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Abstract: The compatibility issue between poly(lactic acid) (PLA) and tannin is a big challenge for preparing PLA/tannin biocomposites with enhanced properties. In this work, composites with enhanced properties have been accomplished using an efficient one-step reactive extrusion method with the help of methylene diphenyl diisocyanate (p-MDI) or 3-aminopropytriethoxysilane (APS). The extent of compatibility achieved via the one-step was evaluated by tensile, morphological, rheological, and thermal properties. The obtained results indicated that the adhesion promoters, especially p-MDI, contributed efficiently to an improved tensile behavior of the resulting composites with a tough tensile-fracture surface compared with incompatibilized PLA/tannin composite. Moreover, these composites displayed a plateau-like rheological behavior, enhanced complex viscosity, higher melting and thermal degradation temperature. This approach can be potentially adapted to other PLA/biopolymers composite systems.

Keywords: poly (lactic acid), condensed tannin, reactive extrusion, isocyanate, silane

1. Introduction

Polylactic acid (PLA) is a promising green polyester that obtained from agricultural products such as corn, sugar cane, and sugar beet via polycondensation or ring-opening polymerization process [1]. It is one of the most promising candidates to replace fossil-

based polymers to develop fully biocomposites as a result of some favorable attributes, such as sustainability, biocompatibility, biodegradability, favorable mechanical properties. PLA is also considered suitable to develop biocomposites with various fibers, fillers and/or polymers [2] through an efficient process like extrusion because of its good thermal processability [3]. Recently, biocomposites consist of PLA and natural fillers are drawing more global attentions since both polymer matrix and fillers are sustainable and degradable, which can minimize the environmental concerns [4–6]. So far, the incorporation of PLA and bio-fillers has been reported to be an efficient and useful approach to develop relatively inexpensive biocomposites with superior characteristics [7,8], such as strength [9,10], flame retardancy [11,12], thermal stability [13], gas barrier [14]. Some of these biocomposites have been successfully applied in the field of packaging, textile sectors, medical devices, and others owing to the improved compatibility between hydrophilic biopolymers and hydrophobic PLA polymer matrix [2].

Condensed tannins, composed of flavonoid units, are one of the most abundant and sustainable biopolymers in the plant. Figure 1 displays a simple flavonoid structure, which represents four main structure of flavonoid units in condensed tannin. Their characteristics like antioxidant, antimicrobial and stabilizing properties are attracting for polymer materials. It has been shown that tannins displayed antioxidant and UV-protective properties on polypropylene [15,16], polyethylene [17], poly (vinyl chloride) (PVC) [18], and polyvinyl alcohol [19]. Recently, a study reported the incorporation of tannins and PLA [20]. However, the presence of highly polarized hydroxyl groups in tannin molecules makes it difficult to achieve good compatibility due to the low polarity PLA matrix, resulting in poor interfacial adhesion and dispersion of tannin in the PLA matrix. Esterification and hydroxypropylation of tannin have performed in order to increase the compatibility and the dispersion capacity with various plastic matrix [21–26], guaranteeing sucessful applications like carbon fiber precusors [22] or functionalized composites [23]. However, a series of complex pretreated processes, involving long-term chemical reaction, precipitation, filtration, and purification, should

be performed before compounding with a polymer matrix. Hence efficient and cost effective modification and continuous processing techniques are required for exploring more possible applications with a competitive prices. Inspired by the chemical reactivity of tannins, it is possible to improve the interfacial adhesion of PLA-tannin via one-step compatibilization approach with suitable compatibilizers/coupling agents [27,28].

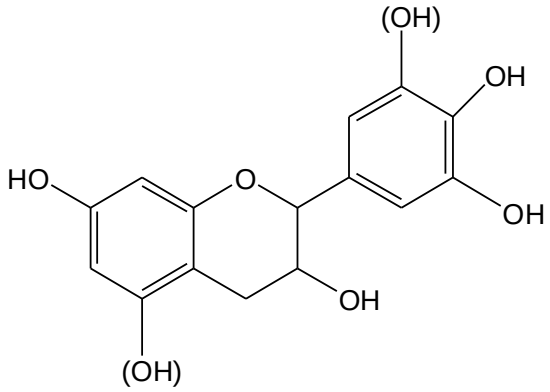


Figure 1. Simple structure of flavonoid unit of condensed tannins

One-step compatibilization is a well documented approach to develop composites with good compatibilization [29–32], through which chemical reaction occurs between each component during the melt blending process with the help of adhesion promoters (e.g. coupling agents, compatibilizers) [2,29]. Hence, this method can promote the interfacial adhesion of components and consequently the dispersion of the fillers in the polymer matrix during melt extrusion [33,34]. However, only few literature reports have addressed biocomposites prepared via reactive extrusion in one step [35,36].

