

Liquefied banana pseudo stem-based epoxy composites: Incorporation of phenol derivative and its characterization



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ABSTRACT

A typical method of synthesizing epoxy composites is to incorporate diglycidyl ether of bisphenol-A (DGEBA) into a bio-based epoxy resin. In this strategy, pure liquefied biomass is typically used as feedstock and is blended with DGEBA. Liquefied banana pseudo stem (LBPS), a bio-based active mixture obtained by liquefaction with phenol as the solvent, was directly utilized without depuration or additional DGEBA to develop a composite blend epoxy resin (cb-LBPSE). The blending process based on an incorporation of phenol-based epoxy resin (PER) was investigated by Fourier transform infrared spectroscopy, gel permeation chromatography, and thermogravimetric analysis. The cb-LBPSE presented a lower molecular weight and an improvement of 38.45% for shear strength than the pure LBPS-based epoxy resin (LBPSE). Also, the cured cb-LBPSE adhesive displayed a thermal stability comparable to that of PER. In addition, the curing behaviour, the activation energy, and the glass transition temperature were analyzed by differential scanning calorimetry and dynamic mechanical analysis. The blend bio-based epoxy composites exhibited an improved performance, confirming its potential as a suitable alternative to commercial PER.

1. Introduction

The currently utilized natural resources, including plant extractives [1,2], lignin [3,4] and liquefied biomass [5,6], can endow bio-based products with different functional groups and make it possible to synthesize high-performance bio-based composites [7]. Among these bio-based composites, the thermoset epoxy resin is considered to be one of the most promising materials due to its outstanding literature [8] and indispensable application for our daily life, especially it can be served as the substitutability for petroleum-based epoxy resins [9] under the threaten of environmental issues and fossil resource shortage. However, the plant extractives-based epoxy resins always have a low glass transition temperature and disillusionary mechanical properties because of the long soft aliphatic chain in plant extractive [10], lack of aromatic rings and low crosslink density with hardener [8]. Lignin, a natural polymer with molecular weight of 2000Da–50000Da [11], has been used to prepare bio-based epoxy resins. But the lignin-based epoxy resins continually are difficult to wet the surface of bonding materials and blend with hardener due to its high viscosity [12]. For liquefied biomass, a large number of phenolic hydroxyl groups is grafted onto liquefied products. Thus, these liquefied biomass-based resins often store significant amounts of aromatic rings [13]. They also possess moderate viscosity, which is beneficial to impair the dispersive hindrance [14].

Liquefied biomass can be obtained through hydrothermal liquefaction [15] or solvent liquefaction [16]. Liquefaction can convert solid biomass into low-polymerized fragments, which has high activity due to more functional groups exposed to the surface of fragments. These active liquefied products can be used to synthesize various bio-based polymers e.g. polyurethane foam [17], blend membrane [18,19] and epoxy resins, especially the epoxy resin can be used in composite matrices [20,21]. For solvent liquefaction, the additional groups such as phenolic or alcoholic hydroxyl are grafted onto the fragments, facilitating the higher activation of liquefied biomass. Recent significant efforts have been exploited to utilize forestry and agricultural wastes including crop straws [22,23] and wood wastes [24,25] to prepare bio-based epoxy resins. Not only can these pure bio-based epoxy resins compete with petroleum-based epoxy resins [26,27], but also the composite bio-based epoxy resins reveal better mechanical performances than pure liquefied biomass-based epoxy resins [28,29]. Normally, there are two approaches to prepare the composite epoxy resins. Based on a physical blending method, the modifier such as hyperbranched polymers can be directly doped into the epoxy adhesives [30]. Nevertheless, an insurmountable limitation of phase separation for network polymer will occur when the composite epoxy resin cured with the hardener [31,32]. Another approach is a chemical blend, where the pure liquefied products first blend with bisphenol-A (BPA) and then

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react with epichlorohydrin to synthesize a composite epoxy [33,34].

During the solvent liquefaction process, the resulting mixture consists of liquefied products and solvent. In order to maximize the recycling use of biomass resources, the excessive solvent is expected to improve the liquefaction rate. Nevertheless, the unreacted solvent with low-molecular weight is unfavourable to the three dimensional cross-linking networks for bio-based epoxy resins. Several strategies such as steam-distillation [35] and vacuum distillation [36] have been exploited to isolate solvent from the resulting mixture, which unfortunately results in large amounts of energy consumption and complex purification steps. A potential approach to bio-based epoxy composite is developed to reduce energy consumption and eliminate the process for removing excess solvent, which even avoid the addition of bisphenol-A or DGEBA from fossil fuel. Therefore, banana pseudo stem (BPS) containing rich cellulose [37] was first liquefied with phenol as solvent and then an acid-catalyzed condensation reaction [38] was carried out to obtain the processed mixture, which finally reacted with epichlorohydrin under alkaline condition to synthesize composite epoxy resins. This process avoids the purification of liquefied products and the addition of modifiers. Moreover, liquefied banana pseudo stem-based epoxy resin (LBPSER) and phenol-based epoxy resin (PER) derived from commercially available phenol monomer were prepared as the comparisons. The chemical structure and molecular weight were investigated using FTIR and GPC, respectively. Polyamide (PA) hardener was used in a stoichiometric amount for curing to build the epoxy-PA adhesive. The mechanical and thermal performances of various cured epoxy adhesives were assessed. Furthermore, the curing kinetic was measured using differential scanning calorimeter (DSC) and the glass transform temperatures were determined by the dynamic mechanical analyser (DMA).

