

Interfacial improvement of poly (lactic acid)/tannin acetate composites via radical initiated polymerization

Jingjing Liao, Nicolas Brosse, Sandrine Hoppe, Xiaojian Zhou, Xuedong Xi,

Guanben Du, Antonio Pizzi

▶ To cite this version:

Jingjing Liao, Nicolas Brosse, Sandrine Hoppe, Xiaojian Zhou, Xuedong Xi, et al.. Interfacial improvement of poly (lactic acid)/tannin acetate composites via radical initiated polymerization. Industrial Crops and Products, 2021, 159, pp.113068. 10.1016/j.indcrop.2020.113068. hal-03032164

HAL Id: hal-03032164 https://hal.univ-lorraine.fr/hal-03032164

Submitted on 21 Nov 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial 4.0 International License

Interfacial improvement of poly (lactic acid)/tannin acetate composites via radical initiated polymerization

Jingjing LIAO ^{1,2,3,4}, Nicolas BROSSE ^{3,*}, Sandrine HOPPE ⁴, Xiaojian ZHOU ^{1,*}, Xuedong XI ³,
 Guanben DU ^{1,2,*}, Antonio PIZZI ³

¹ Yunnan Provincial Key Laboratory of Wood Adhesives and Glued Products, Southwest Forestry
 University, Kunming 650224, Yunnan, P. R. China

7 ² College of Materials Science and Technology, Beijing Forestry University, 35 Tsinghua East Road.

8 Haidian District, Beijing, 100083, P. R. China

9 ³ LERMAB, University of Lorraine, Boulevard des Aiguillettes BP 70239,54506 Vandœuvre-lès-Nancy,
 10 France ;

11 ⁴ LRGP, University of Lorraine, 1, Rue Grandville, BP 451, 54001 Nancy Cedex, France;

* Correspondences: xiaojianzhou@hotmail.com (X. Zhou); gongben9@hotmail.com (G. Du);
 nicolas.brosse@univ-lorraine.fr (N. Brosse).

14

Abstract: A wholly bio-composite based on poly (lactic acid) (PLA) and tannin 15 acetate was successfully prepared via in situ reactive extrusion using dicumyl 16 peroxide (DCP) to improve interfacial adhesion. The composites based on PLA and 17 tannin acetate with high acetylation degree exhibited increased molecular weight as 18 compared with reactive extruded PLA, together with the improvement of Young's 19 modulus and tensile strength. The rheology results showed that reactive extruded 20 PLA/tannin acetate composites exhibited increased complex viscosity and modulus 21 storage, indicating the strong interfacial adhesion of PLA and tannin acetate. Besides, 22 23 Glass transition temperature, thermal stability, and crystallinity degree were all enhanced as a result of better interaction by radical initiated polymerization. From 24 25 contact angle data, free radical extruded composites had a more hydrophobic characteristic compared with PLA, which might be interesting for food packaging 26 application. This approach opens up a pathway to diversify the applications of tannin 27 as a component for bio-composite preparation. 28

Keywords: poly (lactic acid); tannin acetate; peroxide; reactive extrusion; bio composite

31

32 **1. Introduction**

33 Biodegradable polymers from renewable resources have been attracted great interests in past years driven by the depletion of non-renewable petroleum resources and 34 accumulation of non-degradable plastics. Poly (lactic acid) (PLA) is a biodegradable 35 polyester produced from agricultural products (e.g. corn, sugar cane, and sugar beet) 36 with potential applications ranged from biomedical devices to traditional applications 37 in plastics and composites (Ren, 2011). Wholly bio-composites based on PLA and 38 biopolymers have been widely studied due to the low environmental impact and 39 specific functions. For instance, nanocellulose is a good reinforcing component for 40 PLA and it displays excellent oxygen and water vapour barrier properties of resulting 41 composite products (Karkhanis et al., 2018; Yu et al., 2017). Phenolic compounds 42 43 such as lignin generally exhibit functional properties like thermal stability, anti-UV capacity, and flame retardancy (Kumar et al., 2019; Song et al., 2018; Yang et al., 44 45 2020).



46 47

Figure 1. Simple structure of flavonoid unit of condensed tannins

48 Condensed tannins, composed of flavonoid units (Figure 1), are one of the most 49 important phenolic compounds and highly abundant in bark (Pizzi, 1980). They have a range of inherent properties including UV resistance, antioxidant capacity, and 50 antimicrobial activity, which could be considered to design PLA-based composites for 51 outdoor, agricultural, food packaging, and medical applications. The main challenges 52 for the preparation of PLA-tannin composites are the poor dispersion and low 53 compatibility of tannins in PLA, which results in negative effects on mechanical 54 properties (Anwer et al., 2015; García et al., 2016) and functional performances of the 55 resulting composites (Liao et al., 2019a, 2019b). The widely reported strategies to 56 overcome these disadvantages including the introduction of less hydrophilic 57

58 functional groups to tannin and synthesis tannin-based copolymer. For example, anhydride esterification of tannin was widely used for enhancing its miscibility with 59 bioplastics (Grigsby et al., 2014, 2013; Grigsby and Kadla, 2014; Liao et al., 2020b). 60 Tannin was also reported to copolymerize with polycaprolactone (Song et al., 2016) 61 62 before blending with PLA for biomedical applications (Jiang, 2017). Unfortunately, a decrease in mechanical properties and thermal stability were observed due to 63 64 noninteraction between PLA and tannin (García et al., 2016; Liao et al., 2020b). In 65 addition, phase separation was found during 3D printing process (Liao et al., 2020b).