Isocyanate derivatives are widely used as adhesion promoters to improve the interface between PLA and biofillers because isocyanate group is highly reactive towards hydroxyl moieties, yielding a urethane linkage between the polymer and natural fillers [37–40]. As a result, composites based on a high content of lignin (up to 65%) and polybutylene succinate (PBS) using polymeric methylene diphenyl diisocyanate as a compatibilizer were prepared via melt mixing process and displayed an improved interfacial adhesion [41]. Tannins containing various hydroxyl groups and PLA chains bearing functional end-extremities (e.g. hydroxyl and carboxylic acid), can both react with diisocyanate [27,28]. García [42] reported the utilization of polymeric methyl

diisocyanate to improve the compatibility between hydroxypropyl tannin and PLA matrix through a polymerization during the melt-blending in a rheometer chamber. The crosslinking-grafting reaction during the melt-blending was evidenced by the carbamate moiety (R1–O–CO–NH–R2) identified by the FTIR analysis and a typical fluorescence pattern detected by confocal microscopy. Thus, isocyanates can be utilized to enhance the compatibility of hydrophilic tannin with hydrophobic PLA.

The phenolic hydroxyl groups of tannins can easily react with amine even at room temperature [43–46]. On this basis, silane bearing amine functional groups could be a suitable adhesion promoter for processing polymeric composites containing tannin. The work of Zhu reported that the mechanical properties of flax/tannin composites were boosted by aminopropytriethoxysilane (APS) [47]. Amino-silanes are commonly found to improve the interfacial bonding of biofillers containing numerous hydroxyl groups (e.g. fiber, flax, wood flour) and PLA matrix [48–51]. According to the work of Lu and co-workers, the primary amine group of APS can react with PLA via ammonolysis to form covalent bonding between cellulose and PLA under mild conditions [48]. The hydrolysis and condensation reaction of alkoxysilanes are shown in Figure 2. Under suitable conditions, silanes undergo hydrolysis, alcohol condensation, and/or water condensation to create Si-O-Si bonds. Based on this mechanism, Meng created a super tough PLA-silane nanohybrids via in situ crosslinking PLA-silanes [52]. Amino-silane was also reported to improve the interfacial interaction of PLA-nanocellulose based on the successful silane grafting of PLA via melt blending [50]. Therefore, amino-silanes were supposed to improve the interfacial adhesion of PLA-tannin via reactive extrusion.

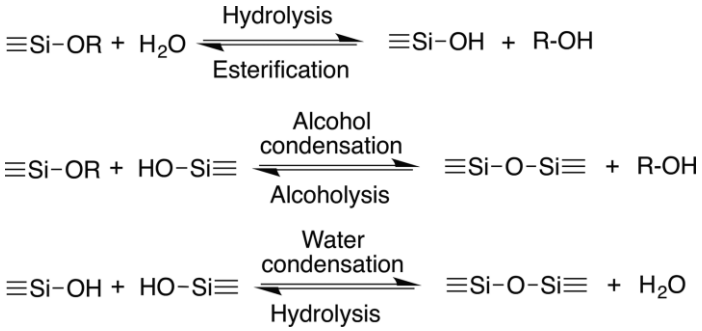


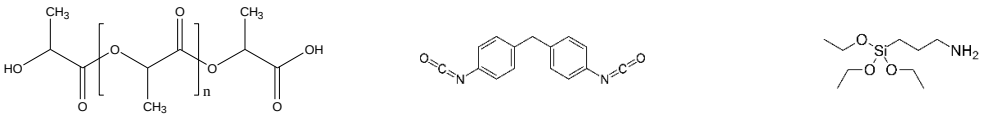
Figure 2. Hydrolysis and condensation reactions of alkoxysilanes [52]

Inspired by those previous studies, we report here a simple one-step efficient method to improve the compatibility between PLA and tannin via reactive extrusion. Methylene diphenyl diisocyanate (p-MDI) and 3-aminopropytriethoxysilane (APS) were chosen as adhesion promoters. The final composites were characterized by tensile, morphological, rheological, and thermal properties.

2. Materials and Methods

2.1. Materials

PLA trademarked under the name of IngeoTM Biopolymer (Grade 3D850), was obtained from Natureworks LLC (Minnesota, USA). Mimosa tannins were purchased from Silva Chimica, in Mondovi, Italy. Methylene diphenyl diisocyanate (p-MDI) was used as a compatibilizer, which is a commercial resin with 57% polyisocyanates content fabricated by Bayer. Silane coupling agent (3-aminopropytriethoxysilane, APS, 98%) was obtained from Alfa Aesar. The chemical structures of the used chemicals and PLA are presented in Figure 3.



PLA p-MDI APS

Figure 3. Chemical structures of PLA, p-MDI, and APS

2.2. Preparation of PLA/tannin composites

PLA was ground into powder by a grinder for better mixing with tannin. PLA and tannin (T) powder were oven-dried at 80°C for more than 12 hours to eliminate possible absorbed water on the surface. The blending ratio of PLA and T was 90/10 (w/w). The silane was fed directly via syringe, while p-MDI was diluted with acetone (p-MDI: acetone=75:25 v/v) to reduce the viscosity before injection.

