
160 temperature and each sample has four repetitions. The tested dog-bone shaped
161 specimens (ISO 527, type 1A) were previously molded with a micro-injection molder
162 (Micro 15, DSM Xplore, Sittard, Netherlands).

163 A scanning electron microscopy (SEM, JSM-6490LV, Tokyo, JAPAN) with an
164 acceleration voltage of 5 kV was applied to observe the morphology of a 3D printed
165 scaffold. The scaffolds were sputter-coated with a thin layer of carbon before scanning.

166 A study on the thermal characteristics, in terms of the melting temperature (T_m) and
167 crystallization temperature (T_c), was undertaken under a nitrogen flow of 50 mL/min by
168 using a METTLER TOLEDO differential scanning calorimeter (DSC). A scanning rate of
169 10°C/min within the temperature range of 30°C to 220°C and 220°C to -10°C in the
170 second scanning cycle was carried out. The measurements were conducted using
171 aluminum crucibles with a total sample weight of $5.00 \pm 1\text{ mg}$. The values for melting
172 temperatures (T_m), enthalpies of melting (ΔH_m) and crystallization (ΔH_c) were analyzed
173 using STARe software. ΔH_m^0 is the enthalpy of melting for 100% crystallized PLA, which is
174 equal to 93.7 J/g (Yamoum et al., 2017), and w is the weight fraction of PLA. The
175 crystallization percentage (X_c %) was estimated using the following equation:

$$X_c (\%) = \frac{\Delta H_m - \Delta H_c}{\Delta H_m^0 \times w} \times 100\% \quad (1)$$

176 The degradation behavior of AT-filled PLA was characterized with the help of a
177 thermogravimetric analyzer (TGA, METTLER TOLEDO, Columbus, Ohio, USA) under air

178 flow of 50 mL/min from 30 to 600°C. The heating rate was controlled at 10°C/min and
179 the weight of each sample was 5-10 mg.

180 **Color measurements.** PLA is a colorless and transparent polymer, thus, it generally
181 colorize with dyes (Hussain et al., 2015; Scheyer and Chiweshe, 2001). Tannin can
182 colorize PLA filaments due to its brown nature, which is a good feature for 3D printed
183 parts. The coloration of PLA filaments with acetylated tannin was investigated by a
184 spectrophotometer (X-rite, model 5P60, Regensdorf, Switzerland) based on the
185 international commission on illumination (CIE) system. Three parameters L*, a* and b*
186 were used to evaluate the colors of filaments, respectively. L* represents the scale of
187 lightness, the value of 0-100 refers to perfect black to white. The value of a* and b*
188 stands for the color of the red-green and the yellow-blue character, respectively, in
189 which positive values represent redness or yellowness while negative values indicate
190 greenness and blueness (Lai So et al., 2014).

191 **Water absorption.** The hydrophobicity of the filaments was characterized by
192 measuring their level of water absorption (Figueira et al., 2017). Each filament was cut
193 into a length of 70 ± 1 mm and submerged into 50 mL of distilled water in a plastic tube
194 for 30 days at room temperature. Before submerging the tested filaments into the
195 water, the filaments were vacuum-dried for 6 h at 80°C and then measured the dried
196 weight (W_0). After 30 days, the specimens were taken out from water and wiped using
197 filter paper. Then the weight was recorded as W_1 . The water uptake of PLA filaments
198 and AT-filled filaments was calculated according to the following equation:

$$\text{Water absorption (\%)} = \frac{|W_1 - W_0|}{W_0} \times 100 \quad (2)$$

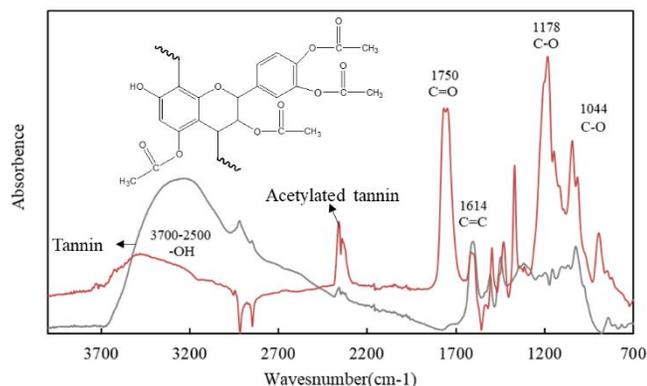
199 **Immersion in solvent.** In order to understand the degradation of PLA/AT composites
200 in aquatic system, printed specimens of dimensions $2.5 \times 30 \times 2$ mm were immersed in
201 buffer solutions (pH=4, pH=10) and PBS solution (pH 7.4) at 40°C for 50 days in an oven.
202 The initial weight (W_0) of each specimen was recorded before soaking into the solvent in
203 glass tube containing 50 mL buffer solution. After 50 days, the samples were removed
204 from the tubes and washed 3 times with distilled water prior to final dry in oven at 40 °C

205 for 12 h. The weight of each specimen was denoted as W_1 . The weight loss was
206 calculated based on the equation (2).

207 3. Results and discussion

208 3.1. Characterization of acetylated tannin

209 The hydrophilic characteristic of tannin render it incompatible with hydrophobic or
210 semi-hydrophobic polymers. This necessitates the modification of tannin for solving this
211 problem. Tannin acetylation was suggested to develop reasonable miscibility with PLA
212 (Grigsby and Kadla, 2014). Figure 3 presents the FTIR spectra of tannin and tannin after
213 being acetylated. The spectrum of tannin reveals a broad band centered at 3250 cm^{-1}
214 and can be ascribed to -OH stretching vibrations while the peak at 1614 cm^{-1} refers to
215 aromatic ring stretching vibration. This latter signal corresponding to a function
216 unaffected by the acetylation reaction which can be considered as an invariant band.
217 Compared to the band at 1614 cm^{-1} , the sharp decrease of the -OH and emergence of a
218 new strong one at 1750 cm^{-1} , which is typical of C=O stretching, representing ester
219 functional group, proves that the acetylation process was undertaken effectively (Luo et
220 al., 2010). Besides, the increased absorption at 1178 cm^{-1} and 1044 cm^{-1} , ascribed to C-O
221 stretching, is also in accordance with the structure of acetylated tannin (Smith, 2018;
222 Vila et al., 2016).



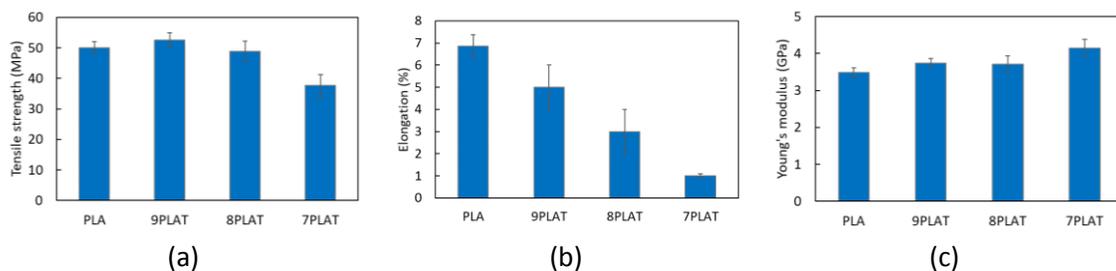
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Figure 3. FTIR spectra of tannin and acetylated tannin

225 3.2. Mechanical properties of PLA/AT composites

226 The mechanical properties of PLA and PLA/AT composites are given in Figure 4.
227 Tensile strength of composite materials generally relies on the stress transfer capacity
228 between fillers and polymer matrix, which is significantly affected by the interfacial
229 adhesion of particle and matrix, particle size, as well as particle distribution (Fu et al.,
230 2008). The dispersion of AT into a thermoplastic polymer without severe agglomeration
231 has been previously achieved by enhancement of the hydrophobic character of tannin
232 (Gaugler et al., 2007; Grigsby et al., 2013). Therefore, unlike native tannin-filled PLA
233 (Anwer et al., 2015), PLA incorporated with 10% and 20% AT did not exhibit significant
234 effects on tensile strength of the resulting composites (Figure 4, a). While PLA
235 incorporated with 30% AT encountered a decrease of tensile strength because higher
236 biopolymer content generally caused filler agglomeration during melt blending process
237 could result in poor particle distribution. Besides, higher loading of AT increases its
238 interfacial area with PLA, which worsens the situation especially in absence of interfacial
239 adhesion due to lack of virtual chemical bonds between AT and PLA. A lower elongation
240 at break was noticed for PLA/AT composites compared with the neat PLA (Figure 4, b),
241 which again highlights the fact that the acetyl part as a modifying agent for tannin does
242 not possess any plasticizing effect to balance the developed interfacial adhesion as a
243 result of acetylation, which causes premature failure. In Figure 4 (c), Young's moduli
244 increased as a function of AT loading since the filling component restricts the molecular
245 mobility of the polymeric chain yielding a better static adhesion (Wacker et al., 1998). A
246 similar result was previously noted for lignin-filled PLA system (Spiridon et al., 2015; Vila
247 et al., 2016).



