



Lignin-based polyurethane and epoxy adhesives: a short review


D.J. dos Santos ^{a,*}, L.B. Tavares ^a, J.R. Gouveia ^a, G.F. Batalha ^b

^a Modelling and Applied Social Sciences Centre, ABC Federal University, Santo Andre, Brazil

^b Department of Mechatronics and Mechanical Engineering, Polytechnic School of Engineering, University of São Paulo, São Paulo, Brazil

* Corresponding e-mail address: demetrio.santos@ufabc.edu.br

ORCID identifier:  <https://orcid.org/0000-0002-4707-2285> (D.J.S.);

 <https://orcid.org/0000-0001-8625-8499> (G.F.B.)

ABSTRACT

Purpose: of this paper was to review and summarize significant papers related to the development and characterization of lignin-containing adhesives: polyurethane and epoxy types. In the last decades, several efforts have been dedicated on the development of renewable raw materials for polymer synthesis, mainly due to petroleum depletion and sustainability. In this context, lignin emerged as a potential candidate to substitute fossil-based raw materials in adhesive synthesis and formulations.

Design/methodology/approach: Recent and other relevant papers were reviewed, aiming to identify the main advantages and limitations involved in lignin incorporation into epoxy and polyurethane adhesives formulations. First, effects of unmodified lignin addition were presented. Afterwards, the main lignin chemical modification methods were presented and discussed, based on thermomechanical results.

Findings: Incorporation of unmodified lignin usually is limited to 30 %wt., otherwise mechanical properties are drastically affected as consequence of poor lignin solubility and excessive brittleness. Lignin chemical modification can be used to increase the reactivity of hydroxyl groups and/or add new moieties in its molecular structure, improving solubility and thermomechanical properties of cured adhesives.

Practical implications: In the last years, some industrial plants started to operate and produce technical grade lignin at industrial scale, with reproducible properties and controlled molecular structure. Therefore, increasing efforts have been dedicated from researchers and chemists to develop lignin-based technologies, in which this work can directly contribute with.

Originality/value: As consequence of the high content of phenol groups in its molecular structure, lignin was mostly applied on the development of phenolic resins applied as wood adhesives. For the first time in the literature, this work summarizes the advances related to synthesis and characterization of polyurethane and epoxy, applied as adhesives. Results can support the development and application of biobased, as well as contribute to the revalorization of this valuable and readily available biomass.

Keywords: Engineering polymers, Adhesives, Polyurethane, Epoxy, Lignin

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MATERIALS

1. Introduction

Structural adhesives are widely applied on technical applications distributed over several industrial segments [1-3]. Among the most significant adhesive families, epoxies, and polyurethanes (PU) hold a prominent position due to their versatility in terms of properties [4]. Despite their technological relevance, epoxy and PU production is still highly dependent on petroleum based raw materials, such as: diglycidyl ether of bisphenol A (DGEBA), polyether and polyester polyols, diisocyanates and others. Aiming to overcome the petroleum based dependency, several efforts have been dedicated on polymer developments based on natural renewable raw materials: castor oil, cellulose, tannin, lactic acid, and lignin [5-8].

Among the above-mentioned materials, lignin emerged in the last decade as a potential and feasible raw material for polymer synthesis, i.e., adhesives developments. Recently, different lignin industrial plants started their operation around the world, producing high volumes of technical grade lignins, industrial biopolymers with reproducible structure and properties. Owing to its current availability at industrial scale and chemical structure, incorporation of lignin into adhesive synthesis became feasible in different methods: (a): direct incorporation without previous lignin modification; (b): chemical modification of lignin [9].

Lignin is an aromatic biopolymer, found in cells of plants, trees and algae, which are chemically bonded to cellulose and hemicellulose. In nature, lignin is in charge of protecting the plant against hazardous microorganisms, transporting water and improving their mechanical behaviour. Still considering lignin in nature, it basically stems from the reaction and combination of three main alcohols, resulting into three monolignols, as presented in Figure 1. The units H, G and S are predominantly bonded by ether, among other linkages [10].

Once subjected to isolation processes, in pulp and paper manufacturers for example, the lignin structure is changed. The main processes are Kraft, Soda, Sulphite and Organosolv. Independent of the process, isolated lignins are abundant in aromatic rings, aliphatic and aromatic hydroxyl, methoxy and carboxyl groups. Molar mass, functional groups and monolignol contents are strongly affected by isolation process and plant or tree species. The above-mentioned lignin industrial plants control the main process parameters, generating technical grade lignins, with constant chemical structure and properties, at some extent. After all, its aromatic structure can contribute to mechanical behaviour improvement of lignin-based polymers, and its functional groups can be functionalized and applied on polymer/adhesive developments as well.