The blending of PLA and T was carried out in a twin-screw extruder (Thermo Scientific^{TM} Process 11, Villebon-sur-Yvette, France). The temperature of the die and the heating zones across the extruder barrel are shown in *Table 1*. The screw speed was 100

rpm and the residence time was 4 min approximately. In the current experiment, the screw profile was designed two mixing zones for obtaining effective mixing perform: zone 1 designed before the addition of compatibilizer for premixing PLA and tannin, while zone 2 aimed to guarantee well blend with compatibilizer. The adhesion promoters were fed by using a syringe, the injecting speed was controlled by a syringe pump (WPI, SP120PZ, MA, USA). The flow rate of PLA/T powder was 6.6 g/min while the flow rate speed of the silane and p-MDI was 0.8 g/min and 1 g/min, respectively, to ensure the ratio of compatibilizer was approximately 12%. The PLA/tannin blend without compatibilizer noted as PLT, while with silane and p-MDI were named as PLTSi and PLTM, respectively.

The extruded composite materials were ground into small particles by a grinder for further use. The tensile test specimens (dumbbell-shaped, ISO 527, type 1A) were carried out by a micro-compounder (Micro 15, DSM Xplore, Sittard, Netherlands) and a micro-injection molder (Xplore, Sittard, Netherlands).

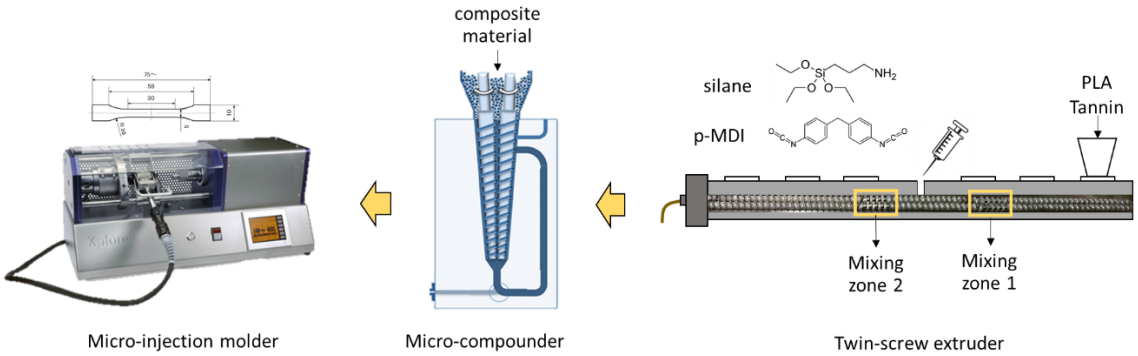


Figure 4. From right to left: reactive extrusion using a twin-screw extruder, the specimens molding process by micro-compounder and micro-injection molder.

Table 1. Temperature of screw profile

Zone	die	8	7	6	5	4	3	2	1
T (°C)	185	155	180	190	190	190	200	200	200

2.3. Characterizations

The tensile test was performed at room temperature on Instron tensile testing

machine (model 5569, Norwood, MA, USA) equipped with a 50 kN load cell. The cross-head speed used was of 1 mm/min according to EN ISO 527:1996. Four replicates were tested for each sample to obtain an average value.

The morphology of fracture surface after the tensile test was characterized by a scanning electron microscopy (SEM, JSM-6490LV, Tokyo, JAPAN) with an acceleration voltage of 5kV. All the samples were coated with a thin layer of gold by using a Polaron SEM coating system (SC7620, Hertfordshire, England) for 5 min at a current between 4 and 5 mA.

Rheological properties of PLA/tannin composites were analyzed on a rheometer (TA instrument, G2 ARES, New Castle, DE, USA) using a parallel-plate geometry (25 mm diameter, 1 mm gap) under a nitrogen atmosphere, in order to prevent thermo-oxidative degradation. Dynamic strain sweep tests to determine the linear viscoelastic region (LVR) was realized at 1 rad/s, in a range of 0.1-1000%, resulting in a strain applied of 10% chosen for frequency tests. Dynamic frequency sweep tests were performed over an angular frequency range of 0.1-623.3 rad/s at 190℃.

The Differential scanning calorimetry (DSC) analysis was carried out using a Metter Toledo DSC 1 (Columbus, Ohio, USA) with a scan rate of 10°C/min within the temperature range of 30°C to 220°C and 220°C to -10°C in the second scanning cycle. A total sample weight 3-4 mg was used for measurement in a aluminum pan under a nitrogen atmosphere (50 mL/min). Melting temperatures (T_m), enthalpy of melting (ΔH_m) and cold crystallization (ΔH_c) were analyzed by STARe evaluation software (version 10.00). ΔH_m^0 is the enthalpy of melting 100% crystallized PLA, which is equal to 93.7 J/g [53], and w is the weight fraction of PLA. The percentage crystallinity X_c (%) was estimated by the following equation (1):

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

Thermogravimetric analysis (TGA) was performed by using a Metter Toledo TGA/DSC (Columbus, Ohio, USA). The samples with a total weight in the 6–7 mg range were scanned in the range of 30-600°C with a heating rate 10°C/min in an air atmosphere (50

mL/min). The obtained data were analyzed by STARe evaluation software (version 10.00).

