Biolignin[TM] Based Epoxy Resins

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ABSTRACT: Wheat straw Biolignin[TM] was used as a substitute of bisphenol-A in epoxy resin. Synthesis was carried out in alkaline aqueous media using polyethyleneglycol diglycidyl ether (PEGDGE) as epoxide agent. Structural study of Biolignin[TM] and PEGDGE was performed by solid-state ^{13}C NMR and gel permeation chromatography, respectively, before epoxy resin synthesis. Biolignin[TM] based epoxy resins were obtained with different ratios of Biolignin[TM] : PEGDGE and their structures were analyzed by solid-state ^{13}C NMR. The crosslinking of PEGDGE with Biolignin[TM] was highlighted in this study. Properties of Biolignin[TM] based epoxy resins were analyzed by differential scanning calorimetry and dynamic load thermomechanical analysis as well as compared with those of a bisphenol-A epoxy-amine resin. Depending on the epoxy resin formulation, results confirmed the high potential of Biolignin[TM] as a biosourced polyphenol used in epoxy resin applications. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Lignin is the second most abundant and renewable macromolecule on earth after cellulose. It is found as a cell wall component in trees and other vascular plants, accounting from 15% to 40% of the biomass matter. It is widely accepted that biosynthesis of lignin takes its origin from the polymerization of three types of phenylpropane units: *p*-Coumaryl, Coniferyl, and Sinapyl alcohols. They are present in different quantities, depending on the origin of the plant. Their oxidative enzymatic polymerization leads to the *p*-hydroxyphenyl, Guaïacyl and Sinapyl units found in lignin structure.[1]

The presence of phenolic hydroxyls in the lignin macromolecule allows its use as a substitute of bisphenol-A in epoxy resin synthesis. The aromatic structure of lignin enhances the stiffness and improves the thermal properties of the epoxy resin obtained.[2] For bisphenol-A substitution, the lignin should be free of impurities, such as salts and sugars. Several studies have been aimed at the modification of lignin before epoxidation. Alkali lignin was mixed with phenols to have a hyperbranched phenolic lignin[3–5] that would have a higher reactivity toward epoxides. The hydroxyalkylation of lignin was studied by Glasser et al.[2,6,7] in epoxy resin synthesis to have a highly soluble lignin in organic solvent. Nevertheless, because of the toxicity and harsh synthesis conditions of the lignin modification process, substitution of bisphenol-A by unmodified lignin seems to be the best method to be used for epoxy resin synthesis. Based on this method, several studies have been conducted using calcium-lignosulfonates,[8] steam exploded lignin,[9,10] or fractionated lignin.[11] Grafted epoxy groups were observed by NMR analysis of lignin-based epoxy resins and showed the compatibility of using lignin as a biosourced phenol in epoxy resin synthesis. Moreover, substitution of epichlorohydrin by polyethyleneglycol diglycidyl ether (PEGDGE) has also been studied. Lignin-based epoxy resins were obtained by using various derivatives of PEGDGE in the works of Nonaka et al.[12] and Hirose et al.[13] The results of these works showed that properties of lignin epoxy resins can be tuned by changing the molecular weight of the PEGDGE, the content of lignin, the nature, and amount of the curing agent, thus allowing a wide range of applications. In most cases, cured epoxy resins based on lignin had similar or better properties than those based on bisphenol-A. However, nowadays, the availability of lignin at industrial scale remains a major problem encountered in the manufacture of lignin-based epoxy resins. In this context, the Compagnie Industrielle de la Matière Végétale (CIMV Company) has developed a biorefinery pilot plant able to extract organosolv lignin by treating 100 kg of dry vegetable matter per hour.[14]

Wheat straw lignin extracted by the CIMV process,[15] and marketed under wheat straw Biolignin[TM] trademark, was analyzed in recent works.[16] Its structural determination and quantification of its hydroxyl content have shown that the biopolymer is a valuable substitute of bisphenol-A. We report in this article the synthesis of Biolignin[TM] and PEGDGE based epoxy resins. The first part of this study will focus on the chemical behaviors of Biolignin[TM] and PEGDGE in basic aqueous medium. The second part will be aimed at the synthesis and structural determination of Biolignin[TM]-PEGDGE epoxy resins. Thermomechanical analysis of epoxy resins will be presented in the last part of this article. The structure and thermomechanical properties of Biolignin[TM] based epoxy resins were determined by solid-state ^{13}C NMR, attenuated total reflectance-Fourier transform infrared (ATR-FTIR), differential scanning calorimetry (DSC), and dynamic load thermomechanical analysis (DLTMA).

MATERIALS AND METHODS

Biolignin[TM] Extraction

Wheat straw Biolignin[TM] ($\approx$97% of purity) was extracted by the CIMV organosolv technology.[14–18] The remaining products in Biolignin[TM] are mainly sugars (<2%) and minerals (<1%). Sugar content was analyzed by using TAPPI standard test methods T 223 cm-01. Mineral content was determined by using Inductively Coupled Plasma Optical Emission Spectroscopy.

Biolignin[TM] Esterification

Biolignin[TM] was esterified using acetic anhydride and pyridine with the same experimental conditions described in a previous work.[16] FTIR-ATR and solid-state ^{13}C NMR analysis of acetylated lignin showed a full esterification of hydroxyl groups.