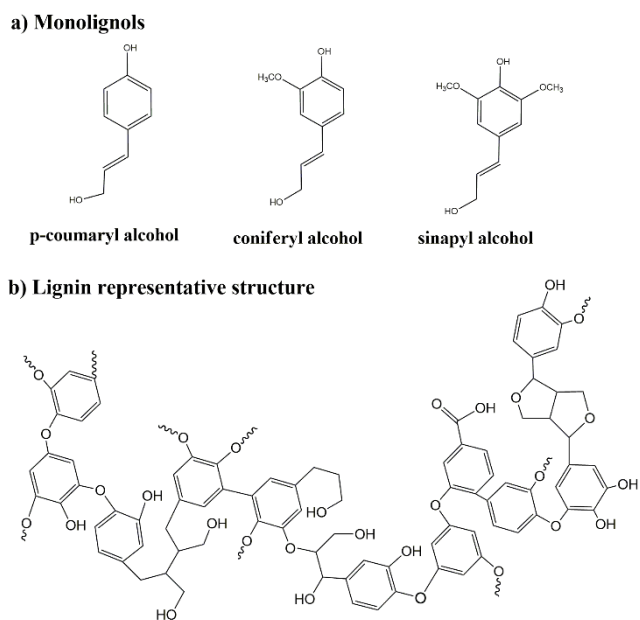


Fig. 1. a) Primary monolignols: para-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol, followed by their respective structure (cumaryl, guaiacyl, and syringyl), and b) Lignin representative structure

Initially, works were dedicated to the development of lignin based phenolic resins, due to the abundance of phenolic groups in its structure. After several efforts, lignin based phenolic resins were developed, formaldehyde free in their preparation. In most cases, the lignin-based resins were applied as wood adhesive since the obtained material usually can attend global standards for this type of application [11].

More recently, lignin-based epoxy and polyurethane received increasing attention. Similar to the initial approach on phenolic resins obtention, the direct incorporation of lignin into epoxy/PU formulations was investigated. Afterwards, some chemical methods for modification were proposed and investigated, thus improving the reactivity of the hydroxyl groups in the lignin structure, or adding new functional groups to its backbone, like oxirane and amine.

Since the development of lignin-based phenolic resins is well established and largely reported, this work aims to present the current contributions to lignin-based epoxies and polyurethanes developments. In this sense, this review can support scientists, chemists, and professionals on the improvement of these structural adhesives, contributing to the development of a circular economy and revalorization of this potential renewable and natural raw material: lignin.

2. Lignin-based polyurethane adhesives

2.1. Unmodified lignin

Direct incorporation of isolated lignin without previous modification prior to incorporation is the first and simplest approach to the development of lignin-based adhesives, including polyurethanes. In this case, lignin is usually employed as the polyol, due to the high amount of hydroxyl groups. Ideally, both hydroxyl types (aliphatic and phenolic) were expected to react towards the isocyanate, however, this has not been observed. The phenolic hydroxyl group is less prone to react with isocyanate groups, probably due to the steric hindrance. Thus, the direct incorporation of lignin results into polyols with lower reactivity and poor dispersion, for high lignin content formulations. Despite some drawbacks, several works were recently reported with promising results.

Nacas et al. solubilized unmodified kraft lignin and MDI in THF for solvent based adhesive development. Several NCO:OH ratios were investigated, aiming to elucidate the reactivity of both hydroxyl types, aliphatic and phenolic, towards MDI in polyurethane synthesis. The adhesive generated high practical adhesion in wood (> 6 MPa), which was comparable to commercial adhesives. In addition, results suggested a dependency between practical adhesion and MDI content, in which the higher the NCO:OH ratio the better the shear strength at rupture, possibly due to reaction of residual MDI with wood hydroxyl groups [12].

Organosolv and kraft lignins were incorporated as filler (up to 20 %wt.) into a commercial monocomponent polyurethane. Among the tested lignin types, PU with 20 %wt. of organosolv lignin provided the highest shear strength and the best delamination behaviour (failure type). Lignin incorporation increased the viscosity and improved the gap filling performance of the PU adhesives [13].

