



**HAL**  
open science

## 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

# 1     **Interfacial improvement of poly (lactic acid)/tannin acetate** 2                   **composites via radical initiated polymerization**

3     Jingjing LIAO <sup>1,2,3,4</sup>, Nicolas BROSSE <sup>3,\*</sup>, Sandrine HOPPE <sup>4</sup>, Xiaojian ZHOU <sup>1,\*</sup>, Xuedong XI <sup>3</sup>,  
4     Guanben DU <sup>1,2,\*</sup>, Antonio PIZZI <sup>3</sup>

5     <sup>1</sup> *Yunnan Provincial Key Laboratory of Wood Adhesives and Glued Products, Southwest Forestry*  
6     *University, Kunming 650224, Yunnan, P. R. China*

7     <sup>2</sup> *College of Materials Science and Technology, Beijing Forestry University, 35 Tsinghua East Road,*  
8     *Haidian District, Beijing, 100083, P. R. China*

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

11    <sup>4</sup> *LRGP, University of Lorraine, 1, Rue Grandville, BP 451, 54001 Nancy Cedex, France;*

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

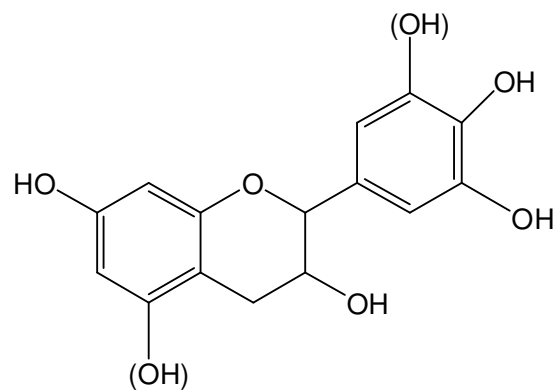
14  
15    **Abstract:** A wholly bio-composite based on poly (lactic acid) (PLA) and tannin  
16    acetate was successfully prepared via in situ reactive extrusion using dicumyl  
17    peroxide (DCP) to improve interfacial adhesion. The composites based on PLA and  
18    tannin acetate with high acetylation degree exhibited increased molecular weight as  
19    compared with reactive extruded PLA, together with the improvement of Young's  
20    modulus and tensile strength. The rheology results showed that reactive extruded  
21    PLA/tannin acetate composites exhibited increased complex viscosity and modulus  
22    storage, indicating the strong interfacial adhesion of PLA and tannin acetate. Besides,  
23    Glass transition temperature, thermal stability, and crystallinity degree were all  
24    enhanced as a result of better interaction by radical initiated polymerization. From  
25    contact angle data, free radical extruded composites had a more hydrophobic  
26    characteristic compared with PLA, which might be interesting for food packaging  
27    application. This approach opens up a pathway to diversify the applications of tannin  
28    as a component for bio-composite preparation.

29    **Keywords:** poly (lactic acid); tannin acetate; peroxide; reactive extrusion; bio-  
30    composite

31

32 **1. Introduction**

33 Biodegradable polymers from renewable resources have been attracted great interests  
34 in past years driven by the depletion of non-renewable petroleum resources and  
35 accumulation of non-degradable plastics. Poly (lactic acid) (PLA) is a biodegradable  
36 polyester produced from agricultural products (e.g. corn, sugar cane, and sugar beet)  
37 with potential applications ranged from biomedical devices to traditional applications  
38 in plastics and composites (Ren, 2011). Wholly bio-composites based on PLA and  
39 biopolymers have been widely studied due to the low environmental impact and  
40 specific functions. For instance, nanocellulose is a good reinforcing component for  
41 PLA and it displays excellent oxygen and water vapour barrier properties of resulting  
42 composite products (Karkhanis et al., 2018; Yu et al., 2017). Phenolic compounds  
43 such as lignin generally exhibit functional properties like thermal stability, anti-UV  
44 capacity, and flame retardancy (Kumar et al., 2019; Song et al., 2018; Yang et al.,  
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  
50 a range of inherent properties including UV resistance, antioxidant capacity, and  
51 antimicrobial activity, which could be considered to design PLA-based composites for  
52 outdoor, agricultural, food packaging, and medical applications. The main challenges  
53 for the preparation of PLA-tannin composites are the poor dispersion and low  
54 compatibility of tannins in PLA, which results in negative effects on mechanical  
55 properties (Anwer et al., 2015; García et al., 2016) and functional performances of the  
56 resulting composites (Liao et al., 2019a, 2019b). The widely reported strategies to  
57 overcome these disadvantages including the introduction of less hydrophilic