2. Experimental

2.1. Materials

Banana pseudo stem (BPS) after harvesting fruits collected from Changjiang Banana Planting Base in Hainan province (China), was oven-dried, milled into a 20–80 mesh, and stored in a desiccator. The used chemicals, including phenol, sulfuric acid, toluene, ethanol, and epichlorohydrin, were purchased from Aladdin and used without further purification. The curing agent polyamide-650 (PA, industrial grade) with a viscosity of 15–50 Pa s and an amine value of 220 ± 20 mg KOH/g was supplied by Sanxiong Chemical Industry (China).

2.2. Methods

2.2.1. Liquefaction of BPS

Liquefaction of the banana pseudo stem (BPS) was accomplished by using phenol as the solvent at a solvent-to-material weight ratio of 4:1 and 7.5% sulfuric acid (based on raw material content) as the catalyst at 160 °C for 40 min according to our previously described procedure [39]. The resulting mixture was filtered through a G4 funnel and washed with anhydrous ethanol. A liquefaction ratio of 70.76% can be calculated through the residue weight. Further, MgO power was added to the filtrate to neutralize the residual sulfuric acid. After filtration and vacuum distillation were conducted at 60 °C to remove the ethanol, a liquefied mixture (*m*-LBPS) composed of liquefied banana pseudo stem (LBPS) and excess phenol was obtained. In addition, the pure LBPS (*p*-LBPS) was obtained by adding deionized water to form a binary phenol-water (1:9) azeotrope system and subsequent running a few cycles of heating at 110 °C to completely remove the excess phenol of the *m*-LBPS.

2.2.2. Synthesis of various epoxy resins

A series of epoxy resins were prepared according to a typical procedure. First, the *m*-LBPS (10 g) was reacted with acetone (4 mL) by

using sulfur acid (6 mL) as the catalyst at 15 °C–20 °C for 2 h. Second, the preprocessed *m*-LBPS (10 g) was dissolved in epichlorohydrin (30 g) in the presence of microwave. The mixture was loaded into a glass flask and heated up to 45 °C–50 °C before the sodium hydroxide solution (10%, 40 mL) was added through the constant pressure funnel in 2 h. Finally, the system was heated to 70 °C–75 °C and kept at this temperature for another 1 h to realize epoxidation. A dual extraction system consisting of toluene and deionized water was added to the resulting mixture. The organic layer was evaporated to remove the extracting agent, and 11.3 g of the composite blend epoxy resin (cb-LBPSER) was obtained under reduced pressure. Meanwhile, a phenol-based epoxy resin (PER) was synthesized by using the phenol monomer as feedstock. To prepare the liquefied banana pseudo stem (LBPSER), the entire procedure was repeated starting at the second step but with the *p*-LBPS.

2.2.3. Curing of various epoxy resins

PA as a curing agent [40] was mixed with LBPSER, cb-LBPSER, and PER at different ratios (w/w, polyamide/epoxy = 2:1, 1:1, 1:2, 1:3). The mixture was coated on the surface of wood plates, and finger-pressing was conducted to realize the mechanical experiments according to a single lap-shear test [41]. The curing profile was arranged at 100 °C for 12 h. The model parameters are described in Fig. 1.

2.3. Characterizations

The FTIR analysis was recorded between 4000 cm^{-1} and 400 cm^{-1} on a TENSOR27 spectrophotometer. According to the physical state of the samples, the pure liquefied products of banana pseudo stem were mixed with dry KBr power to prepare disks and the LBPSER, cb-LBPSER and PER were sandwiched between two pure KBr disks.

The molecular weight distributions of LBPSER, cb-LBPSER and PER were determined using a waters 2515 separation module with a manual injector and a waters 2414 refractive index detector. The samples were dissolved in THF and the mobile phase of THF based on grade with a flow rate of 1 mL min^{-1} was carried out.

The shear strength for various epoxy resins was measured according to a single-lapped method. The specification was $100 \text{ mm} \times 25 \text{ mm} \times 2 \text{ mm}$. The adhesive area was $12.5 \text{ mm} \times 25 \text{ mm}$ and the resin consumption was 480 g/m^2 [42]. Parallel determination for 10 times was carried out on an adhesive tensile shear strength test machine (model: DLD-5). Further, the percentages of different destruction types corresponding to local-plate failure, adhesive concrete interface failure and colloid damage (as Fig. 5 shown) were counted.

The thermal gravimetric analyser (NETZSCH, 209-F3) over a temperature range from 40 °C to 800 °C at a heating rate of $20 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$ was employed to assess the thermal stability of various epoxy resins and cured epoxy/PA adhesives. N_2 as carrier gas with a flow rate of 20 mL min^{-1} was used during tests.

The curing behaviour of phenol-based epoxy/PA system and the two bio-based epoxy/PA systems including LBPSER and cb-LBPSER were investigated by differential scanning calorimetry (NETZSCH, STA 449

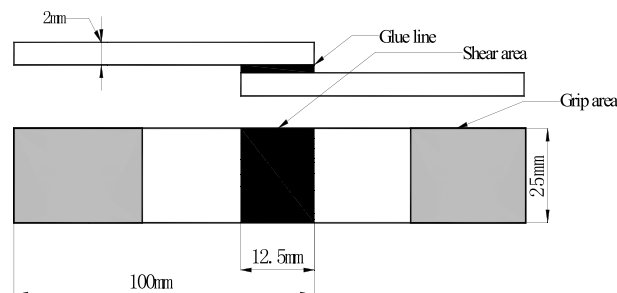


Fig. 1. Single lap shear specimen The resin consumption of $480 \text{ g epoxy resin/m}^2$ and tensile rate of 5 mm s^{-1} were carried out.

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