Tavares et al. obtained polyurethanes, with a wide range of properties, mixing unmodified lignin and castor oils (unmodified and transesterified) under several lignin: oil ratios. Modified and unmodified castor oils have been used in industrial adhesive formulations since many years. Authors incorporated up to 30 %wt. into the oils, and this mixture was employed as the polyol. Polyurethanes from modified castor oil and lignin presented Young's modulus up to 2000 MPa and ultimate tensile strength of 23.0 MPa. As expected, the inclusion of lignin severely affected the elongation behaviour of the synthesized PUs. In short, polyurethanes were developed with high potential to be applied as adhesive, ranging from tough to brittle materials. Afterwards, following a similar approach, this research

group developed a polymer matrix composite using castor oil and unmodified lignin [14].

Aiming to overcome the above mentioned disadvantages, softwood lignin solvent fractioning was recently proposed as a strategy to obtain lignin fractions with different molar mass, hydroxyl contents and properties for PU synthesis. Lignin fractions were mixed with industrial polyols and diisocyanates yielding polyurethanes with high content of unmodified lignin (>40%wt.). Polyurethane morphology was investigated, and micrographs revealed a network assembled by lignin nanoparticles between urethane groups. Among all formulations, the highest measured ultimate tensile stress was 43.2 MPa, while the lower measured strength was 6.8 MPa [15]. Lignin fractioning was carried out by another group for the development of polyurethane coatings [16].

2.2. Modified lignin

Since the early 70's, lignins modification became a tool to improve its reactivity and dispersion in polymers. Hydroxypropylation was one of the first and, yet to this day, the most effective approach for this purpose. Lignin was first hydroxypropylated under high pressure and temperature, generating a liquid lignin, dispersed in homopolymer of propylene oxide [17]. Later, a milder procedure was reported, which was conducted under low temperature and atmospheric pressure, resulting into a powder lignin, with higher reactivity and miscibility [18]. The majority of the studies concerning hydroxypropylated lignins were focused on its use as a polyol in polyurethane rigid foam formulations [19]. Figure 2 shows a scheme of hydroxypropylation reaction.

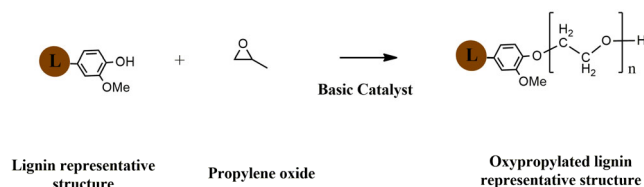


Fig. 2. Scheme of lignin hydroxypropylation and resulting structure (Adapted from Ref. [17])

Hydroxypropylated lignin was recently obtained under high (highT_HPL) and low (lowT_HPL) temperature and pressure and applied as partial polyol in polyurethane adhesives (blended with castor oil). PU with lignin hydroxypropylated at low temperature and pressure (lowT_HPL) showed higher ultimate tensile stress than its counterparts. On the other hand, polyurethanes obtained

with unmodified lignin and lowT_HPL presented cohesive failure and similar ultimate shear stresses (practical adhesion), which were higher than results of highT_HPL-containing samples. Glass transition temperature of PUs was strongly affected by lignin type, arising from 1.1°C (PU from highT_HPL), 21.9°C and 26.0°C for lowT_HPL and unmodified-containing PUs [20].

Steric hindrance strongly decreases the hydroxyl reactivity in lignin toward diisocyanates. Demethylation emerged many years ago as promising candidate to reduce the amount of methoxy groups in lignin and, consequently, decrease hydroxyl steric hindrance (Fig. 3), favouring its reaction toward diisocyanates [21]. Nevertheless, demethylated lignin partially substituted polyethylene glycol in the polyol, in which lignin hydroxyl content, thermal stability and PU ultimate tensile strength were increased, by adding up to 30 %wt. [22].

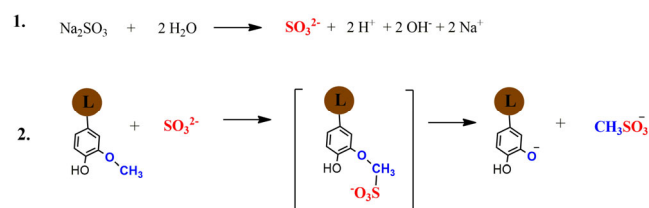


Fig. 3. Decreasing of hydroxyl group's steric hindrance via lignin demethylation (Adapted from Ref. [21])

Despite the high density of phenol groups in lignin structure, thermoplastic polyurethanes have been developed using high lignin contents in the formulation. Methylation and oxypropylation were proposed as modification methods for this purpose, based on molecular structure and thermal properties of the modified biopolymer. However, besides the strong evidence based on the well established material characterization, lignin-containing thermoplastic polyurethanes were not developed in these works [23,24].