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

66 Inducing molecular interactions between tannin oligomers and PLA via trans-  
67 esterification were presented for achieving a strong interfacial adhesion between two  
68 phases (Bridson et al., 2018; Grigsby and Kadla, 2014). Grafting copolymerization  
69 can be also applied to induce covalent bonding in polymer blends, including ring-  
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  
74 special device nor extra purification step is required. This peroxide initiated reactive  
75 grafting method has been successfully applied into PLA/cellulose (Dhar et al., 2016;  
76 Zhou et al., 2018), PHB/cellulose (Wei et al., 2015) and poly(3-hydroxybutyrate-co-  
77 3-hydroxyvalerate) (PHBV)/lignin blends (Luo et al., 2016) to form covalent bonding  
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.

81 In this work, low concentrations of DCP was used as an initiator to induce grafting  
82 copolymerization between PLA and tannin for improving their interfacial adhesion.  
83 Acetylation of tannin hydroxyl groups was required to enhance dispersion and also to  
84 reduce antioxidant character of tannin, guaranteeing free radical reaction (Luo et al.,  
85 2014, 2013, 2016). The radical initiated polymerization of PLA with tannin acetate in  
86 different acetylation degree on the mechanical property, degree of crystallinity,  
87 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  
91 with a melt flow index of 7-9 g/10 min (210°C, 2.16 kg), which trademarked under the  
92 name Ingeo™ Biopolymer (Grade 3D850). Mimosa tannins with molecular weight  
93 range from 400 Da to 1700 Da (Thébault et al., 2015) were obtained from Silva  
94 Chimica, Mondovi, Italy. Acetic anhydride (AR grade), dicumyl peroxide (DCP,  
95 98%), acetone (AR grade) were purchased from Sigma-Aldrich (France). Pyridine  
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  
101 initially reacted with acetic anhydride at a round bottom flask fitted with a condenser.  
102 Partially and totally acetylated tannin were achieved by using pyridine as catalyst.  
103 Continuous stirring was undertaken in the mixture with a magnetic stirrer at 60°C for  
104 6 h (Nicollin et al., 2013). The suspension was precipitated in iced water after  
105 acetylation and centrifuged to separate the solution. The collected tannin acetate (AT)  
106 powders were washed 5 times with distilled water and air-dried for several days at  
107 room temperature. The reaction ratio, catalyst concentration, isolated yield, and  
108 degree of substitution (DS) for tannin acetylation reaction were presented in Table 1.  
109 The DS is calculated using NMR integration (Bridson et al., 2013; Luo et al., 2010;  
110 Thébault et al., 2015). The samples noted as PAT and TAT are tannin acetate with  
111 and without OH groups, respectively.

112 Table 1. Reaction formula of tannin acetate

Product	tannin: acetic anhydride	Pyridine (wt%)	Yield (%)	DS
PAT	1:5	1	69.3% ± 0.3	3.5
TAT	1:5	5	95.3% ± 0.2	6.3

*Notes: <sup>1</sup>H-NMR spectroscopy and related NMR integration were presented in supplementary material, Figure S1.*

### 113 2.2.2. Composite preparation

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

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, named as PLD.

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

#### 130 **2.4. Characterizations**

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

134 The tensile property was carried out using Instron tensile testing machine  
135 (model 5569, Norwood, MA, USA) with a 50 kN load cell and a cross-head speed of  
136 1 mm/min at room temperature. The tensile test specimens (dumbbell-shaped, ISO  
137 527, type 1A) were processed by a micro-compounder (Micro 15, DSM Xplore,  
138 Sittard, Netherlands) and a micro-injection molder (Xplore, Sittard, Netherlands).  
139 Four specimens were tested in each formula, and the average value and standard  
140 deviation were considered.

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

146 Rheological properties of extruded materials were analyzed on a rheometer (TA  
147 instrument, G2 ARES, New Castle, DE, USA) with 25 mm diameter and 1 mm gap  
148 under a nitrogen atmosphere. Dynamic strain sweep tests were performed at 1 rad/s,

149 in a range of 0.1-1000% to determine the linear viscoelastic region (LVR). According  
150 to the LVR, 10% strain was chosen for frequency tests. Dynamic frequency sweep  
151 tests were performed over an angular frequency range of 0.1-623.3 rad/s at 190°C.