3. Results and discussion

3.1. Tensile property

Figure 5 presents the strain-stress curves of PLA/tannin composite with or without adhesion promoters and related data was given in table 2. Compared with PLA, PLA/tannin composite without adhesion promoters (PLT) presented a comparable Young's modulus but a lower tensile strength due to the weak interfacial adhesion of PLA-tannin. With the addition of a compatibilizer (PLTM or PLTSi), an increase of both Young's moduli and tensile strengths were observed. For thermoplastic composite materials, Young's moduli are generally improved by adding a filler because the filled components restrict the chain mobility of the polymer chain [54]. The tensile strength of PLTM and PLTSi are 19.1% and 12.8% higher than that of PLT, respectively, referring to better interfacial adhesion between tannin and PLA matrix. While the elongation of PLA/tannin blends was observed a decrease without exception compared with neat PLA since lack of plasticizers to release the stress concentration between the interface of tannin and PLA [55]. These results are in agreement with the work of García [42].

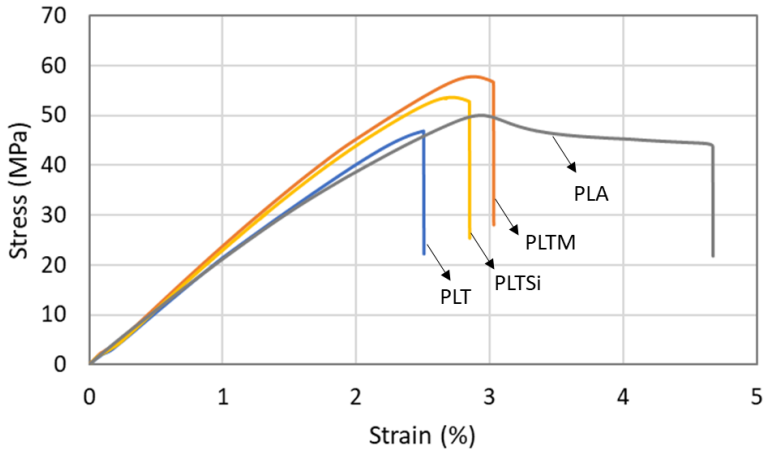


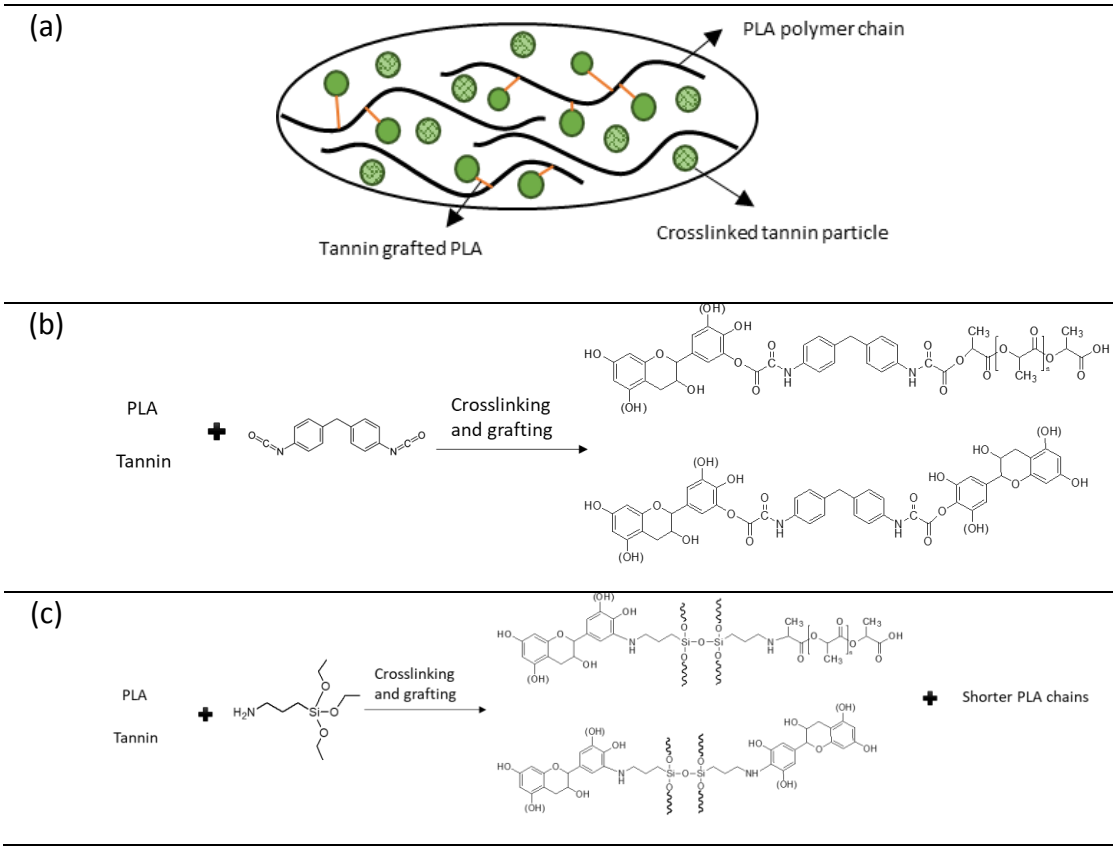
Figure 5. Strain-stress curves of PLA/tannin composites