Inducing molecular interactions between tannin oligomers and PLA via trans-66 esterification were presented for achieving a strong interfacial adhesion between two 67 phases (Bridson et al., 2018; Grigsby and Kadla, 2014). Grafting copolymerization 68 can be also applied to induce covalent bonding in polymer blends, including ring-69 70 opening copolymerization (Song et al., 2016), ion-initiated polymerization (Luo et al., 71 2014, 2013) and radical initiated polymerization (Wei et al., 2015). The latter is 72 considered as a simple and powerful approach of enhancing interfacial adhesion, since 73 it is performed in the molten state with only minor amount of peroxide and neither special device nor extra purification step is required. This peroxide initiated reactive 74 75 grafting method has been successfully applied into PLA/cellulose (Dhar et al., 2016; Zhou et al., 2018), PHB/cellulose (Wei et al., 2015) and poly(3-hydroxybutyrate-co-76 3-hydroxyvalerate) (PHBV)/lignin blends (Luo et al., 2016) to form covalent bonding 77 78 between two phases. However, no literature regarding radical initiated polymerization 79 of PLA/tannin has been reported yet for improving the performance of bio-composite 80 based on PLA and tannin.

In this work, low concentrations of DCP was used as an initiator to induce grafting copolymerization between PLA and tannin for improving their interfacial adhesion. Acetylation of tannin hydroxyl groups was required to enhance dispersion and also to reduce antioxidant character of tannin, guaranteeing free radical reaction (Luo et al., 2014, 2013, 2016). The radical initiated polymerization of PLA with tannin acetate in different acetylation degree on the mechanical property, degree of crystallinity, thermal behaviour and contact angle of resulting composites were investigated.

88 2. Materials and methods

89 2.1. Materials

90 Poly (lactic acid) was purchased from Natureworks LLC (Minnesota, USA) and with a melt flow index of 7-9 g/10 min (210°C, 2.16 kg), which trademarked under the 91 name IngeoTM Biopolymer (Grade 3D850). Mimosa tannins with molecular weight 92 range from 400 Da to 1700 Da (Thébault et al., 2015) were obtained from Silva 93 Chimica, Mondovi, Italy. Acetic anhydride (AR grade), dicumyl peroxide (DCP, 94 98%), acetone (AR grade) were purchased from Sigma-Aldrich (France). Pyridine 95 96 was AR grade from Acros-Organics. All chemicals are used without any further 97 purification.

98 2.2. Sample preparation

99 2.2.1. Tannin acetylation

100 In order to obtain tannin with less hydroxyl functional groups, mimosa tannin was initially reacted with acetic anhydride at a round bottom flask fitted with a condenser. 101 102 Partially and totally acetylated tannin were achieved by using pyridine as catalyst. Continuous stirring was undertaken in the mixture with a magnetic stirrer at 60°C for 103 104 6 h (Nicollin et al., 2013). The suspension was precipitated in iced water after acetylation and centrifuged to separate the solution. The collected tannin acetate (AT) 105 powders were washed 5 times with distilled water and air-dried for several days at 106 107 room temperature. The reaction ratio, catalyst concentration, isolated yield, and degree of substitution (DS) for tannin acetylation reaction were presented in Table 1. 108 109 The DS is calculated using NMR integration (Bridson et al., 2013; Luo et al., 2010; Thébault et al., 2015). The samples noted as PAT and TAT are tannin acetate with 110 and without OH groups, respectively. 111

112

Table 1. Reaction formula of tannin acetate

Product	tannin: acetic anhydride	Pyridine (wt%)	Yield (%)	DS
PAT	1:5	1	$69.3\% \pm 0.3$	3.5
TAT	1:5	5	$95.3\%\pm0.2$	6.3

Notes: ¹H-NMR spectroscopy and related NMR integration were presented in supplementary material, Figure S1.

113 2.2.2. Composite preparation

PLA pellet was ground into powder and blended with tannin acetate in a weight
ratio of 90:10. Each formula was pre-treated with acetone-water solution (80 wt%) of
dicumyl peroxide (DCP) (8 mg/ml) using 0.3 wt% based on under manually stirring at

4

117 room temperature. This concentration of DCP was chosen based on the literature 118 (Yamoum et al., 2017) to guarantee the increased viscosity caused by free radical 119 reaction of PLA will not affect the processability during extrusion. The pre-treated 120 samples were left in a fume hood at room temperature for several hours until acetone 121 evaporated, then, followed by oven-dried at 80°C for 24 hours. The PLA/PAT and 122 PLA/TAT mixtures coated with DCP were labelled as PLPAT and PLTAT, 123 respectively. PLA with DCP was prepared as a control sample, maned as PLD.