152 The differential scanning calorimeter (DSC) was performed with a Mettler  
153 Toledo DSC 1 (Columbus, Ohio, USA). Samples (3-4 mg) were placed in aluminium  
154 crucibles heated from -10 to 220°C at a scanning rate of 10 °C/min and kept for 2 min  
155 to ease the thermal history under a nitrogen atmosphere (50 mL/min). Then cooled to  
156 -10°C and reheated to 220°C with the same scanning rate. The crystallinity ( $X_c$ ) was  
157 calculated from the values of second ramp by the following equation (1):

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

159 where  $\Delta H_m$  is enthalpy of melting,  $\Delta H_c$  is the enthalpy of cold crystallization,  $\Delta H_m^0$  is  
160 the enthalpy of melting for 100% crystallized PLA (93.7 J/g) (Yamoum et al., 2017),  
161 and  $w$  is the weight fraction of PLA.

162 Thermogravimetric analysis (TGA) was carried out with a Mettler Toledo  
163 TGA/DSC (Columbus, Ohio, USA). The samples (6–7 mg) were heated from 30 to  
164 600 °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.

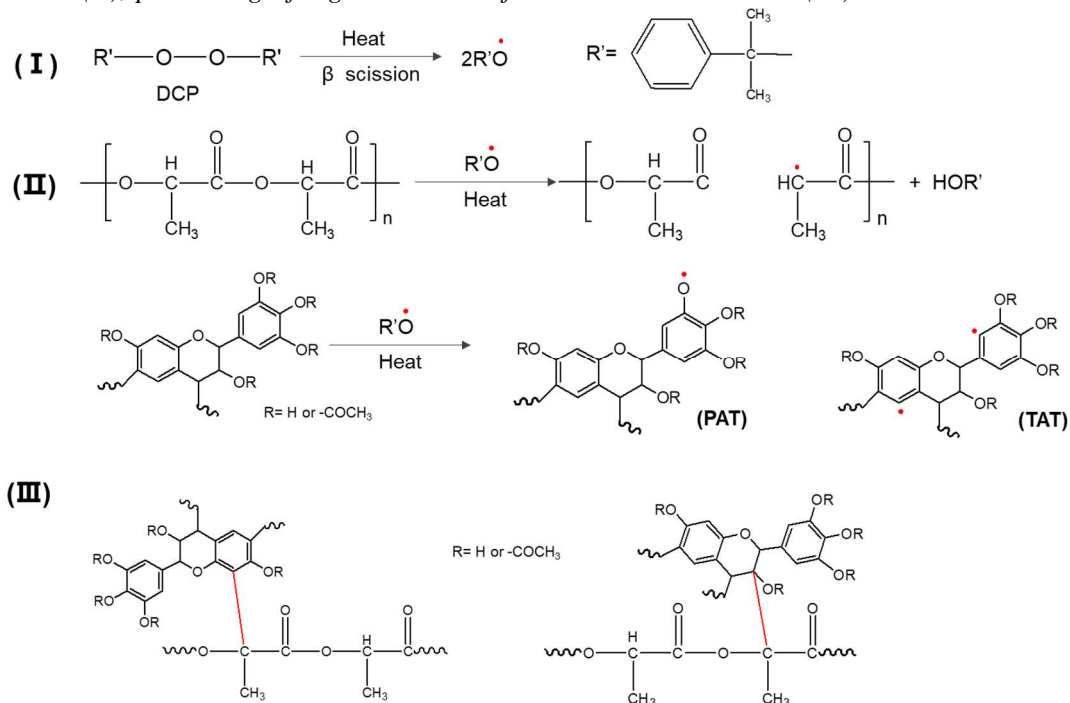
### 169 **3. Results and discussion**

#### 170 **3.1. Plausible reaction mechanism**

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

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

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



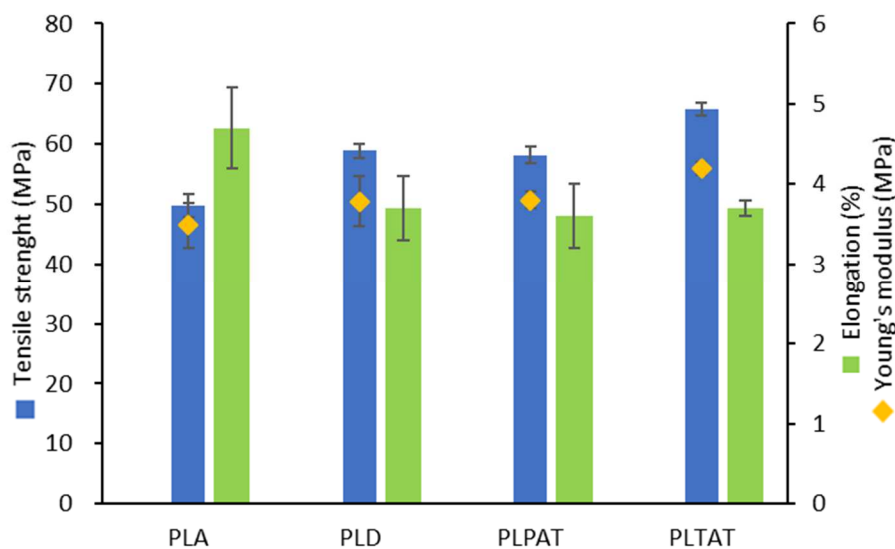
192

### 193 3.2. Mechanical property

194 The mechanical properties of PLA, PLA+DCP (PLD), PLA+PAT+DCP (PLPAT)  
 195 and PLA+TAT+DCP (PLTAT) are presented in Figure 2. The control sample PLD  
 196 display higher Young's modulus and tensile strength with a relatively low elongation  
 197 compared with neat PLA because strong C-C chemical linkages initiated by DCP  
 198 contributes to the formation of crosslinking structure between PLA chains (Yamoum  
 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  
 203 acetate in different sites according to the acetylation degree (Scheme 1). This may  