248 *Figure 4. Tensile parameters of PLA/AT composites: tensile strength (a), elongation (b) and*
249 *Young's modulus (c)*

250 **3.3. Differential scanning calorimeter**

251 DSC was performed in order to detect the glass transition, crystallization and melting
252 temperatures of PLA and PLA/AT composites. DSC thermograms of PLA and PLA
253 incorporated with various contents of AT are shown in Figure 5 and the results from the
254 second heating and first cooling cycles are collected in Table 2. The incorporation of AT
255 showed no significant effect on the melting (T_m) and the glass transition (T_g)
256 temperatures, are consistent with prior studies (Anwer et al., 2015; Grigsby et al., 2014;
257 Grigsby and Kadla, 2014). This means AT has little influence on intermolecular
258 interactions or chain flexibility of PLA polymer chains (Müller et al., 2014). While the
259 enhancement of T_c refers to the composite filaments are more difficult to undergo cold
260 crystallization in comparison with pure PLA filaments and so require higher
261 temperatures (Dong et al., 2017). As can be found in Table 2, the crystallinity of PLA/AT
262 composites` is gradually decreasing with a corresponding decrease in the enthalpy of
263 crystallization as a function of AT content. Therefore, the PLA/AT composites became
264 too amorphous to be more liable to undergo higher degradation rates. This feature
265 most likely benefits to the short-term application like implantable devices in biomedical
266 applications (Lyu and Untereker, 2009) since the degradation of PLA occurs during a
267 generally long period (Karamanlioglu et al., 2017; Tokiwa and Calabia, 2006).