The melt blending of each formula was carried out in a twin-screw extruder (Thermo ScientificTM Process 11, Villebon-sur-Yvette, France) with a screw rotation speed of 100 rpm and the resident time was approximately 4 min. The temperature of the extrusion was 185°C. Two mixing zones were also set in the screw profile for the purpose of effective mixing and reaction between each component. All the extruded materials were grinded into small particles for further use.

130 **2.4. Characterizations**

Proton nuclear magnetic resonance (¹H-NMR) spectra was recorded on a
Bruker AVANCE III HD 300MHz instrument (Switzerland). DMSO was used as a
solvent for tannin and acetylated tannin.

The tensile property was carried out using Instron tensile testing machine (model 5569, Norwood, MA, USA) with a 50 kN load cell and a cross-head speed of 1 mm/min at room temperature. The tensile test specimens (dumbbell-shaped, ISO 527, type 1A) were processed by a micro-compounder (Micro 15, DSM Xplore, Sittard, Netherlands) and a micro-injection molder (Xplore, Sittard, Netherlands). Four specimens were tested in each formula, and the average value and standard deviation were considered.

Molecular weight distributions of samples were measured by size-exclusion chromatography (SEC) using a Styragel column (HR-4) from Waters, with tetrahydrofuran (THF) as a solvent at a flow rate of 1.0 mL/min. The molecular weights (\overline{M}_w and \overline{M}_w) and polydispersity index ($\overline{M}_w/\overline{M}_n$) were calculated from SEC curves using a calibration curve from standard polystyrene.

Rheological properties of extruded materials were analyzed on a rheometer (TA instrument, G2 ARES, New Castle, DE, USA) with 25 mm diameter and 1 mm gap under a nitrogen atmosphere. Dynamic strain sweep tests were performed at 1 rad/s, in a range of 0.1-1000% to determine the linear viscoelastic region (LVR). According
to the LVR, 10% strain was chosen for frequency tests. Dynamic frequency sweep
tests were performed over an angular frequency range of 0.1-623.3 rad/s at 190°C.

The differential scanning calorimeter (DSC) was performed with a Metter Toledo DSC 1 (Columbus, Ohio, USA). Samples (3-4 mg) were placed in aluminium crucibles heated from -10 to 220°C at a scanning rate of 10 °C/min and kept for 2 min to ease the thermal history under a nitrogen atmosphere (50 mL/min). Then cooled to -10°C and reheated to 220°C with the same scanning rate. The crystallinity (X_c) was calculated from the values of second ramp by the following equation (1):

158
$$X_c(\%) = \frac{\Delta H_m - \Delta H_c}{\Delta H_m^0 \times w} \times 100\% \quad (1)$$

where ΔH_m is enthalpy of melting, ΔH_c is the enthalpy of cold crystallization, ΔH_m^0 is the enthalpy of melting for 100% crystallized PLA (93.7 J/g) (Yamoum et al., 2017), and w is the weight fraction of PLA.

Thermogravimetric analysis (TGA) was carried out with a Metter Toledo TGA/DSC (Columbus, Ohio, USA). The samples (6–7 mg) were heated from 30 to 600 °C at a heating rate of 10 °C/min under air atmosphere (50 mL/min).

165 Static contact angle was performed using a Ramé-Hart manual contact angle 166 goniometer (Netcong, USA) by depositing a drop of Millipore water on the surface of 167 specimens ($\sim 2 \times 2 \text{ cm}^2$) at various locations. Each measurement was repeated at 168 three times.

169 **3. Results and discussion**

170 **3.1. Plausible reaction mechanism**

The plausible reaction mechanism of PLA/AT composites using DCP as a free 171 radical initiator during melt extrusion is illustrated in Scheme 1. During reactive 172 extrusion, DCP initially decomposed into cumyloxy radicals at high temperature 173 (around 180 °C), following by the formation of methyl radicals and acetophnone by 174 β -scission (Scheme 1, I). These radicals tend to abstract the protons from both PLA 175 and tannin acetate, and initiate grafting reaction between two phases to form PLA-176 tannin acetate copolymers by C-C cross-links. In the case of PLA, free radicals are 177 liable to attract any theriary -CH along the PLA backbone (Scheme 1, II) (Wei and 178 McDonald, 2015). According to the study of Wei et al., DCP radicals could attack the 179 cellulose at different positions during extrusion, generating carbon radicals on 180

181 glucopyranose ring and alkoxy radicals on OH groups according to the ESR results (Wei and McDonald, 2015). Thus, hydrogen possibly abstracted from the residual free 182 phenolic OH groups since the relatively weak bond dissociation energy of phenolic O-183 H bond (Quideau et al., 2011) and from phenyl and heterocyclic ring of flavonoid 184 units (Scheme 1, II). With the consideration of the formation of quinonic structures 185 from phenolic OH groups is less active (Luo et al., 2018), in situ peroxide radicals 186 187 initiated covalent linkages of PLA/AT composites are possible between phenyl/heterocyclic ring of flavonoid units and PLA backbones. The possible 188 189 covalent bonding between PLA-PAT and PLA-TAT was shown in Scheme 1, III.