 204 result in the formation of more complex products such as cross-linked PLA polymer  
 205 and PLA-tannin acetate copolymer. The intermolecular interactions between two  
 206 components contributed to an enhanced stress transfer between two phases, thus, a  
 207 relatively higher Young's modulus and tensile strength can be observed in PLPAT  
 208 ( $3.8\pm 0.1$  GPa,  $58\pm 1.4$  MPa), especially in PLTAT ( $4.2\pm 0.1$  GPa,  $66\pm 1$  MPa)  
 209 compared with PLA/tannin acetate blends without DCP ( $3.7\pm 0.1$  GPa,  $52\pm 2$  MPa) in  
 210 our previous study (Liao et al., 2020b). It is worth noting that the tensile properties of  
 211 PLTAT is superior to PLD while that of PLPAT is comparable with PLD. This can be  
 212 explained by the scavage capacity of phenolic OH groups limited the free radical  
 213 polymerization since the generated phenoxy radicals (PhO·) is less active that  
 214 prevents the initiation of new radicals in the polymer (Tolinski, 2015).



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

218 The reactive extruded samples were analysed by SEC and values of molecular  
 219 weights ( $\bar{M}_w$  and  $\bar{M}_n$ ) and polydispersity index (PD,  $\bar{M}_w/\bar{M}_n$ ) are reported in Table 2.  
 220 Radical initiated polymerization of PLA and tannin acetate involves a series chemical  
 221 reactions, including chain scission of PLA backbone, crosslinking of PLA chains and  
 222 grafting copolymerization of PLA-tannin acetate (Monika et al., 2018; Yamoum et al.,  
 223 2017). These reactions simultaneously occur in melt extrusion, promoting the  
 224 generation of both the high- and low- molecular weight fraction, therefore, a relatively

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

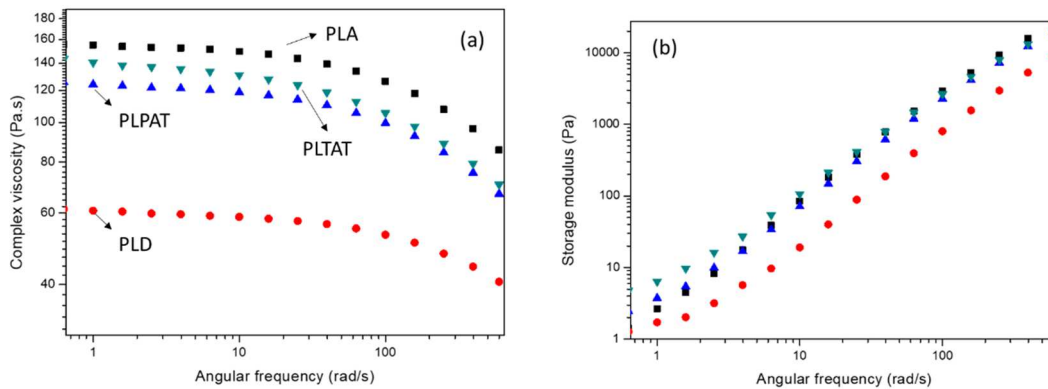
235 *Table 2. SEC data of PLA and reactive extruded samples using DCP*

	$\bar{M}_w$ (g/mol)	$\bar{M}_n$ (g/mol)	PD
PLA	1115000	1711000	0.65
PLD	304900	142800	2.14
PLPAT	213400	130200	1.64
PLTAT	386200	140000	2.76

