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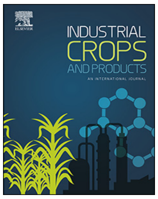

Fully bio-based soybean adhesive in situ cross-linked by interactive network skeleton from plant oil-anchored fiber

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ABSTRACT

The fiber-reinforcement is an attractive strategy to enhance composites under the green development concept. However, the poor dispersion/interactivity of natural fiber and most petroleum-based modification strategies impede development of fiber-reinforced environmental composites. In this study, we employed a soybean oil derivative as a multi-functional cross-linker that reacted with kenaf fiber (KF) to synergistically improve the soybean flour (SF)-based adhesive. The biobased cross-linker, phosphate and epoxy groups-containing soybean oil (PESO), was synthesized via phosphoric acid ring-opening reaction from epoxidized soybean oil in certain extent. To provide reaction sites, the KF was surface-coated by poly (tannic acid) (PTA) to obtain a PTA-coated KF (TKF). The PESO cross-linker, with the role of epoxy groups, constructed an interactive network skeleton with TKF and formed in situ cross-linking reactions with SF matrix. In addition, the incorporated phosphate groups of PESO gave rise to interactions with hydroxyl of TKF and polysaccharide of SF further stabilizing cross-linking network as confirmed by fourier transform infrared (FTIR), nuclear magnetic resonance (NMR), X-ray diffraction (XRD) and scanning electron microscopy (SEM) measurements. As expected, compared to pristine SF adhesive, the modified adhesive showed a significant increment in wet shear strength by 236.4% and also exhibited a favorable thermal stability. We envisage that this design may provide a new avenue for developing high-performance fully sustainable biomass composites.

1. Introduction

Because of the increasing depletion of nonrenewable resources, researchers are diligently working to find alternative renewable biomass for these materials (Song et al., 2011). Natural fiber (NF) (e.g. kenaf, flax, hemp, jute and bamboo fiber), as one of the most abundant agricultural crops, has acquired wide applications in many fields because of its novel qualities such as stiffness and biodegradation, and its rheological properties (Akil et al., 2011; Alavudeen et al., 2015; Saba et al., 2015). In recent years, it has been a powerful comparator to synthetic polymers in ecological characteristics, but considerable mechanical improvement is required for satisfactory integrative performance (Krishna and Kanny, 2016; Yusoff et al., 2016). The poor surface activity of NF leads to weak interfacial bonding that limits the transference of stress in fiber-reinforced composites, resulting in undesirable concentration of stress in certain areas (Väisänen et al., 2018; Xia et al., 2016). Accordingly, extensive research has been carried out to improve interfacial interactions between fibers and matrix (e.g. acetylation and acrylic acid treatment), while the most incorporated modifiers introduced hydrophilic groups, which decrease water resistance property after exposure to water (Abraham et al., 2016; Jannah et al., 2009).

There has been considerable interest in developing hydrophobic fiber-reinforced composites in recent years. Hydrophobic surface modification with polyurethane, poly(butyl acrylate) and methyltrimethoxysilane remarkably improved the hydrophobic properties of fibers-reinforced composites, while the nature of nonrenewable resources still gives rise to environmental concerns (Li et al., 2011; Wang et al., 2015; Yao et al., 2014; Zhang et al., 2016; Zhao et al., 2016). As a natural renewable hydrophobic resource, it has been a common practice to enhance the hydrophobicity of composites with plan oil (PO). The unique chemical structure of PO with its ester groups and unsaturated sites endows this oil with satisfactory hydrophobicity and enables it to undergo various chemical functional transformations for many applications (Alagi et al., 2018). Among various modifications,

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the in situ epoxidation reaction of the double bonds in PO (EPO) has gained increasing attention because the formed active epoxy groups can form a stable cross-linking network with the matrix to improve integrative properties (Diez-Pascual and Diez-Vicente, 2014; Huang et al., 2015). Huang et al. reported an efficient method to utilize EPO to graft cellulose fibers with the prepared composites exhibiting enhanced interfacial interactions (Huang et al., 2016). The EPO was also employed as a coupling agent to bridge poly (lactic acid) and hazelnut shell flour, where the EPO formed a cross-linking network and clearly enhanced integrated composites properties (Balart et al., 2016). The application of EPO was a viable approach toward superior composites with outstanding hydrophobic property and integrated mechanical performances.

For further improvement, grafting functional groups onto EPO can be seen as a feasible strategy whereby the groups serve as a multifunctional cross-linker to construct a strong cross-linking network that optimizes composite performances (Quiles-Carrillo et al., 2018; Yadav et al., 2018). Acrylated epoxidized soybean oil (AESO), produced via a ring-opening reaction of epoxy groups with acrylic acid, was confirmed as a multifunctional and reactive polymer and has been applied in highly cross-linked thermosets (Mauck et al., 2016). L. Quiles-Carrillo et al. employed AESO as a multiple functional enhancer to modify polyactide, resulting in significantly improved properties due to efficient interactions and cross-linking by reactive acrylate and epoxy groups, which provided a new avenue for high-performance composites (Quiles-Carrillo et al., 2018).