Scheme 1. Mechanism of DCP decomposition (I); hydrogen abstraction from PLA and tannin
acetate (II); potential grafting mechanism of PLA and tannin acetate (III)



192

193 **3.2. Mechanical property**

The mechanical properties of PLA, PLA+DCP (PLD), PLA+PAT+DCP (PLPAT) 194 and PLA+TAT+DCP (PLTAT) are presented in Figure 2. The control sample PLD 195 display higher Young's modulus and tensile strength with a relatively low elongation 196 197 compared with neat PLA because strong C-C chemical linkages initiated by DCP contributes to the formation of crosslinking structure between PLA chains (Yamoum 198 199 et al., 2017). For filled polymer systems, where weak filler/matrix interfacial adhesion 200 predominates, they show generally poor tensile strength due to poor stress transfer 201 capacity between fillers and polymer matrix (Fu et al., 2008). In the presence of DCP,

202 the initiated PLA radicals provided additional reacting sites for grafting with tannin acetate in different sites according to the acetylation degree (Scheme 1). This may 203 result in the formation of more complex products such as cross-linked PLA polymer 204 and PLA-tannin acetate copolymer. The intermolecular interactions between two 205 components contributed to an enhanced stress transfer between two phases, thus, a 206 relatively higher Young's modulus and tensile strength can be observed in PLPAT 207 208 (3.8±0.1 GPa, 58±1.4 MPa), especially in PLTAT (4.2±0.1 GPa, 66±1 MPa) compared with PLA/tannin acetate blends without DCP (3.7±0.1 GPa, 52±2 MPa) in 209 our previous study (Liao et al., 2020b). It is worth noting that the tensile properties of 210 PLTAT is superior to PLD while that of PLPAT is comparable with PLD. This can be 211 explained by the scavage capacity of phenolic OH groups limited the free radical 212 polymerization since the generated phenoxy radicals (PhO·) is less active that 213 prevents the initiation of new radicals in the polymer (Tolinski, 2015). 214



215

216 Figure 2. Tensile test results of PLA and reactive extruded samples using DCP

217 3.3. Molecular weight and rheological behaviour of PLA/AT blends using DCP

The reactive extruded samples were analysed by SEC and values of molecular weights (\overline{M}_w and \overline{M}_n) and polydispersity index (PD, $\overline{M}_w/\overline{M}_n$) are reported in Table 2. Radical initiated polymerization of PLA and tannin acetate involves a series chemical reactions, including chain scission of PLA backbone, crosslinking of PLA chains and grafting copolymerization of PLA-tannin acetate (Monika et al., 2018; Yamoum et al., 2017). These reactions simutaneously occur in melt extrusion, promoting the generation of both the high- and low- molecular weight fration, therefore, a relatively

high PD was found in all reactive extruded samples compared with PLA. Compared 225 with the extruded PLA, the depletion in the \overline{M}_w and \overline{M}_n values of reactive extruded 226 samples was observed in Table 2, implying the thermal degradation was dominated 227 during reactive extrusion; this phenomenon was commonly found in reactive 228 extrusion using DCP (Monika et al., 2018). However, the chain scission of PLA 229 caused by DCP radicals provide more reaction sites for the formation of covalent 230 bonding in two phases (Yamoum et al., 2017), contributing to the improvement of 231 interfacial adhesion of PLA/AT composites. A relatively low \overline{M}_w and \overline{M}_n values of 232 PLPAT was observed in reactive extruded samples, which might blame to the 233 234 generation of less active phenoxy radicals.

	M_w (g/mol)	M_n (g/mol)	PD			
PLA	1115000	1711000	0.65			
PLD	304900	142800	2.14			
PLPAT	213400	130200	1.64			
PLTAT	386200	140000	2.76			

235 Table 2. SEC data of PLA and reactive extruded samples using DCP

236

The variation of the melt rheological properties is useful to investigate changes in 237 molecular structure and interfacial adhesion property during the reactive extrusion 238 239 (Yamoum et al., 2017). Figure 3 (a) shows the complex viscosity of reactive extruded samples as a function of angular frequency at 190 °C. The complex viscosity 240 decreases with the increasing angular frequency, showing a shear thinning behaviour 241 of PLA polymer in the resulting composites. DCP radicals promoted the chain 242 scission of PLA polymer chain led to decrease of molecular weight in PLD, PLPAT 243 and PLTAT (Table 2), thus a significant drop of complex viscosity of reactive 244 extruded samples compared with PLA. As reported by Dorgan et al., PLA 245 homopolymers with comparable molecular weights presents similar complex viscosity 246 (Dorgan et al., 1999). One this basis, the introduction of filler in polymers was 247 generally found a decrease of complex viscosity since the poor interfacial adhesion 248 249 (Liao et al., 2020a, 2019a). In the case of PLPAT and PLTAT, their complex viscosity is much higher than that of PLD, referring the strong interfacial adhesion 250 251 between PLA and tannin acetate in the presence of DCP. This phenomenon was 252 commonly observed in polymer blends using DCP (Luo et al., 2016; Wei and