236

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

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



265 Figure 3. Rheological behavior of PLA and reactive extruded samples

### 266 3.4. Thermal behaviour

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

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

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

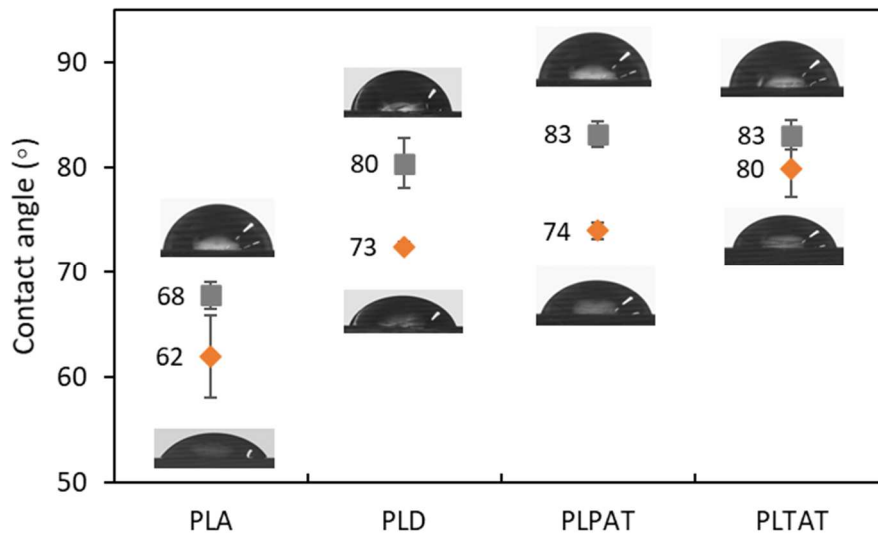
Samples	DSC				TAG-Weight loss (%)		
	$T_g$ (°C)	$T_c$ (°C)	$T_{m1}; T_{m2}$ (°C)	$X_c$ (%)	$T_{90}$ (°C)	$T_{max}$ (°C)	$T_{10}$ (°C)
PLA	55.6	120.2	152.5; 162.8	7.4	322.8	357.5	367.2
PLD	55.1	116.3	149.6; 157.8	1.2	318.7	358.2	367.0
PLPAT	56.8	122.8	152.3; 161.6	2.1	316.8	352.2	370.3
PLTAT	57.0	121.5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

286 The thermal stability of PLA and reactive extruded samples was explored by  
 287 TGA under an air atmosphere and thermal degradation data was presented in Table 3.  
 288 The decomposition process of composites relies on the thermal stability of each  
 289 component, interfacial adhesion between the two components and molecular weight  
 290 of the polymer matrix (García et al., 2018; Yu et al., 2011). In our previous work, the  
 291 addition of PAT in PLA results in a decrease of thermal stability since the weak  
 292 interfacial adhesion between the filler and the polymer matrix (Liao et al., 2020b).  
 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.

### 296 **3.5. Contact angle analysis**

297 The wettability is an important property for PLA-based composites in the  
 298 application of food packaging for preventing the food items from humidity during  
 299 transport to the consumption stage (Monika et al., 2018). The wettability can be  
 300 characterized by depositing a water drop on the surface of material. Figure 4 is the  
 301 contact angle data of resulting samples at 1 s and 180 s. The contact angles of PLD  
 302 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  
 305 tannin acetate, contact angles mainly rely on degree of roughness that will be affected  
 306 by the dispersion of tannin acetate in PLA matrix. In our previous experiment, PLA  
 307 blended with PAT generated a rough surface (Figure S2, supplementary material)  
 308 because of the aggregation of tannin acetate. The dispersion of AT in PLA can be  
 309 ameliorated via free radical copolymerization (Monika et al., 2018). The contact  
 310 angle of PLPAT has a lower value compared with PLA + PAT ( $88^\circ \pm 1$ , Table S1,  
 311 supplementary material), indicating good dispersion of tannin acetate in PLA.  
 312 Therefore, it can be concluded from contact angle data, PLA/AT composites prepared  
 313 by free radical copolymerization exhibited high degree of hydrophobicity, which are  
 314 potentially applied in packaging applications.