Table 2. Main tensile properties of PLA/tannin composites

Sample	Young's modulus (GPa)	tensile strength (MPa)	Elongation (%)
PLA	3.5±0.1	50±1	4.7±0.5
PLT	3.5±0.3	47±3	2.5±0.2
PLTM	3.9±0.3	56±1	3.0±0.2
PLTSi	3.8±0.3	53±1	2.8±0.1

The changes of tensile property can be explained by the interaction of PLA, tannin, and p-MDI/Silane, forming crosslinked tannin particles and/or local crosslinking and interpenetrating network structure of tannin-PLA during the melt blending process. The proposed representative microstructure of PLA/tannin composites compatibilized by p-MDI/APS was represented in Scheme 1 (a) and all possible reactions have been listed in Scheme 1 (b-c). Taking into account the well known high reactivity of tannins with nucleophilic reagents in general and the reaction of PLA by both hydroxyl and carboxylic acid groups with isocyanates under mild conditions [56]. The chemical reaction of PLA and tannin was achieved using p-MDI via melt-blending as reported by García and his colleagues Scheme 1 (b)) [42]. For silane coupling agent, PLA and tannin were proposed to crosslink with APS through electrophilic substitution and / or ester-amide exchange reaction (Scheme 1 (c)) [48,52]. In the blending system, tannin was proposed to crosslink with p-MDI/APS leading to the formation of stiff thermoset particles, these particles will be dispersed in the PLA matrix as internal crosslinked domains. Considering that these particles are still functionalized with a variety of reactive function groups thereby it will act further as local crosslinking points to connect the chains of PLA. Thus, the crosslinking-grafting reactions between PLA, tannin and p-MDI/APS created a complicated network, with upgraded interfacial adhesion and remarkable stress transfer between the two phases. This contributes to the improvement of tensile strength compared with PLT.

Scheme 1. The proposed representative microstructure of PLA/tannin composites and illustration of the proposed crosslinking-grafting reactions between PLA, tannin and p-MDI/APS



The morphology of tensile-fracture surface of each sample was observed by SEM microscopy and the SEM micrographs are displayed in Figure 6. The fracture surface of PLA is relatively smooth and PLA/tannin composites present a distinct coarse fracture surface. Similar with the study of Answer et al [20], it is difficult to identify tannin particles between PLA and tannin since tannin was generally wetted by PLA matrix. The coarse region of PLA-tannin blends is the deboned interface (marked in yellow arrows) at regions of higher stress intensity during fracture. From these areas, composites with compatibilizer displayed tougher and deeper interfacial gaps compared with native PLA/tannin composite, referring a stronger interfacial adhesion between filler and polymer matrix. Similar phenomena can be found in the PLA/starch composites compatibilized by isocyanate [38] and chemical crosslinked PLA [53].