McDonald, 2015). Figure 3 (b) presents the storage modulus as a function of 253 frequency of all tested samples, which corresponds to the elastic character of the 254 blends or the energy stored during the deformation (Wei and McDonald, 2015). The 255 domination of chain scission on PLD results in a drop of storage modulus due to the 256 257 shorter polymer chains and less chains entanglement. In PLA/AT system, the presence of radicals induced covalent bonds between PLA and tannin acetate. The 258 259 grafting between PLA and tannin acetate can increase the entanglement density, resulting in an increase of storage modulus (Dorgan et al., 1999). In the present study, 260 the relatively lower storage modulus of PLPAT reveals most likely a less covalent 261 linkage in PLA/PAT blending system. This can be explained by the presence of free 262 phenolic -OH moieties of tannin acetate, which are competing to react with the DCP 263 radicals. As a result, less grafting reactions can be undertaken between PLA and PAT. 264



Figure 3. Rheological behavior of PLA and reactive extruded samples

266 **3.4. Thermal behaviour**

The temperature of glass transition (T_g) , melt (T_m) , cold crystalline (T_c) , and 267 degree of crystallinity (X_c) was investigated using DSC and the related data presented 268 in Table 3. As reported in previous section, the molecular weight of extruded samples 269 (PLD, PLPAT, PLTAT) in presence of DCP is lower than extruded PLA without 270 DCP. Thus, PLD displayed relatively low grass transition, melting and cold crystal 271 temperature. For PLA/AT with DCP, Tg shifted to a higher temperature compared 272 with PLD, referring the formation of covalent bonding between PLA and tannin 273 acetate since the mobility of polymer chain required more thermal energy (Wei and 274 McDonald, 2015). PLPAT and PLTAT have a higher T_c because the introduction of 275 tannin acetate in PLA and the generation of less regular polymer chains from radical 276

277 reaction results in the difficulty of chain reorganization and chain folding during crystallization process (Dong et al., 2017). As chain scission of PLA backbone and 278 recombination of polymer chain occur simutaneously during the reactive extrusion 279 using DCP, the formation of inhomogeneous polymer chain segments inhibited the 280 281 crystallinity in PLD, PLA/AT blends. However, it should be noted that the X_c values increased with the addition of tannin acetate, especially for PLTAT, which might due 282 283 to the improved interfacial adhesion of two components and dispersion of tannin acetate in PLA matrix because of C-C grafting of PLA-AT (Dhar et al., 2016). 284

	DSC			TAG-Weight loss (%)			
Samples	$T_{g}(^{\circ}C)$	T _c (°C)	$T_{m1}; T_{m2} (^{\circ}C)$	X _c (%)	T ₉₀ (°C)	$T_{max}(^{\circ}C)$	T ₁₀ (°C)
PLA	55.6	120.2	152.5; 162.8	7.4	322.8	357.5	367.2
PLD	55.1	116.3	149.6; 157.8	1.2	318.7	358.2	367.0
PLPAT	56.8	122.8	152.3; 161.6	2.1	316.8	352.2	370.3
PLTAT	57.0	121.5	150.8; 157.4	4.6	319.2	356.2	368.2

285 Table 3. DSC data and weight loss of PLA and reactive extruded samples using DCP

The thermal stability of PLA and reactive extruded samples was explored by 286 287 TGA under an air atmosphere and thermal degradation data was presented in Table 3. The decomposition process of composites relies on the thermal stability of each 288 289 component, interfacial adhesion between the two components and molecular weight of the polymer matrix (García et al., 2018; Yu et al., 2011). In our previous work, the 290 291 addition of PAT in PLA results in a decrease of thermal stability since the weak interfacial adhesion between the filler and the polymer matrix (Liao et al., 2020b). 292 293 Thus, the degradation temperature of PLA/AT composites is comparable to PLA, 294 suggesting that interfacial adhesion of PLA and tannin acetate can be promoted by 295 free radical copolymerization.

_...

3.5. Contact angle analysis

The wettability is an important property for PLA-based composites in the application of food packaging for preventing the food items from humidity during transport to the consumption stage (Monika et al., 2018). The wettability can be characterized by depositing a water drop on the surface of material. Figure 4 is the contact angle data of resulting samples at 1 s and 180 s. The contact angles of PLD exhibited a higher contact angle compared with PLA either at 1 s or 180 s, indicating 303 reactive extruded PLD tend to be more hydrophobic than PLA. This might associate 304 to covalent bonding of polymer chain initiated by free radicals. With the addition of tannin acetate, contact angles mainly rely on degree of roughness that will be affected 305 by the dispersion of tannin acetate in PLA matrix. In our previous experiment, PLA 306 blended with PAT generated a rough surface (Figure S2, supplementary material) 307 because of the aggregation of tannin acetate. The dispersion of AT in PLA can be 308 309 ameliorated via free radical copolymerization (Monika et al., 2018). The contact angle of PLPAT has a lower value compared with PLA + PAT ($88^\circ \pm 1$, Table S1, 310 supplementary material), indicating good dispersion of tannin acetate in PLA. 311 Therefore, it can be concluded from contact angle data, PLA/AT composites prepared 312 by free radical copolymerization exhibited high degree of hydrophobicity, which are 313 potentially applied in packaging applications. 314