315

316 *Figure 4. Contact angle at 1s (up) and 180 s (bottom) of PLA and reactive extruded samples*  
 317 *at 25 °C*

318

319

#### 320 4. Conclusions

321 In current work, PLA/AT composites have been prepared via in situ free  
 322 radical copolymerization using DCP. The composites based on PLA and tannin  
 323 acetate with high acetylation degree presented improved Young's modulus and tensile  
 324 strengths as compared with PLA because the initiated DCP radicals contributed to the  
 325 formation of covalent bonding between PLA and tannin acetate. The promoted  
 326 intermolecular interaction of PLA/AT composites results from free radical

327 copolymerization, which can be investigated by the rheology test. The increased  
328 complex viscosity and modulus storage indicates the strong interfacial adhesion of  
329 PLA and tannin acetate. In addition, glass transition temperature, thermal stability and  
330 crystallinity degree of PLA/AT composites were all improved as a result of better  
331 interaction by free radical copolymerization. The enhanced hydrophobicity of  
332 PLA/AT composites may suggest a possible application towards packaging  
333 applications. It is expected that this free radical copolymerization can expand the  
334 application of tannin as a sustainable component for bio-composite preparation.

### 335 **Acknowledgements**

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

### 344 **Notes**

345 The authors declare no competing financial interest.

346

### 347 **Reference:**

- 348 Anwer, M.A.S., Naguib, H.E., Celzard, A., Fierro, V., 2015. Comparison of the  
349 thermal, dynamic mechanical and morphological properties of PLA-Lignin &  
350 PLA-Tannin particulate green composites. *Composites Part B: Engineering* 82,  
351 92–99. <https://doi.org/10.1016/j.compositesb.2015.08.028>
- 352 Bridson, J.H., Grigsby, W.J., Main, L., 2018. One-pot solvent-free synthesis and  
353 characterisation of hydroxypropylated polyflavonoid compounds. *Industrial*  
354 *Crops and Products* 111, 529–535.  
355 <https://doi.org/10.1016/j.indcrop.2017.11.028>
- 356 Bridson, J.H., Grigsby, W.J., Main, L., 2013. Synthesis and characterization of  
357 flavonoid laurate esters by transesterification. *J Appl Polym Sci* 129, 181–186.  
358 <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>

367 Dorgan, J.R., Williams, J.S., Lewis, D.N., 1999. Melt rheology of poly(lactic acid):  
368 Entanglement and chain architecture effects. *Journal of Rheology* 43, 1141–  
369 1155. <https://doi.org/10.1122/1.551041>

370 Fu, S.-Y., Feng, X.-Q., Lauke, B., Mai, Y.-W., 2008. Effects of particle size,  
371 particle/matrix interface adhesion and particle loading on mechanical  
372 properties of particulate–polymer composites. *Composites Part B: Engineering*  
373 39, 933–961. <https://doi.org/10.1016/j.compositesb.2008.01.002>

374 García, D., Carrasco, J., Salazar, J., Pérez, M., Cancino, R., Riquelme, S., 2016. Bark  
375 polyflavonoids from *Pinus radiata* as functional building-blocks for polylactic  
376 acid (PLA)-based green composites. *eXPRESS Polymer Letters* 10, 835–848.  
377 <https://doi.org/10.3144/expresspolymlett.2016.78>

378 García, D.E., Salazar, J.P., Riquelme, S., Delgado, N., Paczkowski, S., 2018.  
379 Condensed Tannin-Based Polyurethane as Functional Modifier of PLA-  
380 Composites. *Polymer-Plastics Technology and Engineering* 57, 709–726.  
381 <https://doi.org/10.1080/03602559.2017.1344855>

382 Grigsby, W.J., Bridson, J.H., Lomas, C., Elliot, J.-A., 2013. Esterification of  
383 Condensed Tannins and Their Impact on the Properties of Poly(Lactic Acid).  
384 *polymers* 5, 334–360. <https://doi.org/10.3390/polym5020344>

385 Grigsby, W.J., Bridson, J.H., Lomas, C., Frey, H., 2014. Evaluating Modified Tannin  
386 Esters as Functional Additives in Polypropylene and Biodegradable Aliphatic  
387 Polyester: Modified Tannin Esters as Plastic Additives. *Macromol. Mater. Eng.*  
388 299, 1251–1258. <https://doi.org/10.1002/mame.201400051>

389 Grigsby, W.J., Kadla, J.F., 2014. Evaluating Poly(lactic acid) Fiber Reinforcement  
390 with Modified Tannins: Evaluating Poly(lactic acid) Fiber Reinforcement ....  
391 *Macromol. Mater. Eng.* 299, 368–378.  
392 <https://doi.org/10.1002/mame.201300174>

393 Jiang, S., 2017. Blending PLLA/tannin-grafted PCL fiber membrane for skin tissue  
394 engineering. *J Mater Sci* 8.

395 Karkhanis, S.S., Stark, N.M., Sabo, R.C., Matuana, L.M., 2018. Water vapor and  
396 oxygen barrier properties of extrusion-blown poly(lactic acid)/cellulose  
397 nanocrystals nanocomposite films. *Composites Part A: Applied Science and*  
398 *Manufacturing* 114, 204–211.  
399 <https://doi.org/10.1016/j.compositesa.2018.08.025>

