Industrial Crops & Products 112 (2018) 225–235

Contents lists available at ScienceDirect

Industrial Crops & Products

journal homepage: www.elsevier.com/locate/indcrop

Evaluation of Ligno Boost™ softwood kraft lignin epoxidation as an approach for its application in cured epoxy resins

Antons Jablonskis[a], Alexandr Arshanitsa[a,*], Alexandr Arnautov[b], Galina Telysheva[a], Dmitry Evtuguin[c]

[a] Laboratory of Lignin Chemistry, Latvian State Institute of Wood Chemistry, 27 Dzerbenes Street, LV-1006, Riga, Latvia
[b] Institute of Polymer Mechanics, University of Latvia, 23 Aizkraukles Street, LV-1006, Riga, Latvia
[c] Department of Chemistry, CICECO, Campus Universitario de Santiago, University of Aveiro, Aveiro, Portugal

ARTICLE INFO

Keywords:
Kraft lignin
Glycidylation
Lignin-based epoxies
Epoxy equivalent weight
Viscosity
Young's modulus

ABSTRACT

In this study, modification of LignoBoost™ softwood kraft lignin with epichlorhydrin in water-organic solvents media was realized. Lignin-based epoxy resins were obtained by two ways: acetone extraction of glycidylated lignin or glycidylation of the acetone soluble lignin fraction. The effect of glycidylation regimes on the yields of acetone soluble fractions, their functional composition and physical-chemical characteristics was investigated using wet chemistry methods, FTIR spectroscopy, size exclusion chromatography (SEC) and differential scanning calorimetry (DSC). The positive effect of the biphasic phase transfer catalytic system – KOH/quaternary ammonium salt – on glycidylation of both phenolic and aliphatic hydroxyl groups was testified, exemplified using a lignin-like model compound – 4-hydroxy-3-methoxylbenzyl alcohol (vanillyl alcohol). The partial substitution (up to 10%) of commercial epoxy resin on the basis of bisphenol A (Araldite® LY1564) by lignin-based epoxy resin significantly increased the viscosity of resin. Therefore, the possible practical application of lignin-containing epoxies as adhesive, mastic or crack filler instead of binder for fiber reinforced composites was considered. A tendency towards increasing Young's modulus of cured lignin-containing epoxies, compared with the case of the reference composition, was observed. The lignin chemically incorporated into the matrix of cured commercial epoxy resin acts as a charcoal formation promoter in high temperature treatment.

1. Introduction

Cured epoxy resins are thermosetting heat-stable polymers with high mechanical properties and chemical resistance (He et al., 2014). The coatings, adhesives and reinforced composites on the basis of epoxy resins are widely used in many industrial applications, including electrical engineering, electronics, automobile and air craft industries, etc. (Wanga et al., 2016; Katunina et al., 2017; Çakır et al., 2014; Murakami et al., 2016).

Commercial epoxy resins are currently produced mainly (almost 90%) from petroleum-derived chemicals: bisphenol A (BPA) and epichlorhydrin (ECH) (Abdul Khalil et al., 2011).

BPA is responsible for numerous favorable properties of the final material, but unfortunately, it exhibits an estrogenic activity and, therefore, is referred to as an environmental hormone that negatively influences the human health (Sasaki et al., 2013). BPA and its derivatives possess high potential as an endocrine disruptor. Exposure to BPA may induce harmful, reproductive, developmental and metabolic disorders (Fischnaller et al., 2016).

Besides, the depletion of fossil resources and the environmental problems induced by their processing and extensive utilization have encouraged the industry and science all over the world to seek for renewable resources for the production of bio-based polymerics, particularly epoxy resins (Ferdosian et al., 2016).

Recently, several researches have been reported on the synthesis of bio-based epoxy resins from various renewable resources such as vanillin (Fache et al., 2014), gallic acid and catechin (Aouf et al., 2013), isosorbide (Lukaszczyk et al., 2011), tannins (Aouf et al., 2014; Benyahya et al., 2014), vegetable oils (Shah and Ahmad, 2012) and lignins (Delmas et al., 2013; Hirose et al., 2012).

Nowadays, cellulose and other carbohydrates, derived from plant biomass, are successfully used in the paper industry and as a feedstock for bioethanol production. However, only 2% of the lignin obtained as by-products in pulp and fuel ethanol processing is used commercially (Li et al., 2012). The biorefinery conception assumes the most profitable usage of all components extracted from the lignocarbohydrate

* Corresponding author.
E-mail address: arshanica@edi.lv (A. Arshanitsa).

https://doi.org/10.1016/j.indcrop.2017.12.003
Received 25 April 2017; Received in revised form 23 November 2017; Accepted 3 December 2017

complex at its processing. Therefore, lignin utilization for the fabrication of value added products is a worldwide bio economic task.

Lignin in situ is a three-dimensional amorphous biopolymer formed by three major monolignols: *p*-coumaryl (P), coniferyl (C) and sinapyl (S) alcohols with different ratios, linked together by various types of ether and carbon−carbon bonds (Laurichesse and Avérous, 2014). The technical lignins extracted from plant biomass as by-products differ from native lignins; however, the aromatic structure of lignins and the presence of a significant amount of OH groups (phenolic, aliphatic and carboxylic) make technical lignins an attractive raw material for BPA substitution, capable of modification via the reaction of OH groups with epichlorohydrin.

The direct utilization of lignin for the synthesis of epoxy resins is challenging due to the large molecular weight and heterogeneity of lignins, their restricted solubility in common organic solvents, different electronic constraints and steric hindrance of the available OH groups. Overcoming these challenges, different approaches have been used, including the de-polymerization and chemical modification of lignin.