315

316 Figure 4. Contact angle at 1s (up) and 180 s (bottom) of PLA and reactive extruded samples 317 at 25 $^{\circ}$ C

- 318
- 319

320 **4.** Conclusions

In current work, PLA/AT composites have been prepared via in situ free radical copolymerization using DCP. The composites based on PLA and tannin acetate with high acetylation degree presented improved Young's modulus and tensile strengths as compared with PLA because the initiated DCP radicals contributed to the formation of covalent bonding between PLA and tannin acetate. The promoted intermolecular interaction of PLA/AT composites results from free radical 327 copolymerization, which can be investigated by the rheology test. The increased complex viscosity and modulus storage indicates the strong interfacial adhesion of 328 PLA and tannin acetate. In addition, glass transition temperature, thermal stability and 329 crystallinity degree of PLA/AT composites were all improved as a result of better 330 interaction by free radical copolymerization. The enhanced hydrophobicity of 331 PLA/AT composites may suggest a possible application towards packaging 332 333 applications. It is expected that this free radical copolymerization can expand the application of tannin as a sustainable component for bio-composite preparation. 334

335 Acknowledgements

This work was supported by the National Natural Science Foundation of 336 China (NSFC 31971595, 31760187) and the Program for Leading Talents of Science 337 338 and Technology (grant No. 2017HA013) as well as the Yunnan Provincial Youth and Yunnan Provincial Reserve Talents for Middle & Young Academic and Technical 339 Leaders (2019HB026). LERMAB is supported by the French National Research 340 Agency through the Laboratory of Excellence ARBRE (ANR-12-LABXARBRE-01). 341 China Scholarship Council is gratefully acknowledged. The authors also thank 342 Richard Laine for precious technical support. 343

- 344 Notes
- 345

The authors declare no competing financial interest.

346

347 **Reference:**

- Anwer, M.A.S., Naguib, H.E., Celzard, A., Fierro, V., 2015. Comparison of the thermal, dynamic mechanical and morphological properties of PLA-Lignin & PLA-Tannin particulate green composites. Composites Part B: Engineering 82, 92–99. https://doi.org/10.1016/j.compositesb.2015.08.028
- Bridson, J.H., Grigsby, W.J., Main, L., 2018. One-pot solvent-free synthesis and characterisation of hydroxypropylated polyflavonoid compounds. Industrial Crops and Products 111, 529–535.
 https://doi.org/10.1016/j.indcrop.2017.11.028
- Bridson, J.H., Grigsby, W.J., Main, L., 2013. Synthesis and characterization of
 flavonoid laurate esters by transesterification. J Appl Polym Sci 129, 181–186.
 https://doi.org/10.1002/app.38731
- 359 Dhar, P., Tarafder, D., Kumar, A., Katiyar, V., 2016. Thermally recyclable polylactic
 360 acid/cellulose nanocrystal films through reactive extrusion process. Polymer
 361 87, 268–282. https://doi.org/10.1016/j.polymer.2016.02.004
- 362 Dong, J., Li, M., Zhou, L., Lee, S., Mei, C., Xu, X., Wu, Q., 2017. The influence of