400 Kumar, A., Tumu, V.R., Ray Chowdhury, S., S.v.s., R.R., 2019. A green physical  
401 approach to compatibilize a bio-based poly (lactic acid)/lignin blend for better  
402 mechanical, thermal and degradation properties. *International Journal of*  
403 *Biological Macromolecules* 121, 588–600.  
404 <https://doi.org/10.1016/j.ijbiomac.2018.10.057>

405 Liao, J., Brosse, N., Hoppe, S., Du, G., Zhou, X., Pizzi, A., 2020a. One-step  
406 compatibilization of poly(lactic acid) and tannin via reactive extrusion.  
407 *Materials & Design* 191, 108603.  
408 <https://doi.org/10.1016/j.matdes.2020.108603>

409 Liao, J., Brosse, N., Pizzi, A., Hoppe, S., 2019a. Dynamically Cross-Linked Tannin as  
410 a Reinforcement of Polypropylene and UV Protection Properties. *Polymers* 11,  
411 102. <https://doi.org/10.3390/polym11010102>

412 Liao, J., Brosse, N., Pizzi, A., Hoppe, S., Xi, X., Zhou, X., 2019b. Polypropylene

413 Blend with Polyphenols through Dynamic Vulcanization: Mechanical,  
414 Rheological, Crystalline, Thermal, and UV Protective Property. *Polymers* 11,  
415 1108. <https://doi.org/10.3390/polym11071108>

416 Liao, J., Brosse, N., Pizzi, A., Hoppe, S., Zhou, X., Du, G., 2020b. Characterization  
417 and 3D printability of poly (lactic acid)/acetylated tannin composites.  
418 *Industrial Crops and Products* 149, 112320.  
419 <https://doi.org/10.1016/j.indcrop.2020.112320>

420 Luo, C., Grigsby, W., Edmonds, N., Eastal, A., Al-Hakkak, J., 2010. Synthesis,  
421 characterization, and thermal behaviors of tannin stearates prepared from  
422 quebracho and pine bark extracts. *Journal of Applied Polymer Science* 117,  
423 352–360. <https://doi.org/10.1002/app.31545>

424 Luo, C., Grigsby, W.J., Edmonds, N.R., Al-Hakkak, J., 2014. Rubber-Like Materials  
425 Prepared from Copolymerization of Tannin Fatty Acid Conjugates and  
426 Vegetable Oils. *Macromolecular Materials and Engineering* 299, 65–74.  
427 <https://doi.org/10.1002/mame.201300039>

428 Luo, C., Grigsby, W.J., Edmonds, N.R., Al-Hakkak, J., 2013. Vegetable oil  
429 thermosets reinforced by tannin–lipid formulations. *Acta Biomaterialia* 9,  
430 5226–5233. <https://doi.org/10.1016/j.actbio.2012.08.048>

431 Luo, S., Cao, J., McDonald, A.G., 2018. Cross-linking of technical lignin via  
432 esterification and thermally initiated free radical reaction. *Industrial Crops and*  
433 *Products* 121, 169–179. <https://doi.org/10.1016/j.indcrop.2018.05.007>

434 Luo, S., Cao, J., McDonald, A.G., 2016. Interfacial Improvements in a Green  
435 Biopolymer Alloy of Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) and  
436 Lignin via in Situ Reactive Extrusion. *ACS Sustainable Chem. Eng.* 4, 3465–  
437 3476. <https://doi.org/10.1021/acssuschemeng.6b00495>

438 Monika, Pal, A.K., Bhasney, S.M., Bhagabati, P., Katiyar, V., 2018. Effect of  
439 Dicumyl Peroxide on a Poly(lactic acid) (PLA)/Poly(butylene succinate)  
440 (PBS)/Functionalized Chitosan-Based Nanobiocomposite for Packaging: A  
441 Reactive Extrusion Study. *ACS Omega* 3, 13298–13312.  
442 <https://doi.org/10.1021/acsomega.8b00907>

443 Nicollin, A., Zhou, X., Pizzi, A., Grigsby, W., Rode, K., Delmotte, L., 2013. MALDI-  
444 TOF and <sup>13</sup>C NMR analysis of a renewable resource additive—Thermoplastic  
445 acetylated tannins. *Industrial Crops and Products* 49, 851–857.  
446 <https://doi.org/10.1016/j.indcrop.2013.06.013>

447 Pizzi, A., 1980. Tannin-Based Adhesives. *Journal of macromolecular science* 18,  
448 247–315.

449 Quideau, S., Deffieux, D., Douat-Casassus, C., Pouysegue, L., 2011. Plant polyphenols:  
450 chemical properties, biological activities, and synthesis. *Angewandte Chemie*  
451 *International Edition* 50, 586–621.