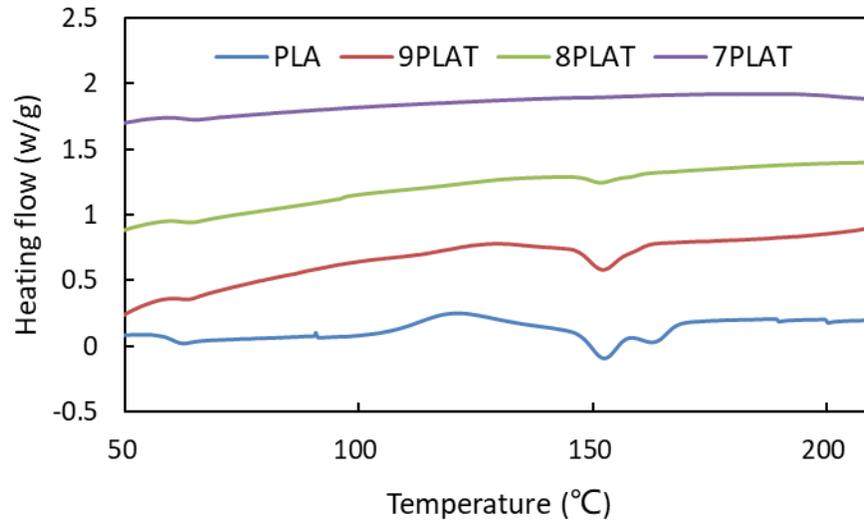


Figure 5. DSC thermograms of PLA and PLA/AT composites

Table 2. DSC results of PLA and PLA/AT composites

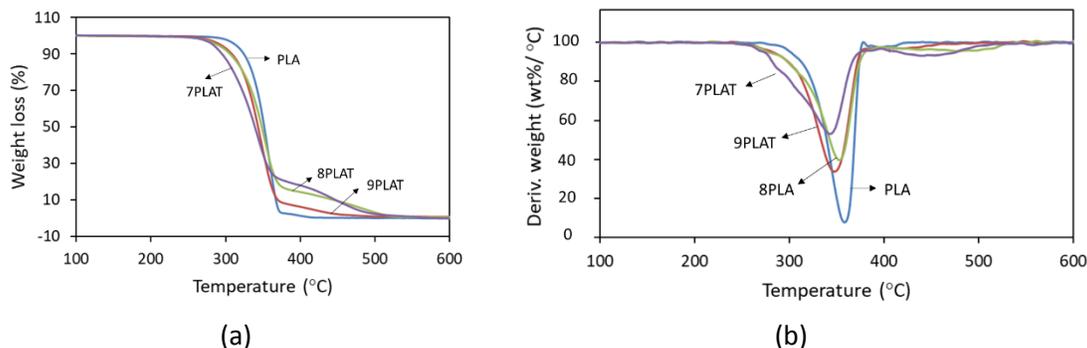
Sample	T_g (°C)	ΔH_c (J/g)	T_c (°C)	ΔH_m (J/g)	T_m (°C)	X_c (%)
PLA	56.7	14.2	120.2	20.4	152.5	6.6
9PLAT	56.3	4.23	127.5	10.9	152.6	7.9
8PLAT	56.8	0.78	129.4	3.01	151.9	3.0
7PLAT	58.6	0.26	129.7	0.06	151.1	--

Note: "--" means that no crystallization percentage.

3.4. Thermogravimetric analysis

The thermal behavior of PLA and PLA/AT composites was studied via thermogravimetric analysis under air atmosphere. The weight loss and DTG data are plotted in Figure 6 as a function of temperature. Each sample sharply degraded in a one-step process started at 250°C and continued to 370°C, which is also corroborated from the single peak in the DTG profile. The results demonstrated additionally that the incorporation of AT into to PLA matrix resulted in a decrease of the thermal stability, presumably due to the drop in crystallinity (see Table 2). This observation is generally found in PLA biocomposites (Boruvka et al., 2019; Grigsby et al., 2014; Zhang et al.,

282 2017). The onset of degradation for all PLA/AT composites was very close to pristine
283 PLA (250°C) while the major decomposition took place at 350°C. Consequently, a
284 printing temperature below 250°C is considered suitable for PLA/AT composites and no
285 decomposition should be undertaken under these conditions.



286 *Figure 6. Thermal gravimetric traces of PLA and PLA/AT composites (a) and their relevant DTG*
287 *curves (b).*

288 3.5. Water absorption and degradation in solvent

289 PLA is a well-known degradable polymer, however, the total degradation of PLA into
290 carbon dioxide, water, and methane in the environment generally lasts from several
291 months to two years (Karamanlioglu et al., 2017). Moisture easily results in the
292 hydrolyzation of PLA, therefore, water absorption capacity has been considered as an
293 important factor to the degradability of PLA (Yew et al., 2005) when exposed to humid
294 atmosphere. Degradation behavior of material in different pH condition is an important
295 characteristic for many applications.

296 As presented in Figure 7 (a), PLA/AT composites exhibited a higher water absorption
297 compared with the neat PLA, which may result from the decrease of crystallinity. The
298 water absorption is related to its rate of diffusion into the composites and responsible
299 for faster degradation of PLA/AT composites in various aqueous solutions (Figure 7, b).
300 This characteristic is positive for medical applications because the PLA-based implants
301 are firstly hydrolyzed in vivo by body fluids after absorbing water, which causes the
302 breaking of the ester bonds (Yew et al., 2005). In this study, the phosphate-buffered
303 saline (PBS) solution (pH=7.4) was used to represent the body fluids in neutral

304 conditions, while phosphate buffer (pH=4.0) and sodium carbonate buffer (pH=10) are
 305 applied to investigate the degradation of composite material in acidic and basic
 306 conditions. All tested samples in aqueous environments exhibited higher degradation
 307 rate with increasing the AT content. The faster degradation that appeared in strongly
 308 basic condition is the easier random ester cleavage, whereas, under acidic conditions, it
 309 proceeds via chain-end cleavage, which is more time-consuming (Elsawy et al., 2017).