In recent decades, different lignin de-polymerization methods have been introduced. Base and acid catalyzed reactions at high temperatures and pressure were performed on a laboratory scale. The mechanical and thermal properties of cured epoxy resins on the basis of depolymerized kraft, hydrolysis and organosolv lignins were found to be inferior to those for reference commercial epoxy resins (Wang et al., 2013).

Another approach is demethylation of lignin and obtaining of lignin products with free phenolic groups in the 3 and 5 ring positions; these lignins could be used as a feedstock for lignin based hyperbranched epoxy production. However, at the moment, catalytic pathways do not exist, and the widely used reagents (alkyl halides) are harmful and undesirable for large scale production (Ferhan et al., 2013; Hu et al., 2014).

Phenolation, as another modification method for increasing the content of phenolic groups in lignin, has a potential for making more favorable conditions for lignin reaction with ECH. However, the release of formaldehyde to generate new reactive sites and cyclization via etherification of phenol with lignin side chain carbons was also detected, that diminished the advantages of this approach (Podschun et al., 2015).

Hofmann and Glasser prepared epoxy resins from hydroxyalkyl lignin (alkali extracted lignin from steam exploded yellow poplar) derivatives with varying degrees of alkoxylation. To obtain lignin derivatives, containing only high reactive primary OH groups, the consequent modification of lignin with propylene oxide and ethylene oxide was performed before glycidylation. The prepared epoxy prepolymers were cured into stiff thermosets having a high glass transition temperature (Hofmann and Glasser, 1993).

The complexity and labor expensive processing can be considered as the disadvantages of this modification from the viewpoint of its practical application.

It is known that lignin properties and its ability towards various chemical modifications depend strongly on the biomass origin and the technology of lignin isolation (Gosselink et al., 2010).

Different novel processes of lignin isolation in the framework of the biorefinery approach are currently under development, although only single of them are realized on a commercial scale. The LignoBoost concept developed by Innventia AB and Chalmers University (Sweden) is one of them (Tomani, 2010). LignoBoost lignin meets the requirements for a material pure enough to be used as a chemical feedstock for green chemicals and for quality fuel production.

The objectives of the present work were: (i) to provide the controlled covalent incorporation of the epoxy function in the LignoBoost™ softwood lignin structure via the glycidylation reaction, (ii) to investigate the tensile and thermal characteristics of cured lignin containing epoxy resins, (iii) to study the effect of quaternary ammonium salt as a phase transfer catalyst, combined with an alkali catalyst, on the glycidylation of both phenolic and aliphatic OH groups using vanillyl alcohol as a lignin-like model compound (LMC).

To obtain a lignin-based epoxy resin prospective for substitution of commercial BPA-based epoxy resin in amine cured composites, two pathways were used, i.e. extraction of glycidylated LignoBoost™ softwood lignin with acetone and glycidylation of the acetone soluble lignin fraction.

2. Experimental

2.1. Materials

LignoBoost™ softwood kraft lignin (KL), isolated from the original black liquor using the LignoBoost process, was kindly presented by Innventia AB.

Epichlorohydrin (ECH), acetone, dichloromethane, vanillyl alcohol, potassium hydroxide, dimethyl sulfoxide and sodium dihydrogen phosphate dihydrate ($NaH_2PO_4{\cdot}2H_2O$) were all of analytical grade and were sourced from Sigma Aldrich Company Ltd. and Lach-Ner Ltd. 2-Methoethanol was gas chromatographic grade from Fluka. Commercial BPA-based epoxy resin Araldite® LY1564 (epoxy equivalent weight, EEW = 170 g eq^{-1}), cured by the amine hardener Aradur®3486 (amine hydrogen equivalent weight, AHEW = 111 g eq^{-1}) containing cycloaliphatic polyamines: 5-amino-1,3,3-trimethyl isophoronediamine cyclohexanamine, cyclohexanemethanamine, 4,4′-methylenebis(2-methylcyclohexylamine) and polyoxy(methyl-1,2-ethanediyl), was sourced from Huntsman Chemical Company.

2.2. Klasson lignin content and functional characteristics of KL

Klasson lignin (96 ± 1%) was determined according to the TAPPI T222 Standard.

The content of total OH groups in KL was determined via acetylation of samples with acetic anhydride followed by potentiometric titration of free acetic acid in excess with 0.1 N NaOH in water. The content of phenolic and carboxylic OH groups in KL was determined by acid-base conductometric titration using an automatic titration device ABU901, coupled with a Conductometer CDM 210 and a titration manager TIM 900. The methoxyl groups (OCH_3) content was measured according to the Viebock-Schwappach method (Zakis, 1994). The functional composition of KL is shown in Table 1.

2.3. Extraction of non-modified KL and glycidylated lignin with acetone

The acetone soluble fraction of kraft lignin (KLAF) was isolated by double solid-liquid extraction of 10 g of KL with 100 mL of acetone in a round flask at room temperature. Each extraction step was done by vigorous stirring of the suspension for 60 min. The undissolved material was filtered off and resuspended for a second identical extraction. The acetone solutions of each extraction step were collected. After filtration, the acetone was distilled off in a rotary evaporator and the residue was oven dried in vacuum at 50 °C. Three replicate fractionations were made.

The acetone soluble fraction of lignin-based epoxy resin (GLAF) was isolated from glycidylated lignin (GL) by two times solid-liquid extraction with 100 mL of acetone in a round flask at room temperature.

Table 1
Functional groups of KL.

Functional group	Content (mmol g^{-1})
OH, total	7.3 ± 0.3
OH, phenolic	1.4 ± 0.2
COOH	2.4 ± 0.3
OCH_3	4.1 ± 0.1