452 Ren, J., 2011. *Biodegradable Poly(Lactic Acid): Synthesis, Modification, Processing*  
453 *and Applications*. Springer Berlin Heidelberg, Berlin, Heidelberg.  
454 <https://doi.org/10.1007/978-3-642-17596-1>

455 Song, P., Jiang, S., Ren, Y., Zhang, X., Qiao, T., Song, X., Liu, Q., Chen, X., 2016.  
456 Synthesis and characterization of tannin grafted polycaprolactone. *Journal of*  
457 *Colloid and Interface Science* 479, 160–164.  
458 <https://doi.org/10.1016/j.jcis.2016.06.056>

459 Song, Y., Zong, X., Wang, N., Yan, N., Shan, X., Li, J., 2018. Preparation of  $\gamma$ -  
460 Divinyl-3-Aminopropyltriethoxysilane Modified Lignin and Its Application in  
461 Flame Retardant Poly(lactic acid). *Materials* 11, 1505.  
462 <https://doi.org/10.3390/ma11091505>



463 Thébault, M., Pizzi, A., Essawy, H.A., Barhoum, A., Van Assche, G., 2015.  
464 Isocyanate free condensed tannin-based polyurethanes. *European Polymer*  
465 *Journal* 67, 513–526. <https://doi.org/10.1016/j.eurpolymj.2014.10.022>

466 Tolinski, M., 2015. Additives for polyolefins: getting the most out of polypropylene,  
467 polyethylene and TPO, Second edition. ed, PDL handbook series. Elsevier,  
468 William Andrew is an imprint of Elsevier, Kidlington, Oxford, UK.

469 Wei, L., McDonald, A.G., 2015. Peroxide induced cross-linking by reactive melt  
470 processing of two biopolyesters: Poly(3-hydroxybutyrate) and poly(l-lactic  
471 acid) to improve their melting processability. *Journal of Applied Polymer*  
472 *Science* 132. <https://doi.org/10.1002/app.41724>

473 Wei, L., McDonald, A.G., Stark, N.M., 2015. Grafting of Bacterial  
474 Polyhydroxybutyrate (PHB) onto Cellulose via In Situ Reactive Extrusion  
475 with Dicumyl Peroxide. *Biomacromolecules* 10.

476 Yamoum, C., Maia, J., Magaraphan, R., 2017. Rheological and thermal behavior of  
477 PLA modified by chemical crosslinking in the presence of ethoxylated  
478 bisphenol A dimethacrylates: Rheological and Thermal Behaviors of PLA  
479 with Bis-EMA Crosslinking. *Polym. Adv. Technol.* 28, 102–112.  
480 <https://doi.org/10.1002/pat.3864>

481 Yang, W., Weng, Y., Puglia, D., Qi, G., Dong, W., Kenny, J.M., Ma, P., 2020.  
482 Poly(lactic acid)/lignin films with enhanced toughness and anti-oxidation  
483 performance for active food packaging. *International Journal of Biological*  
484 *Macromolecules* 144, 102–110.  
485 <https://doi.org/10.1016/j.ijbiomac.2019.12.085>

486 Yu, H.-Y., Zhang, H., Song, M.-L., Zhou, Y., Yao, J., Ni, Q.-Q., 2017. From  
487 Cellulose Nanospheres, Nanorods to Nanofibers: Various Aspect Ratio  
488 Induced Nucleation/Reinforcing Effects on Polylactic Acid for Robust-Barrier  
489 Food Packaging. *ACS Appl. Mater. Interfaces* 9, 43920–43938.  
490 <https://doi.org/10.1021/acsami.7b09102>

491 Yu, L., Petinakis, E., Dean, K., Liu, H., Yuan, Q., 2011. Enhancing compatibilizer  
492 function by controlled distribution in hydrophobic polylactic acid/hydrophilic  
493 starch blends. *Journal of Applied Polymer Science* 119, 2189–2195.  
494 <https://doi.org/10.1002/app.32949>

495 Zhou, L., He, H., Li, M., Huang, S., Mei, C., Wu, Q., 2018. Enhancing mechanical  
496 properties of poly(lactic acid) through its in-situ crosslinking with maleic  
497 anhydride-modified cellulose nanocrystals from cottonseed hulls. *Industrial*  
498 *Crops and Products* 112, 449–459.  
499 <https://doi.org/10.1016/j.indcrop.2017.12.044>

500