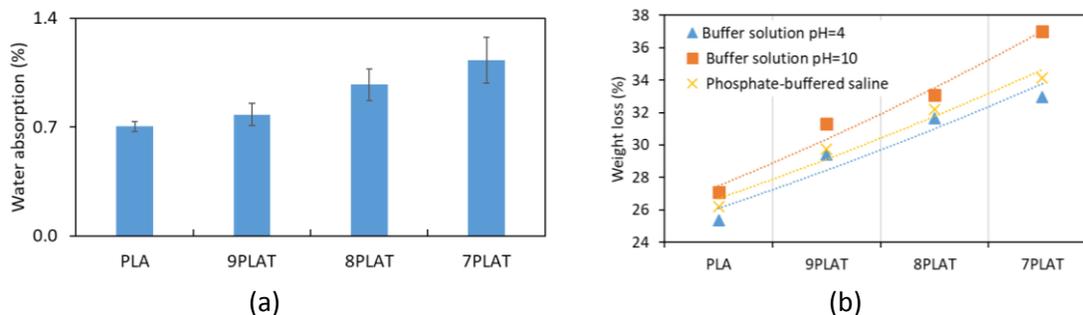


Figure 7. Water absorption of PLA with various AT contents over 30 days(a) and degradation in different solvent media over 50 days (b).

310 3.6. PLA/AT composites for 3D printing application

311 Color is an important appearance factor for 3D printing products. As can be seen
 312 from Table 3, PLA is a colorless transmitting polymer. The combination of PLA with dyes
 313 for producing vibrant colors is necessary for commercial applications (Scheyer and
 314 Chiweshe, 2001). From the optical image of the filaments (Table 3), PLA/AT composites
 315 displayed brown colors and lost transmitting characteristic. These composites had lower
 316 L* value which translates into a decrease of lightness. When PLA was compounded with
 317 more AT, an increasing trend was observed from the increasing a* and b* values,
 318 exhibiting more green hue and blue hue, respectively. Therefore, PLA/AT composites
 319 could be promising colored filaments for 3D printing products.

Table 3. Color measurements of PLA and PLA/AT composite

sample	Image of PLA and PLA/AT composites	L*	a*	b*
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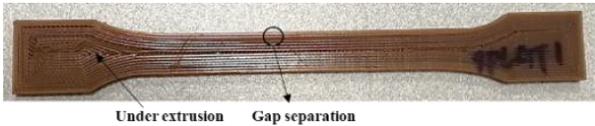
PLA		70.93	+0.91	+5.43
9PLAT		28.07	+7.91	+7.80
8PLAT		29.77	+9.09	+10.05
7PLAT		31.42	+10.22	+8.41

321 The model of dog bone specimens for tensile testing was used to evaluate the
322 printability of PLA/AT composites, the printed specimens and their tensile strength
323 results are collected in Table 4. The digital images of printed PLA/AT composites

324 revealed that the specimens exhibited some defects during printing, either under-
 325 extrusions or in fill and outline separations. These printed issues are not only due to the
 326 setting of the printing parameter but also may be caused by the imperfect dispersion
 327 and agglomeration of the filler (Filgueira et al., 2017). Imperfect printing is commonly
 328 found in composite materials given that the presence of fillers in polymeric matrixes
 329 change their characteristics and consequently affect their printability (Nguyen et al.,
 330 2018). Therefore, a correlation between the features of printing process with the AT-
 331 filled composite filaments is a key factor to obtain qualified printed objects. This issue
 332 will be considered more intensively in our future work.

333 The materials derived from the melt-extrusion 3D printing process commonly
 334 showed a lower tensile strength compared to comparable specimens obtained by
 335 traditional manufacturing methods (Cruz Sanchez et al., 2017). The relatively higher
 336 porosity of the dog bones caused during 3D printing may probably justify this finding
 337 (Filgueira et al., 2017). Another possible reason could be related to the poor interlayer
 338 adhesion of the printed specimens because the mechanical properties of printed part
 339 depends on the interlayer adhesion (Bakrani Balani et al., 2019). As a whole, the
 340 strength of printed specimen was very close to that processed by traditional
 341 manufacturing methods (Figure 4).