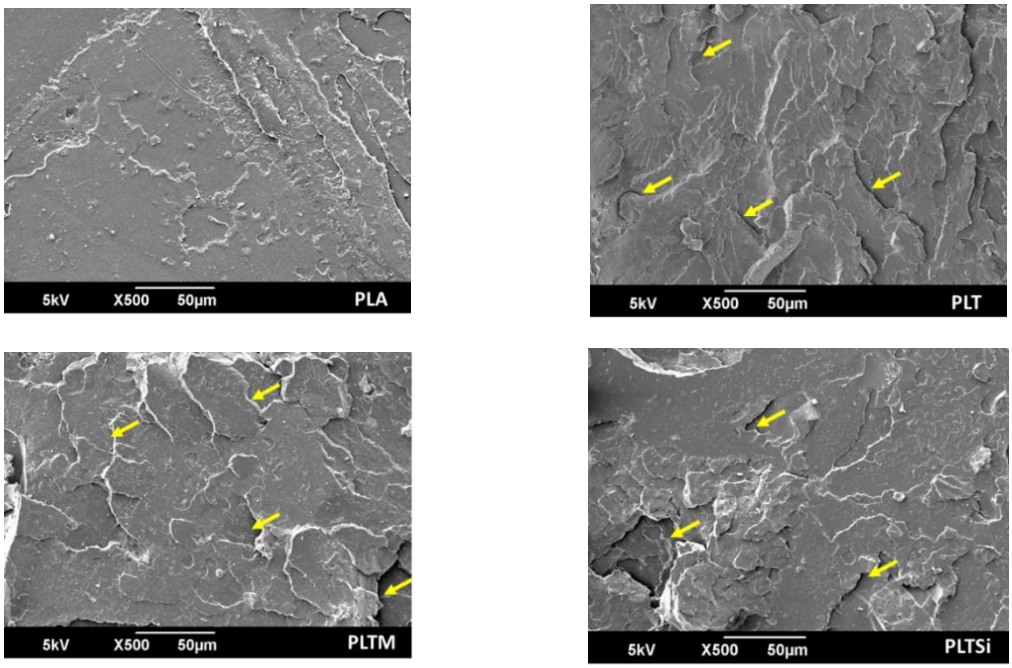


Figure 6. SEM micrographs of the tensile-fracture surface of PLA and PLA/tannin composites.

3.2. Rheological property

The measurement of rheological properties of polymeric materials under the molten state is useful to detect changes in the molecular structure via a one-step compatibilization process. The complex viscosity and storage modulus were used to explore the flow behavior as a result of all acting interactions in PLA-tannin composites. As presented in Figure 7, complex viscosity in all curves decreased as a function of angular frequency, exhibiting a typical shear-thinning behavior. The introduction of tannin in PLA results in a sharply decrease of complex viscosity because of poor interfacial adhesion between PLA and tannin and absence of uniform distribution. However, PLA/tannin composite compatibilized with APS or p-MDI (PLTSi or PLTM) displayed an enhanced complex viscosities compared with incompatibilized composite (PLT), suggesting the formation of bonding between tannin and PLA polymer chain and/or crosslink of tannin (see Scheme 1). This increase in complex viscosity is particularly marked for PLTM and with the association of improved tensile strength and tougher tensile-fracture surface, indicating a stronger interfacial adhesion between two components. As previously described for filled polymer systems, a plateau-like behavior

of storage modulus was observed in all PLA/tannin composites at low frequency (<5 rad/s), suggesting that the presence of tannin limited the mobility of polymer chains and reinforced the internal network structure [57,58]. For PPTM and PPTSi, the network structure created by the crosslinking-grafting reaction of PLA could also contribute to such plateau-like behavior. PLTSi exhibited lower complex viscosity and storage modulus compared with PLTM since the reaction between APS and PLA generated shorter chain since the amine group on APS reacted with PLA through ester-amide exchange reactions, resulting in chain scission [52], see Scheme 1 (c). These results are in accordance with the work of Meng [52].

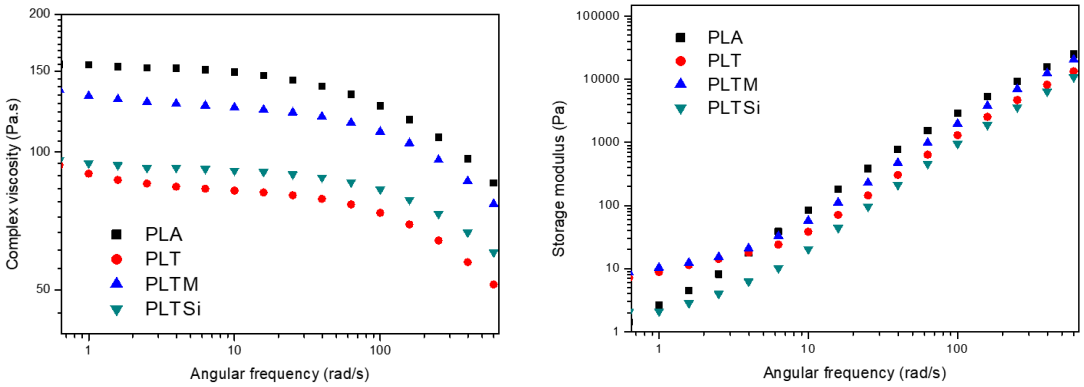


Figure 7. Rheological behavior of PLA and PLA/tannin composites

3.3. Crystallization and melting behavior

The effect of tannin and compatibilizers on the glass transition temperature, crystallization and melting behavior of PLA and PLA/tannin composites were characterized by differential scanning calorimetry (DSC), and are shown in Figure 8. The related results from the second heat-cool circle are given in Table 3. All samples displayed clear glass transition, cooling crystallization and melting peak. Compared with PLA, a slight shift to a higher temperature for T_g and T_c of PLA/tannin composites was observed indicating a decrease in the mobility of polymer molecules in the vicinity of the interface [59]. This is generally found in the blends of PLA and bio-fillers even without compatibilizers, such as starch [4], cellulose [50], coconut shell powder [51], etc. PLA exhibited two obvious melting peaks revealing two kinds of lamellae structure. The low-melting peak is attributed to an imperfect crystal structure, while the high-melting peak

refers to a more orderly crystal structure [60]. The addition of tannin inhibited the crystallization of PLA, thus, PLT has a broad melting enthalpy and the crystallinity of PLA disappeared. However, T_m of PLA/tannin composites shifts to a higher temperature by adding p-MDI or APS, referring to an improvement of the interfacial interaction between tannin and PLA matrix. Similar results can be found in PLA biocomposites compatibilized by either isocyanates [38,42,61,62] or silanes [50,63]. The crosslinking structure in PLA polymer may also inhibit chain segments motion for crystallization [53], thus, a decrease of X_c can be found in PLTM and PLTSi.

