



Cyclocarbonated lignosulfonate as a bio-resourced reactive reinforcing agent for epoxy biocomposite: From natural waste to value-added bio-additive

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ABSTRACT

A lignin-based industrial waste was converted to a value-added reinforcing agent for epoxy matrix composites. Thus, a facile three-step strategy including methylation, epoxidation and carbonation (i.e., CO₂ fixation) was conducted to prepare the reactive filler as a cyclocarbonated lignosulfonate (CLS). Then, CLS (10, 20, and 30 wt %) was blended with DGEBA epoxy resin followed by amine-curing to produce the biocomposites. Spectral, thermal, thermomechanical, mechanical and morphological properties of the CLS-epoxy composites were studied by FTIR, DSC/TGA, DMTA, tensile/flexural testing and SEM, respectively. In comparison with the neat DGEBA network, by increasing the CLS% in the biocomposite, tensile strength decreased, flexural modulus was well-preserved, and the Young's and storage modulus were greatly improved. It was attributed to stiffening effect of the modified lignin particles as well as the formation of urethane bonds and intermolecular interactions such as hydrogen bonding. The glass transition temperature for the biocomposites with 10 and 20 wt% of CLS showed negligible change. The incorporation of the carbonated lignin into epoxy resin could provide an eco-effective approach toward inexpensive high performance biocomposites.

1. Introduction

Epoxy resins have been known as one of the most important and widely used thermoset resins around the world, mainly due to their chemical resistance, thermal stability, high adhesion, and their critical role in surface coatings, adhesives, polymer composites, etc. [1–3]. Due to the depletion of fossil resources, finding new ways to replace renewable resources, particularly biomass, have been one of the main research topics [4]. The biomass is mainly composed of natural polymers such as lignocelluloses, that consists of three biopolymers including lignin, cellulose and hemicellulose [5,6]. Among them, lignin is the only valuable aromatic biopolymer with high availability and very complicated polyphenolic structure [7–9]. Its attractive properties are considered to be used as filler in polymer blends and composites [4,10,11].

Lignin has been produced as waste, annually millions of tons, in transformation of wood into paper products. The only small percentage of it just is used as natural stabilizers and surfactants for making of hard materials [12–14]. However, it has been mostly trashed away or burnt, due to lack of appropriate conversion technologies [15]. Lignin is

located on the external wall of the plant cells and functionalizes in the plants as a binding agent in internal structure of supportive tissues, which prevents them from premature decay and maintains plant's rigidity for long time. Amorphous lignin is composed of phenylpropanoid units connected by etheric bounds. The main monomers of lignin are coniferyl, sinapyl and *p*-comaryl alcohols [16].

Some industrial lignins, like lignosulfonates and kraft, contain sulfur, being produced in large quantities, while others such as organosolv and soda as a second category do not have sulfur, which have been named as sulfur-free lignins [17]. The application of lignin as rigid biopolymer incorporated into the composite structures has become popular over the past decade [18,19], because of its excellent bio-alternative role in substituting bisphenol A (BPA) for preparing epoxy resins [20–22]. However, lignin structural nature may limit its reactivity with epoxy resin [23,24]. Reactive oxirane groups of the epoxidized lignin can be converted to other functional groups. For instance, cyclic carbonate was synthesized through addition of CO₂ onto epoxy groups [21].

Carbon dioxide as the best steady-state oxidized form of carbon is mainly responsible for greenhouse gases crisis, leading to some unusual

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changes in global climate. It could be obtained through combustion processes as a side product, and has been utilized for production of other materials [25,26]. The cyclic carbonates are receiving considerable attention because of their application in various polymeric fields as a monomer. For instance, they could be utilized for production of polycarbonates and thermoplastic polyurethanes compositions. Also, they have been applied in the field of adhesives and aeronautic industries. Recently, five-membered cyclic carbonates with its superior properties have drawn many attentions as a green substitute [27–32]. Morphological, mechanical and thermal properties as well as network behavior of epoxy resins have been analyzed in many academic endeavors [12,33,34], but incorporation of carbonated lignin for cross-linking into the epoxy network has not been yet reported in the literature. Actually, there is no report on reinforcement of epoxy matrix by carbonated lignosulfonate particles, and this can be considered as the essential novelty of the present work.

Recently, diglycidyl ether of bisphenol A (DGEBA) cross-linked by isophorone diamine was modified using glycidylated organosolv lignin (GOL) as a filler [34]. The resultant epoxy thermosets prepared from various percentage of GOL were cured to study mechanical and thermal properties. It was indicated that using lignin content of 8–33%, the cross-linking density, stiffness and Young modulus, could be improved comparing to pristine epoxy.

Kong et al. [3] blended hydrolyzed lignin in different ratios with conventional epoxy resin. Its properties and curing kinetics were studied, demonstrating that in the lignin content of 5%, the highest shear strength could be achieved. Sun et al. [35] investigated epoxy matrix with 0.5, 1 and 1.8 wt% depolymerized lignin epoxide. The morphology and mechanical properties analysis showed that in the weight ratio of 1, the highest fracture toughness was attained without any significant reduction in elastic modulus, tensile strength and elongation at break. In another attempt, two types of de-polymerized lignin including Kraft and Organosolv were mixed with conventional epoxy resin [36,37]. The results showed that limiting oxygen index was increased by increasing the lignin content within the conventional epoxy resin. Furthermore, modification of epoxy resin by lignin had significant impact on the activation energy during thermal decomposition process.