- 363 grafted cellulose nanofibers and postextrusion annealing treatment on selected
 364 properties of poly(lactic acid) filaments for 3D printing. Journal of Polymer
 365 Science Part B: Polymer Physics 55, 847–855.
 366 https://doi.org/10.1002/polb.24333
- Borgan, J.R., Williams, J.S., Lewis, D.N., 1999. Melt rheology of poly(lactic acid):
 Entanglement and chain architecture effects. Journal of Rheology 43, 1141–
 1155. https://doi.org/10.1122/1.551041
- Fu, S.-Y., Feng, X.-Q., Lauke, B., Mai, Y.-W., 2008. Effects of particle size,
 particle/matrix interface adhesion and particle loading on mechanical
 properties of particulate-polymer composites. Composites Part B: Engineering
 39, 933–961. https://doi.org/10.1016/j.compositesb.2008.01.002
- García, D., Carrasco, J., Salazar, J., Pérez, M., Cancino, R., Riquelme, S., 2016. Bark
 polyflavonoids from Pinus radiata as functional building-blocks for polylactic
 acid (PLA)-based green composites. eXPRESS Polymer Letters 10, 835–848.
 https://doi.org/10.3144/expresspolymlett.2016.78
- García, D.E., Salazar, J.P., Riquelme, S., Delgado, N., Paczkowski, S., 2018.
 Condensed Tannin-Based Polyurethane as Functional Modifier of PLAComposites. Polymer-Plastics Technology and Engineering 57, 709–726.
 https://doi.org/10.1080/03602559.2017.1344855
- Grigsby, W.J., Bridson, J.H., Lomas, C., Elliot, J.-A., 2013. Esterification of
 Condensed Tannins and Their Impact on the Properties of Poly(Lactic Acid).
 polymers 5, 334–360. https://doi.org/10.3390/polym5020344
- Grigsby, W.J., Bridson, J.H., Lomas, C., Frey, H., 2014. Evaluating Modified Tannin
 Esters as Functional Additives in Polypropylene and Biodegradable Aliphatic
 Polyester: Modified Tannin Esters as Plastic Additives. Macromol. Mater. Eng.
 299, 1251–1258. https://doi.org/10.1002/mame.201400051
- Grigsby, W.J., Kadla, J.F., 2014. Evaluating Poly(lactic acid) Fiber Reinforcement
 with Modified Tannins: Evaluating Poly(lactic acid) Fiber Reinforcement
 Macromol. Mater. Eng. 299, 368–378.
 https://doi.org/10.1002/mame.201300174
- Jiang, S., 2017. Blending PLLA/tannin-grafted PCL fiber membrane for skin tissue
 engineering. J Mater Sci 8.
- Karkhanis, S.S., Stark, N.M., Sabo, R.C., Matuana, L.M., 2018. Water vapor and
 oxygen barrier properties of extrusion-blown poly(lactic acid)/cellulose
 nanocrystals nanocomposite films. Composites Part A: Applied Science and
 Manufacturing 114, 204–211.
 https://doi.org/10.1016/i.composites 2018.08.025
- 399
 https://doi.org/10.1016/j.compositesa.2018.08.025
- Kumar, A., Tumu, V.R., Ray Chowdhury, S., S.v.s., R.R., 2019. A green physical approach to compatibilize a bio-based poly (lactic acid)/lignin blend for better mechanical, thermal and degradation properties. International Journal of Biological Macromolecules 121, 588–600. https://doi.org/10.1016/j.ijbiomac.2018.10.057
- Liao, J., Brosse, N., Hoppe, S., Du, G., Zhou, X., Pizzi, A., 2020a. One-step
 compatibilization of poly(lactic acid) and tannin via reactive extrusion.
 Materials & Design 191, 108603.
 https://doi.org/10.1016/j.matdes.2020.108603
- Liao, J., Brosse, N., Pizzi, A., Hoppe, S., 2019a. Dynamically Cross-Linked Tannin as
 a Reinforcement of Polypropylene and UV Protection Properties. Polymers 11,
 102. https://doi.org/10.3390/polym11010102
- 412 Liao, J., Brosse, N., Pizzi, A., Hoppe, S., Xi, X., Zhou, X., 2019b. Polypropylene

Blend with Polyphenols through Dynamic Vulcanization: Mechanical, 413 Rheological, Crystalline, Thermal, and UV Protective Property. Polymers 11, 414 1108. https://doi.org/10.3390/polym11071108 415 Liao, J., Brosse, N., Pizzi, A., Hoppe, S., Zhou, X., Du, G., 2020b. Characterization 416 and 3D printability of poly (lactic acid)/acetylated tannin composites. 417 Industrial Crops Products 149, 112320. 418 and https://doi.org/10.1016/j.indcrop.2020.112320 419 Luo, C., Grigsby, W., Edmonds, N., Easteal, A., Al-Hakkak, J., 2010. Synthesis, 420 characterization, and thermal behaviors of tannin stearates prepared from 421 422 quebracho and pine bark extracts. Journal of Applied Polymer Science 117, 352-360. https://doi.org/10.1002/app.31545 423 Luo, C., Grigsby, W.J., Edmonds, N.R., Al-Hakkak, J., 2014. Rubber-Like Materials 424 425 Prepared from Copolymerization of Tannin Fatty Acid Conjugates and Vegetable Oils. Macromolecular Materials and Engineering 299, 65-74. 426 https://doi.org/10.1002/mame.201300039 427 Luo, C., Grigsby, W.J., Edmonds, N.R., Al-Hakkak, J., 2013. Vegetable oil 428 429 thermosets reinforced by tannin-lipid formulations. Acta Biomaterialia 9, 5226-5233. https://doi.org/10.1016/j.actbio.2012.08.048 430 Luo, S., Cao, J., McDonald, A.G., 2018. Cross-linking of technical lignin via 431 esterification and thermally initiated free radical reaction. Industrial Crops and 432 Products 121, 169-179. https://doi.org/10.1016/j.indcrop.2018.05.007 433 Luo, S., Cao, J., McDonald, A.G., 2016. Interfacial Improvements in a Green 434 435 Biopolymer Alloy of Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) and Lignin via in Situ Reactive Extrusion. ACS Sustainable Chem. Eng. 4, 3465-436 3476. https://doi.org/10.1021/acssuschemeng.6b00495 437 438 Monika, Pal, A.K., Bhasney, S.M., Bhagabati, P., Katiyar, V., 2018. Effect of Dicumyl Peroxide on a Poly(lactic acid) (PLA)/Poly(butylene succinate) 439 (PBS)/Functionalized Chitosan-Based Nanobiocomposite for Packaging: A 440 Reactive Extrusion Study. ACS Omega 3, 13298-13312. 441 https://doi.org/10.1021/acsomega.8b00907 442 Nicollin, A., Zhou, X., Pizzi, A., Grigsby, W., Rode, K., Delmotte, L., 2013. MALDI-443 TOF and 13C NMR analysis of a renewable resource additive—Thermoplastic 444 tannins. Industrial Crops and Products 49. 851-857. 445 acetylated https://doi.org/10.1016/j.indcrop.2013.06.013 446 Pizzi, A., 1980. Tannin-Based Adhesives. Journal of macromolecular science 18, 447 448 247-315. Quideau, S., Deffieux, D., Douat-Casassus, C., Pouysegu, L., 2011. Plant polyphenols: 449 chemical properties, biological activities, and synthesis. Angewandte Chemie 450 451 International Edition 50, 586–621. Ren, J., 2011. Biodegradable Poly(Lactic Acid): Synthesis, Modification, Processing 452 Applications. Springer and Berlin Heidelberg, Berlin. Heidelberg. 453 https://doi.org/10.1007/978-3-642-17596-1 454 Song, P., Jiang, S., Ren, Y., Zhang, X., Qiao, T., Song, X., Liu, Q., Chen, X., 2016. 455 Synthesis and characterization of tannin grafted polycaprolactone. Journal of 456 457 Colloid and Interface Science 479. 160-164. https://doi.org/10.1016/j.jcis.2016.06.056 458 Song, Y., Zong, X., Wang, N., Yan, N., Shan, X., Li, J., 2018. Preparation of y-459 460 Divinyl-3-Aminopropyltriethoxysilane Modified Lignin and Its Application in Flame Retardant Poly(lactic acid). Materials 11. 1505. 461 https://doi.org/10.3390/ma11091505 462

