



Research Paper

“Green” bio-thermoset resins derived from soy protein isolate and condensed tannins



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ABSTRACT

The condensed tannins (CTs) have a similar catechol structure compared with mussel protein's high water resistance structure, thus, CTs was used to mix with soy protein isolate (SPI) to develop a thermoset resin. Different pH condition was applied to catalyze the reaction of CTs and SPI. The chemical structure, thermal degradation behavior, fracture morphology, and physical characteristics of the resulting resins were tested. The resultant resin was applied on plywood fabrication and its wet shear strength was measured. Results showed that, in the acid condition, the catechol structure on B ring was protected and the active sites (C6 and C8) of A-ring reacted with functions and formed a crosslinking network with SPI, which effectively brought catechol into SPI. In the alkaline condition, the catechol structure on B ring of CTs was oxidized and formed an ortho-quinone to crosslink SPI and then formed a denser structure. This crosslinked structure formed by both ways improved the water resistance of the resultant resin, also, the structure led to a better thermostability and created a homogeneous fracture surface of the resin, which further increased the resin's water resistance. The wet shear strength of the plywood bonded by the ac ST 2.5 and al ST 5 resin reached at 1.07 and 0.95 MPa, which was a 75.4% and 55.7% higher than that of SPI resin. The resultant resins had favorable water resistance, suitable viscosity, cost-effective, and easy to handle, which were potential for industry application.

1. Introduction

Thermoset resins are a crucial component in a vast array of manufacturing fields such as plasticizers, coatings, aerospace, and housing construction (Bakare et al., 2014). Most thermoset resins are utilizing petroleum as the raw material, including epoxies, unsaturated polyesters, and formaldehyde-based resins (Yao et al., 2016; Ureñabenaides et al., 2013; Shukla et al., 2014). However, these resins have hazardous emission issue and are non-biodegradable. Thus the search for alternative, eco-friendly thermoset resins from renewable resources has garnered a great deal of research attention in recent years.

Soy protein-based resins show notable advantages including low cost, ease of handling, and ready availability. It was commonly applied as wood adhesive for the production of plywood between the 1930s and 1960s. After the 1960s, the soy protein adhesive was gradually replaced by formaldehyde-based adhesives (Gao et al., 2012). In recent years, under the threat of formaldehyde emissions and petroleum scarcity issues, soy protein materials have again been explored as potential thermoset resins. However, their low bonding strength and poor water resistance limit their application.

Researchers have explored chemical modifications to improve soy

protein resin's properties. Recently, the polyamidoamine-epichlorohydrin (PAE) and epoxide (Luo et al., 2015a) have been proved used as effective cross-linkers, which could react with the $-NH_2$, $-COOH$, and other exposed groups of protein to increase the cross-linking density of soy protein resins, so that, the wet shear strength of the resultant plywood meet the interior use of China National Standard (GB/T 9846.3-2004) requirement (Gui et al., 2013). However, the addition of these cross-linkers exceeded 50% compared to the soy protein content in the formulation, which means the soy protein adhesive also depended on petroleum-derived materials. Further, the use of these cross-linkers would result in a large amount of waste at the end of the product life. Though methods of recycling similar products are available, they are far from ideal (Kim and Netravali, 2016).

Due to the exceptional adhesive performance in wet and turbulent environments, mussels represent attractive targets for biomimetic research. An important structural component of these proteins is 3,4-dihydroxyphenylalanine (DOPA, Fig. 1a), which has catecholic functionality (Lee and Konst, 2014; Lee et al., 2011). According to Martinez-Rodriguez et al. (2015), DOPA serves as a key cross-linking mediator in the material's outstanding mechanical properties. For the purpose of improving the performance of soy protein-based thermoset resin, DOPA

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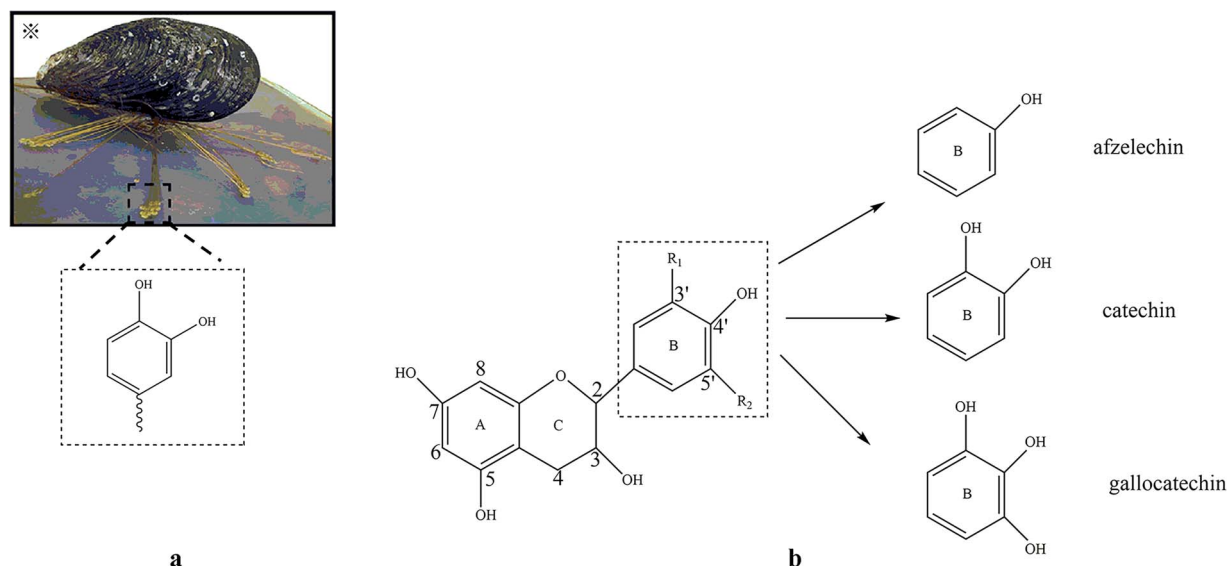