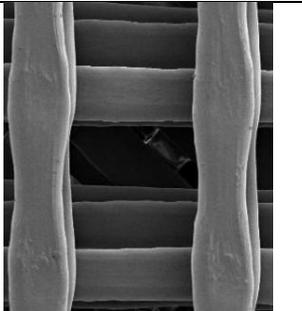
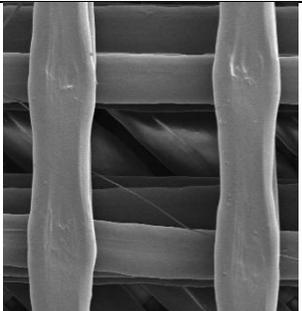
342 *Table 4. Printed dog bone specimens and their tensile parameters*

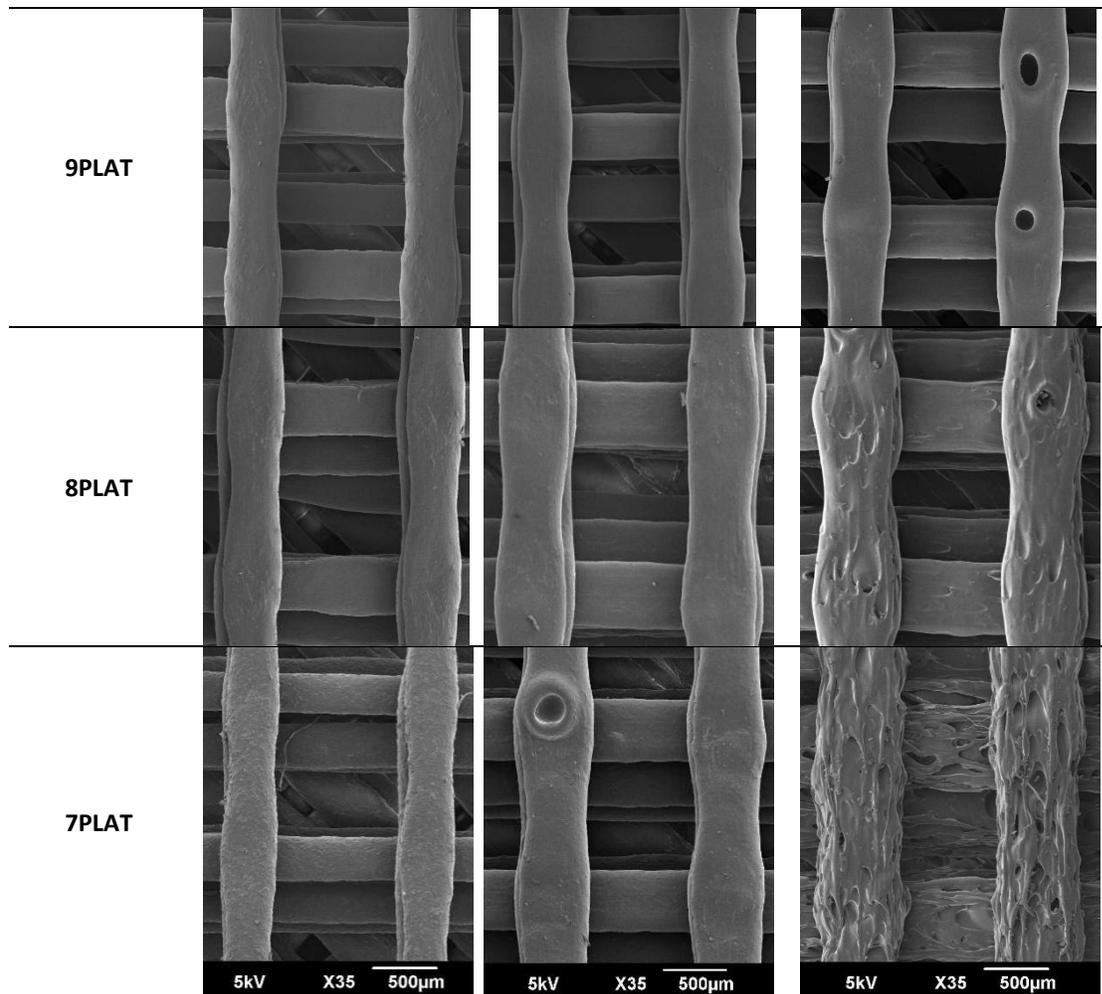
specimen	Image	Young's modulus GPa	Tensile strength MPa
PLA		2.6	27
9PLAT		2.1	26
7PLAT		2.9	31