Phosphorus-functional modification is a fascinating path because of the variety of its merits such as complexation, biocompatibility, flame retardancy, and especially adhesion, and it has been reported as a crucial tool for wide applications such as coatings, structural adhesives and biomedicals (Breucker et al., 2015; Gaddam et al., 2017; Mourão et al., 2017; Pethsangave et al., 2017). Most importantly, there has been a report describing how phosphate was used as a cross-linker to cross-link polysaccharide, which obviously improving the strength and water resistance of a soy protein isolated matrix (Yuan et al., 2017). Hence, considering the similar basic unit between polysaccharide and fiber, it is believed that the functionalizing EPO by grafting phosphorus groups is a satisfactory method to construct a double cross-linking system with fiber toward superior composites.

As well known, soybean flour (SF) is an attractive by-product of oil industry with merits of low cost and good film-forming property, showing applications in biomedical, resin and packaging fields, while the presence of vast water-soluble polysaccharide and poor cross-linking network could decrease the integrated properties of SF composites (Li et al., 2014; Thakur et al., 2015). In this work, kenaf fiber (KF) was firstly coated by the poly (tannic acid) (PTA) with a dip-coating method given the TKF and then reacted with phosphorylated epoxidized soybean oil (PESO) to in situ cross-link SF composites. Additionally, we hypothesized the phosphate groups of PESO could serve as a "bridge" forming interactions between KF and polysaccharide for further improving SF composites performances, which could realize utilizing all components of soybeans. The effect of PESO-TKF on SF based composites (SF/PESO-TKF) was determined via mechanical and thermal properties, and additionally, the modification mechanism was explained by attenuated total reflection, X-ray diffraction, and scanning electron microscopy analysis.

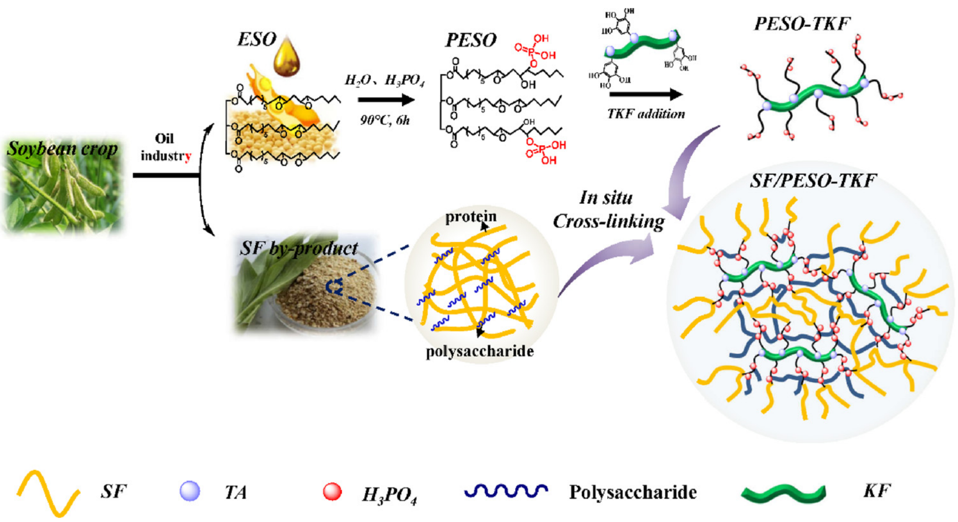
2. Materials and methods

2.1. Materials

Soybean flour (SF) with 46% soy protein content was obtained from Xiangchi Grain Oil Company, Shandong, China. Kenaf fiber (FB) was chopped into pieces approximately 5 mm in length before use. Epoxidized soybean oil (ESO) with an oxirane value greater than 5% was purchased from Aladdin Biochem Co., Ltd. Formic acid (FA, 85%), phosphoric acid (H_3PO_4, 85%), sulfuric acid (98%), tertiary butanol, ethyl acetate, tannic acid (TA), and tris(hydroxymethyl) aminomethane (Tris) were obtained from Tianjin Heowns Biochem Co., Ltd. Hydrogen peroxide (H_2O_2), anhydrous Na_2SO_4 and other chemical reagents were supplied by Beijing Chemical Reagents Co., Ltd (Beijing, China) and used as received. Poplar veneer (8% moisture content) was purchased from Wen'an (Hebei, China).

2.2. Fiber surface functionalization

The kenaf fiber (KF) was treated with alkali aqueous solution (NaOH) to remove interior lignin. The resulting KF was thoroughly washed using deionized water until the PH value approached neutrality and was then oven dried at 80 °C for 24 h. Subsequently, functionalized KF was prepared according to the method of Wang et.al (Wang et al., 2017a). Briefly, KF aqueous solution (5 mg/ml) was prepared by mixing TA (4 mg/ml) and Tris (100 mM), and then, KF was added and the solution was stirred for 24 h under ambient conditions. Finally, the as-prepared KF/TA (TKF) fiber was washed with deionized water and oven-dried at 80 °C for further application.



Scheme 1. Synthetic procedure of SF/PESO-TKF and the interactions in SF/PESO-TKF matrix.