On the other hand, partial lignin acetylation was applied by different authors to decrease the content of lignin hydroxyl groups, or its functionality [25,26]. In this sense, partially acetylated lignin with lower hydroxyl content enabled the synthesis of thermoplastic materials with a large range of mechanical properties, starting from brittle up to elastomeric (large deformation) polyurethanes. Figure 4 illustrates the proposed method.

Lignin-containing thermoplastic polyurethanes were developed from partial acetylated lignin and polyethylene glycols, with different molecular weights, under several NCO:OH ratios. Lignin content strongly affected TPU glass transition temperature, which raised from -30°C to above -10°C by increasing its content. NCO:OH ratio and

molecular weight of polyethyleneglycol presented a more significant influence on TPU thermomechanical properties above 100°C. At last, the lignin-containing TPUs were applied as hotmelt adhesive for wood substrate, resulting in some cases into shear strengths higher than 5 MPa, the same strength level as industrial adhesives for this application [26].

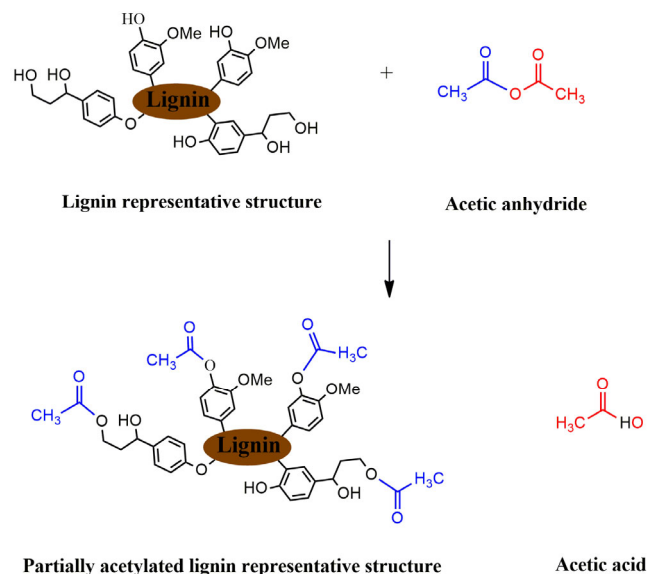


Fig. 4. Partial acetylation of lignin for synthesis of thermoplastic polyurethane to be applied as hotmelt adhesive (Adapted from Ref. [26])

3. Lignin-based epoxy adhesives

Following the same approach used for polyurethanes, unmodified lignin can also be incorporated in formulations of epoxy adhesives, without previous chemical modification. In a recent effort, the authors reported a slight increase in shear strength and practical adhesion using steel laps by incorporation up to 15 wt.% of lignin as filler, in room temperature cured epoxy resin. DSC curves suggested a chemical reaction between lignin OH-groups and the oxirane rings from epoxy resins at elevated temperatures, which might affect thermomechanical properties of one component epoxies, cured at high temperatures [27]. The same reaction between lignin OH groups and oxirane rings was verified by Li et al, in which this mechanism was proposed as an alternative to formaldehyde-based wood adhesives [28].

In the case of epoxies cured at elevated temperature, the above proposed reaction might strongly affect the material properties, increasing the crosslinking density, temperature

resistance and shear strength. Kong et al. reported the increase in shear strength with the inclusion of unmodified lignin in epoxy resin, which was more pronounced at higher temperatures, as result of higher thermal resistance and crosslinking density. However, unmodified lignins also presented limitations such as the increase of epoxy brittleness, which might be overcome by its chemical modification or functionalization [29].

3.1. Lignin epoxidation

As previously mentioned, DGEBA is the most used epoxy resin, which is obtained from the reaction between bisphenol A and epichlorohydrin. Several efforts have been dedicated in the search for a renewable substitute for bisphenol A, due to its toxicity and carcinogenic character. The abundance of phenolic groups in the lignin structure enhances its use as epoxy precursor. First, similar methodologies were employed, i.e., lignin phenolic groups reacted towards epichlorohydrin in an alkaline medium, as shown in Figure 5. Gouveia et al. compared the incorporation of pristine and epoxidated lignin in epoxy adhesive. Results revealed that the addition of epoxidated lignin increased the impact resistance and practical adhesion of cured epoxies (the last one was verified through lap shear tests with steel as substrates) [27]. The optimal condition, concerning both properties, was verified by incorporating 15 wt.% of modified lignin in the neat epoxy resin. Furthermore, the incorporation of 30 wt.% decreased the mechanical properties, in comparison with samples with 15 wt.%, but were still slightly higher than the results obtained with neat epoxies.