Chemical modification of epoxy resin was also conducted through conversion of oxirane ring to cyclic carbonates [38]. CO₂ fixation method was supplied to produce bi-functional carbonated resin and after curing process, the final product showed an extraordinary toughness. Curing behavior of lignin-based epoxy was evaluated by differential scanning calorimetry (DSC) and the obtained results were reported in several scientific papers [21,39,40]. In the present study, using methylation reaction, hydroxyl functional groups were substituted on sodium lignin sulfonate (LS) backbone and subsequently, they were epoxidized by epichlorohydrin. The resulting oxirane groups were finally cyclo-carbonated via CO₂ fixation. Different weight ratios (i.e., 10, 20 and 30 wt%) of carbonated lignin was incorporated into conventional epoxy resin and amine-cured. Morphology, structure and thermal/mechanical properties of carbonated lignin re-enforced epoxy composite were assessed using various techniques.

2. Experimental

2.1. Materials

Sodium lignosulfonate (LS) was purchased from East China Chemicals Co. (elemental analysis: C% 46.80, H% 4.67, S% 7.24). Diglycidylether of bisphenol A epoxy resin (DGEBA, EEW 187–194 g/eq) was purchased from Khuzestan petrochemical Co., Iran. Bio-based epichlorohydrin (96%) was prepared from glycerol according to the literature [41]. Diethylenetriamine (DETA) was prepared from Daejung Chemical Co., China. Tetrabutylammonium bromide (TBAB, %98), 37% formaldehyde solution, the solvent dimethylacetamide (DMAc) and other reagents were provided from Merck (Germany) and used without

further purification.

2.2. Methylation of lignosulfonate

LS was dissolved in 80 mL NaOH solution 3 wt% so that the NaOH/lignin weight ratio was 0.08, and then 7.8 g formaldehyde solution was added (CH₂O/lignin weight ratio of 0.26). The temperature was raised to 50 °C with vigorous stirring for 4 h to complete the reaction as spectrally indicated by FTIR. The modified lignosulfonate was precipitated by lowering the pH to 1.5–2 with a 1 N HCl solution. The product was centrifuged at 10,000 rpm for 15 min., and repeatedly washed by distilled water [42,43]. It was dried in an oven at 50 °C overnight to give methylolated lignosulfonate (MLS) as black powder.

2.3. Epoxidation reaction

Methylolated lignin (MLS, 15.0 g) and bio-resourced epichlorohydrin (150.0 g) were added into a three-necked flask equipped with magnetic stirrer, thermometer and reflux condenser. TBAB (1.50 g) with 90 mL of distilled water was then slowly added and the reaction mixture was refluxed at 70 °C for 4 h under vigorous stirring. Subsequently, the mixture was cooled down to 25 °C and then 63 mL of NaOH aqueous solution (50% w/w) was added dropwise under stirring (while the temperature of mixture was kept at 25 °C for another 3 h) to reconstruct the oxirane ring. Finally, the extra epichlorohydrin was removed by rotary evaporator at 70 °C under a reduced pressure. The precipitate was filtrated using a sintered glass funnel, then washed by acetone and then by distilled water for three times. Epoxidized lignosulfonate (ELS) was obtained as a brown powder (13.8 g) after drying in an oven at 50 °C overnight.

2.4. Carbonation reaction

ELS (10.0 g) and TBAB (1.0 g) were slowly dissolved/dispersed in 100 mL of DMAc and the mixture was stirred for 24 h. Afterwards, the sample was charged in a three-necked flask equipped with bubbling of the pure CO₂ gas. The pressure of purging CO₂ was 2 bars and the flask temperature was raised to 80 °C in an oil bath and maintained for 12 h. The solvent was removed by rotary evaporator at 80 °C under a reduced pressure. The synthesized carbonated lignin (CLS) was filtered on Buchner glass funnel and washed with distilled water. It was then dried in an oven at 50 °C overnight. Cyclocarbonated lignin (CLS) was obtained as a light brown powder and used as reactive filler in the subsequent experiments.

2.5. Preparation of carbonated lignin composites

Carbonated lignin, CLS, was ground using a ball mill for 90 min. Then DGEBA resin was mixed with ground CLS in various weight ratios of 10, 20 and 30%. The number of active hydrogen in triethylenetriamine (DETA) for oxirane and carbonated group are 3 and 5, respectively. It means that 1 mol of DETA reacts with 5 mol of oxirane group and 3 mol of carbonated group. Therefore, CLS and DGEBA were mixed homogeneously and heated to 70 °C and kept at this temperature under vigorous stirring for 12 h. Then, temperature was decreased and the stoichiometric amount of DETA was added as a hardener into the above prepared mixture, and uniformly dispersed. The blends were casted into dog bone shaped molds. Then, they were degassed in a vacuum oven for 15 min until the bubbles were completely removed. The molds were placed at room temperature for 24 h to be cured. Finally, the samples were post-cured at 75 °C for 6 h and 120 °C for 2 h.

2.6. Characterization

2.6.1. Epoxy/carbonate content

The cyclocarbonate content was assessed via determination of the

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