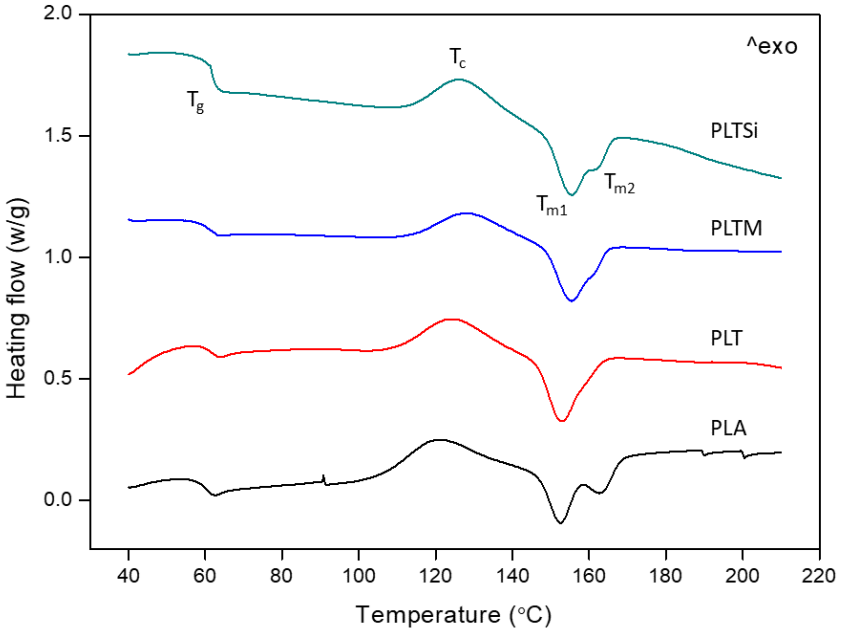


Figure 8. DSC thermograms of PLA and PLA/tannin composites

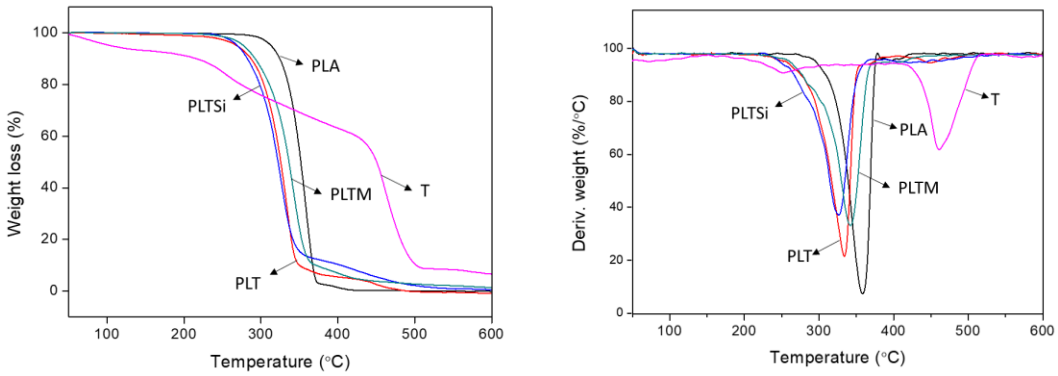
Table 3. DSC data of PLA and PLA/tannin composites

Sample	T_g (°C)	ΔH_c (J/g)	T_c (°C)	ΔH_m (J/g)	T_{m1}; T_{m1} (°C)	X_c (%)
PLA	55.9	14.0	120.4	20.7	152.5;162.9	8.0
PLT	58.6	17.8	125.2	14.7	152.8	--
PLTM	57.2	9.6	128.0	15.7	155.3;161.4	7.3
PLTSi	60.0	15.9	126.8	17.0	155.4;161.9	1.2

Note: no crystallinity: --.

3.4. Thermal property

The thermal degradation behavior of tannin, PLA and PLA/tannin blends was determined by thermogravimetric analyses in an air atmosphere. Their weight losses as a function of temperature and differential thermal gravity (DTG) data are presented in Figure 9. Tannin exhibits a three-step degradation process, which include the loss of adsorbed water, the decomposition of linkage between flavonoid units and pyrolytic degradation [64]. PLA and PLA/tannin blends showed a one-step degradation process, which was represented by a single peak as shown in the DTG curves, while char formation can be observed with the addition of tannin at high temperature (~350°C) during the pyrolysis process. The char acts as a protective barrier that can suppress the thermal decomposition of the PLA matrix [51]. Tannin results in a lower onset decomposition temperature which can be explained by the reduction of crystallinity of PLA/tannin blends. Besides, the decomposition process of composites also relies on the thermal stability of each component, interfacial adhesion between the two components and molecular weight of the polymer matrix [38,42]. The higher decomposition temperature of PLTM can be further confirmed the improvement of interfacial adhesion, which can be found PLA/biopolymer composites compatibilized with isocyanate [38,61]. In accordance with Meng [52], the decomposition temperature of PLTSi is close to that of PLT, probably due to ester-amide exchange reactions of PLA and APS, causing chain scissions. The higher residues of PLTSi and PLTM at a high temperature can be rationalized by the crosslinked network between PLA and tannin.