- Thébault, M., Pizzi, A., Essawy, H.A., Barhoum, A., Van Assche, G., 2015.
 Isocyanate free condensed tannin-based polyurethanes. European Polymer
 Journal 67, 513–526. https://doi.org/10.1016/j.eurpolymj.2014.10.022
- Tolinski, M., 2015. Additives for polyolefins: getting the most out of polypropylene,
 polyethylene and TPO, Second edition. ed, PDL handbook series. Elsevier,
 William Andrew is an imprint of Elsevier, Kidlington, Oxford, UK.
- Wei, L., McDonald, A.G., 2015. Peroxide induced cross-linking by reactive melt
 processing of two biopolyesters: Poly(3-hydroxybutyrate) and poly(1-lactic
 acid) to improve their melting processability. Journal of Applied Polymer
 Science 132. https://doi.org/10.1002/app.41724
- Wei, L., McDonald, A.G., Stark, N.M., 2015. Grafting of Bacterial
 Polyhydroxybutyrate (PHB) onto Cellulose via In Situ Reactive Extrusion
 with Dicumyl Peroxide. Biomacromolecules 10.
- Yamoum, C., Maia, J., Magaraphan, R., 2017. Rheological and thermal behavior of
 PLA modified by chemical crosslinking in the presence of ethoxylated
 bisphenol A dimethacrylates: Rheological and Thermal Behaviors of PLA
 with Bis-EMA Crosslinking. Polym. Adv. Technol. 28, 102–112.
 https://doi.org/10.1002/pat.3864
- Yang, W., Weng, Y., Puglia, D., Qi, G., Dong, W., Kenny, J.M., Ma, P., 2020.
 Poly(lactic acid)/lignin films with enhanced toughness and anti-oxidation
 performance for active food packaging. International Journal of Biological
 Macromolecules 144, 102–110.
 https://doi.org/10.1016/j.ijbiomac.2019.12.085
- Yu, H.-Y., Zhang, H., Song, M.-L., Zhou, Y., Yao, J., Ni, Q.-Q., 2017. From 486 Cellulose Nanospheres, Nanorods to Nanofibers: Various Aspect Ratio 487 488 Induced Nucleation/Reinforcing Effects on Polylactic Acid for Robust-Barrier Packaging. ACS Mater. Interfaces 9, 43920-43938. 489 Food Appl. https://doi.org/10.1021/acsami.7b09102 490
- Yu, L., Petinakis, E., Dean, K., Liu, H., Yuan, Q., 2011. Enhancing compatibilizer
 function by controlled distribution in hydrophobic polylactic acid/hydrophilic
 starch blends. Journal of Applied Polymer Science 119, 2189–2195.
 https://doi.org/10.1002/app.32949
- Zhou, L., He, H., Li, M., Huang, S., Mei, C., Wu, Q., 2018. Enhancing mechanical properties of poly(lactic acid) through its in-situ crosslinking with maleic anhydride-modified cellulose nanocrystals from cottonseed hulls. Industrial Crops and Products 112, 449–459. https://doi.org/10.1016/j.indcrop.2017.12.044
- 500