Aiming to achieve a higher conversion rate of hydroxyl groups to oxirane rings, some studies have proposed a previous lignin modification before epoxidation. For this purpose, hydroxypropylation was applied to convert aromatic hydroxyl into aliphatic ones by etherification. Afterwards, hydroxypropylated lignin was reacted with epichlorohydrin for epoxidation. Epoxy resins were obtained from hydroxypropylated lignin, and results revealed a low influence of lignin's molar mass and content on epoxy curing kinetic. In addition, the activation energy of lignin-based epoxies presented similar level as commercial epoxy resins [13,30].

Furthermore, several works reported alternative catalysts and optimized synthesis parameters. However, the reaction between phenol groups in the lignin structure and epichlorohydrin is still the most employed chemical reaction for lignin epoxidation. In a different approach, other lignin modification methods were proposed for the development of hardener for epoxy systems, as discussed in the next section.

3.2. Lignins amination

Mannich reaction is the most reported approach to produce aminated lignin, therefore, the recent works on this topic have been focused on the optimization of the synthesis conditions and outcome, such as: the concentration of primary and secondary amines and their effects on the properties of cured epoxies.

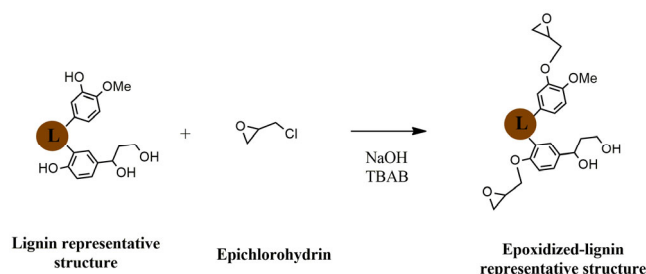


Fig. 5. Epoxidation of kraft lignin by the reaction of phenolic groups with epichlorohydrin in presence of NaOH (Adapted from Ref. [27])

Ott et al. investigated the effects of diamine molecular weights on the flexibility of cured epoxies. The authors emphasized the presence of homopolymerization during lignin amination via Mannich reaction and its dependency on the type of amine. Furthermore, a relationship between molecular structure and mechanical properties was proposed, based on flexural tests and nanomechanical analysis. Results confirmed the strong influence of lignin stiffness on the epoxy mechanical properties [31].

Nikafshar et al. proposed the lignin amination in three steps. First, the steric hindrance of reactive groups was decreased by lignin demethylation. Afterwards, an intermediate reaction was developed, in order to increase the functional group reactivity. At last, lignin was aminated. Authors confirmed the possibility of employing lignin as the hardener of epoxy systems. They defined specific lignin concentrations, in which the biobased hardener provided good mechanical properties, comparable with commercial ones [32].

Pan et al. introduced oxirane groups in the lignin structure, prior to their amination [33]. Then, authors investigated the effects of the inclusion of aminated lignin as a hardener in epoxy synthesis, and its effect on the final epoxy thermal properties. The results revealed that the incorporation of aminated lignin improved the thermal resistance of the cured resin in comparison to the neat epoxy [34].

In short, Mannich template reaction can yield aminated lignin that can be applied as a hardener for epoxy system, with good mechanical and thermal properties. Some other

modification methods were reported in the literature, among them the functionalization of lignin with NCO groups might support the development of polyurea and thermal activated adhesives, in a near future [27].

4. Conclusions

Technical grade lignin emerged as a potential candidate for the replacement of petroleum-based raw materials, in polyurethane and epoxy adhesives. Small concentrations of unmodified lignin can be incorporated in polyurethane and epoxy formulations, improving polymer mechanical properties. On the other hand, high concentrations of unmodified lignin can cause phase separation and brittle behaviour. Chemical modification of lignin overcomes most drawbacks, improving its reactivity, solubility, and practical adhesion. Modified lignin allows developing polyurethane adhesives with a wide range of properties, i.e., from highly brittle wood adhesives to largely flexible thermoplastic polyurethanes. In the case of epoxy adhesives, chemically modified lignin can substitute both components of the system: epoxy resin and hardener. Indeed, lignin-based adhesives appears as potential materials towards the substitution of fossil-based ones.

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