(a) (b)

Figure 9. Thermal analysis profile of PLA and PLA/tannins composites: (a) TGA curves; (b) DTG curves.

4. Conclusions

PLA/tannin biocomposite showing good compatibility can be successfully processed via one-step reactive extrusion with the help of p-MDI or APS. The compatibilized composites acquire a stronger interfacial adhesion between PLA and tannin, leading to superior tensile strength and Young's modulus compared with incompatibilized PLA/tannin composite. The compatibilized composites acquire a stronger interfacial adhesion between PLA and tannin, leading to superior tensile strength and Young's modulus compared with incompatibilized PLA/tannin composite. Moreover, higher melting temperature and onset of thermal degradation of resulting composite evidenced an elevated capacity for compatibility using p-MDI. Thus, this approach could be applied to efficiently prepare similar PLA-based biocomposites.

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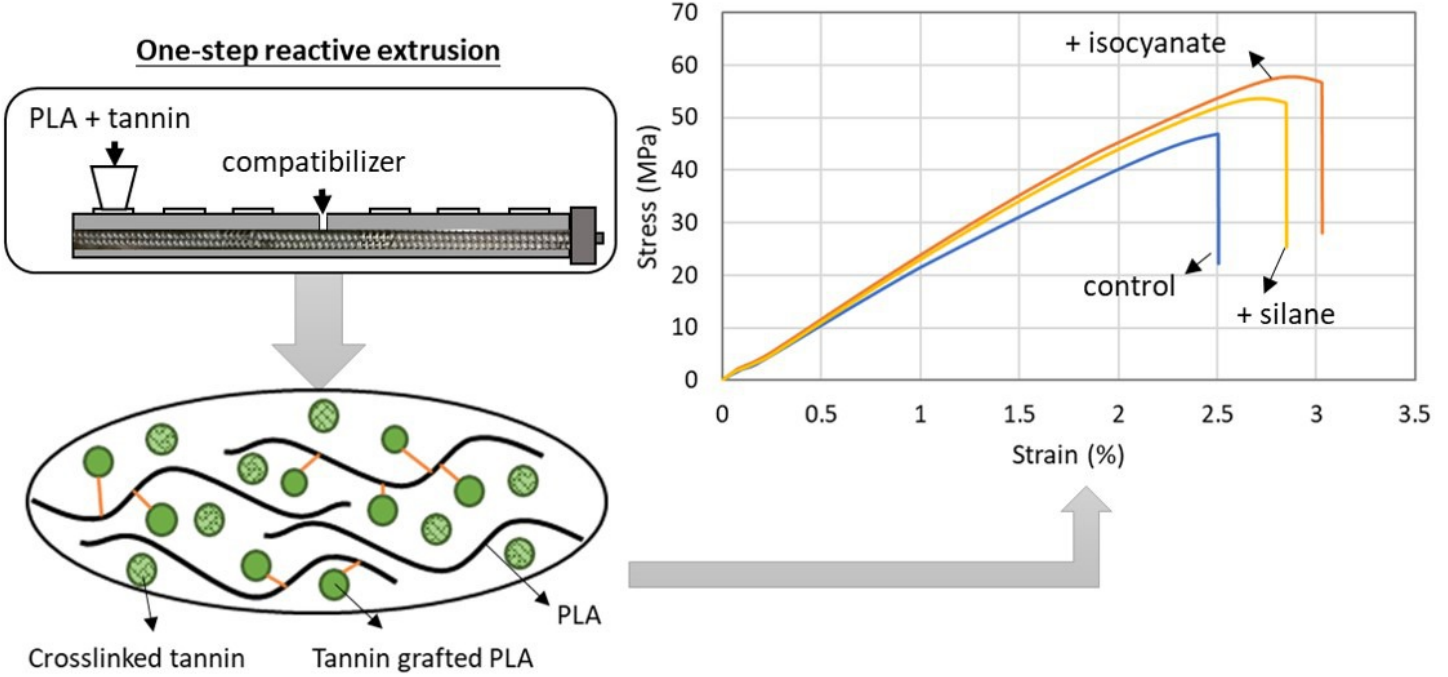
One-step reactive extrusion
PLA + tannin
compatibilizer
Crosslinked tannin
Tannin grafted PLA
PLA
Stress (MPa)
Strain (%)
+ isocyanate
control
+ silane
0
10
20
30
40
50
60
70
0
0.5
1
1.5
2
2.5
3
3.5