Fig. 1. Chemical structures of DOPA (a) and flavonoid ring system of CTs (b). (✱Martinez-Rodriguez et al., 2015).

was introduced into soy protein-based thermoset resin. The high cost of mussel proteins restricts their application, however; therefore, an inexpensive, sustainable material containing DOPA structure mimicking mussel proteins is an attractive research object in regards to enhancing the performance of soy protein-based resins. The condensed tannins (CTs) show intriguing potential for mimicking mussel proteins based on their catechol-laden structural features. The common skeleton of CTs are shown in Fig. 1b (Chen et al., 2014). The B ring of CTs has a similar catechol ring to DOPA. While the position of the hydroxyl groups on the A ring can be referred to as a meta-substitution pattern. The most famous reaction associated with the A ring is the polycondensation reaction mediated by acetaldehyde under acidic conditions, in which the meta-substitution pattern becomes electrophilic aromatic substitution. Based on their inherent structural features, CTs have a high reactivity and been explored for many applications including phenol-formaldehyde resins, leather dyeing, and ion exchange resins in recent years (Zhou et al., 2013; Falcão and Araújo, 2014; Vidal and Pereira, 2015).

Recent years there are continually increasing demand for eco-friendly products manufactured via sustainable processes. Based on these principles, the goal of the present study was to develop novel bio-thermoset resins derived from soy protein isolate (SPI) and CTs. The proposed synthesis process is “green”, as it does not necessitate the addition of any catalyst or external initiator. The technology can be easily extended to other bio-based thermoset resins when the two components are protein and catechol. The functions, thermal behavior, morphological, and mechanical properties of the resultant adhesive was tested to understand the reaction mechanism between the adhesive components.

2. Materials and methods

2.1. Materials

SPI with 95% protein content was obtained from Yuwang Ecological Food Industry Co., Ltd. (Shandong, China) and milled to 250 mesh. CTs were obtained from Tian’guan Biotech Co. (Henan, China) with the following components: 60.1% condensed tannins, 27.4% non-tannin, 9.5% moisture, and 3% insoluble substance. Formic acid (HCOOH, AR) ($\geq 88\%$) and sodium hydroxide (NaOH, AR) were purchased from Tianjin Chemical Reagent Co. and diluted to 20% and 30% (w/w) solutions, respectively. Poplar (*Populus tomentosa*) veneers (40 × 40 × 1.5 cm, 8% moisture content) were provided from Hebei

Province, China.

2.2. Preparation of bio-thermoset resins in different pH

For pure SPI resin, SPI (15 g) was mixed with water (85 g) and stirred for 30 min at 20 °C and labeled as “SPI”. For SPI-CT resins, CTs (2.5, 5, 7.5 and 10 g) were mixed with water (85 g) and stirred for 15 min at 20 °C. SPI (15 g) was then added into the mixture and stirred for 30 min to obtain a homogeneous substance; the resulting resins were labeled “ST 2.5”, “ST 5”, “ST 7.5”, and “ST 10” indicating the different CT additions.

For acid SPI-CT resin samples, HCOOH solution was used to adjust the pH of the water-CT mixture to 3.2. For alkaline SPI-CT, NaOH solution was used to adjust the pH to 9.0 after adding SPI into the water-CT mixture and stirring it vigorously. The same subsequent steps were taken to prepare SPI-CT resins. The acid resin samples were labeled “ac ST 2.5”, “ac ST 5”, “ac ST 7.5”, and “ac ST 10”, respectively, and the alkaline resin samples were labeled “al ST 2.5”, “al ST 5”, “al ST 7.5”, and “al ST 10”, respectively. The pH of pure SPI was also adjusted as a control and labeled “ac SPI” and “al SPI”. As an additional control, 20 g CTs were mixed with 85 g water and stirred for 15 min at 20 °C to develop CT resin and labeled “CTs”. The pH values of two such samples were adjusted to 3.2 and 9.0 and labeled “ac CTs” and “al CTs”.

2.3. FTIR, TG, and SEM analysis

The samples were placed in an oven at 120 ± 2 °C to cure completely then ground into powder. The powder samples were mixed with KBr crystals at a mass ratio of 1/70 and pressed in a mold to form a sample folium. The FTIR spectra were recorded on a Nicolet 6700 spectrometer (Nicolet Instrument Corporation, Madison, WI) over the range of 4000^{-1} – 400 cm^{-1} with a 4 cm^{-1} resolution using 32 scans.

TG measurements were recorded on a TGA instrument (TA Q50, Waters Company, USA); 5 ± 0.1 mg powdered sample was weighed in a platinum cup and scanned from 10 to 610 °C at a heating rate of 10 °C min^{-1} in a nitrogen environment while recording the weight change.

The thermoset resin was cured in an oven at 120 ± 2 °C. The cured resin films, about 1.5 mm in thickness, were fractured and their cross-sections were examined under a Hitachi S-4800 emission scanning electron microscope (Hitachi Scientific Instruments, Tokyo, Japan). The fractured cross-sections were coated with 10 nm Au/Pd film using a Q150T S Turbo-Pumped Sputter Coater/Carbon Coater (Quorum

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