343 For a specific material, the temperature is one of the most important parameters to
 344 control the shear viscosity and flow rate for offering successive layer deposition. The
 345 dimensional stability of each printed layer depends on the rapid solidification capacity
 346 via improved heat dissipation (Nguyen et al., 2018). Thus, the temperature should be
 347 carefully selected for validating the balance between flowability and solidification. For
 348 this purpose, the effects of temperature on the printability of PLA/AT composites and
 349 morphology of printed specimens were investigated by printing a scaffold prototype.

350 SEM images of the printed scaffolds at different temperatures are displayed in Table
 351 5. Filaments made from PLA/AT composites are printable at a temperature range from
 352 180 to 220°C. However, the surface morphology was mostly affected especially at higher
 353 temperatures. It is worth to notice that both lower and higher printing temperatures
 354 result in unsatisfying faults on the surface, namely, high roughness and phase
 355 separation, respectively, when PLA incorporated with a higher AT content (e.g. 7PLAT).
 356 This highlights a strong correlation between high AT loading in the filaments and the
 357 sensitivity to encounter phase separation at high temperatures. Similar results were
 358 found for a system based on hemicellulose-filled filaments (Xu et al., 2018). The
 359 unsuccessful printing of PLA scaffold at 180°C is referred to the failure of the first layer
 360 that should be stuck to the building platform. This might due to the fast cooling of
 361 extruded PLA before bonding to the building platform or to the poor flowability of PLA
 362 at 180°C. In other words, the addition of AT reduced the melting viscosity of PLA
 363 polymer (rheology behavior data in supplementary material, Figure S1), thus improved
 364 the printability even at low temperature.

365 *Table 5. SEM images of printed scaffolds at different 3D printing temperatures*

Temperature	180°C	200°C	220°C
PLA	Failed to print the scaffold.		



366 **4. Conclusions**

367 This study investigated the properties and 3D printability of a composite made from
 368 PLA and acetylated tannin. The acetylation of tannin contributed to its well dispersion
 369 within PLA matrix, guaranteeing successful fabrication of PLA/AT composite filaments
 370 via a twin-screw extruder. PLA incorporated with 20 wt% acetylated tannin did not
 371 significantly encounter deterioration in tensile property of the final product. Meanwhile,
 372 the incorporation of various AT contents caused no significant effect on the melting and
 373 glass transition temperatures of PLA because it has little influence on intermolecular
 374 interactions or chain flexibility of PLA polymer chain. A decrease of crystallinity was
 375 found in PLA/AT composites, resulting in higher rates of degradation in aquatic system
 376 especially under alkaline conditions, which would definitely benefit in short-term
 377 applications like implantable devices in biomedical field. A 3D printing temperature

378 below 250°C is suggested for safe processing of PLA/AT composites without
379 encountering decomposition according to the data of thermogravimetric analysis.
380 Although PLA systems loaded with acetylated tannin showed good printability in
381 general, this is limited to temperatures reasonably below 220°C to avoid printing defects
382 caused by phase separation and aggregation of acetylated tannin, especially at high
383 loading content.

384

385 **Author contributions**

386 The manuscript was written through contributions of all authors. All authors have
387 given approval to the final version of the manuscript.

388

389 **Conflict of interest**

390 The authors declared that they have no conflicts of interest.

391 **Acknowledgement**

392 This work was supported by the National Natural Science Foundation of China
393 (NSFC 31760187, 31971595); Natural Science Foundation of Yunnan (2017FB060); and
394 the Yunnan provincial youth and middle-age reserve talents of academic and technical
395 leaders (2019HB026). LERMAB is supported by the French National Research Agency
396 through the Laboratory of Excellence ARBRE (ANR-12-LABXARBRE-01). Pascal
397 Xanthopoulos and Polybridge® are thanked for the fruitful discussions. Financial support
398 from China Scholarship Council is gratefully acknowledged. The authors also thank
399 Richard Laine for precious technical support.

400

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