Gel Permeation Chromatography

Gel permeation chromatography (GPC) analysis was conducted using a Waters, Versailles, France 1515 isocratic high-performance liquid chromatography (HPLC) pump, a column oven, and a Waters 2414 Refractive detector. The system was equipped with 3× GPC columns PL-Gel (100 Å, 500 Å, 1000 Å—particle size: 5 μm) connected with a guard-column (Agilent Technologies, Massy, France). Tetrahydrofuran (THF) was used as eluent and sample solvent. Refractive detector and columns were constantly maintained at 30°C. Flow was maintained at 1.2 mL/min with a sample injection volume at 20 μL. Calibration was made using Polystyrene standards. Sample concentration was 10 mg/mL in THF.

Poly(Ethyleneglycol) DiGlycidyl Ether (PEGDGE)

PEGDGE (M_n = 526 g/mol) was supplied by Sigma-Aldrich.

Solid-State ^{13}C NMR

The solid-state ^{13}C NMR analysis was recorded on a Bruker (Wissembourg, France) Advance 700 MHz instrument equipped with a 4 mm MAS Probe DVT [31]P-^{15}N/^{1}H GRD.

Experiments were performed at 23°C. Samples were placed in a zirconium rotor of 4 mm diameter and positioned at the magic angle at a speed of 10 kHz. Cross polarization have been implemented with a ramp of 80–100% for ^{1}H impulse and another impulse of 50 kHz on [13]C. These Hartmann-Hahn conditions were applied during a contact time of 2 ms. A decoupling of 100 kHz on ^{1}H channel has been used during 17 ms. A total of 2048 scans were accumulated with a recurrence delay of 3 s. [13]C chemi-

cal shifts were calibrated using the carbonyl signal of glycine as external reference.

Attenuated Total Reflectance-Fourier Transform InfraRed

Analysis was performed on a PerkinElmer (Courtaboeuf, France) Spectrum 100 Universal ATR-FTIR instrument equipped with a diamond/ZnSe crystal in single reflection configuration. Dried samples were placed on the crystal plate with a constant applied pressure of 85 N.mm^{-2}. For each sample, 10 scans were performed at a resolution of 4 cm^{-1}.

Differential Scanning Calorimetry

DSC measurements were performed on a Setaram (Caluire, France) DSC131 with alumina pans under static air using the following temperature program: Isothermal state at 30°C during 10 min, heat ramp from 30°C to 350°C at 5°C min^{-1}, isothermal state at 350°C during 1 min and cooling to room temperature at 20°C min^{-1}.

Dynamic Load Thermomechanical Analysis

DLTMA measurements were performed on a Mettler-Toledo (Viroflay, France) TMA SDTA840 equipped with a quartz film clamping device in dynamic tensile mode under N$_2$ flow (80 mL/min). The size of all epoxy resins samples were 1.5 × 0.6 mm with a thickness from 0.2 mm to 2 mm.

In a first part, analysis of epoxy resins were carried out using the following force and temperature program: isothermal state at 25°C during 10 min with a constant force applied at 0.01 N—then, a dynamic tensile force is applied from 0.1 N to 0.5 N with a frequency of 6 s during a heat programming ramp from 25°C to 190°C at 10°C min^{-1} followed by a cooling process to 25°C at 10°C min^{-1} with a constant force applied at 0.01 N.

In a second part, a preheating process was run before analysis of epoxy resins using this force and temperature program: isothermal state at 190°C for 15 min followed by another isothermal state at 25°C for 90 min with a constant applied force at 0.01 N. Then, a dynamic tensile force is applied from 0.1 N to 0.5 N at a frequency of 6 s with a force and temperature program: isothermal state at 25°C during 15 min, heat ramp from 25°C to 190°C at 10°C min^{-1} then cooling to 25°C at 10°C min^{-1}.

Dissolution of Wheat Straw Biolignin[TM] in Basic Aqueous Media

Dried wheat straw Biolignin[TM] (6.5 g) was dispersed in 43.5 g of water at room temperature with an Ultra-Turrax T18 disperser (IKA, Staufen, Germany) at 13,000 rpm for 2 min. Under vigorous mechanical stirring, 2.6 g of a NaOH solution (10.7 mol L^{-1}) is quickly added to obtain a Biolignin[TM] solution with a pH > 12. Filtration is carried out over a Buchner funnel. The filtrate is oven dried at 50°C for 48 h, and finally, a dark brown powder is obtained. Dissolved product, after analysis, was determined to be ionized wheat straw Biolignin[TM].

PEGDGE Hydrolysis in Basic Medium

In a 100 mL flask, 30 mL of distilled water and 9 g of PEGDGE are added. The system is mounted by a reflux condenser and heated to reflux under magnetic stirring. Seven grams of a NaOH solution (10.7 mol·L^{-1}) is added to the mixture. Stirring is maintained under reflux during 2 h. The colorless solution turns into a clear yellow solution at the end of the reaction. The mixture is cooled to room temperature and a 2M HCl solution is added until neutrality. The product is extracted twice with methylene
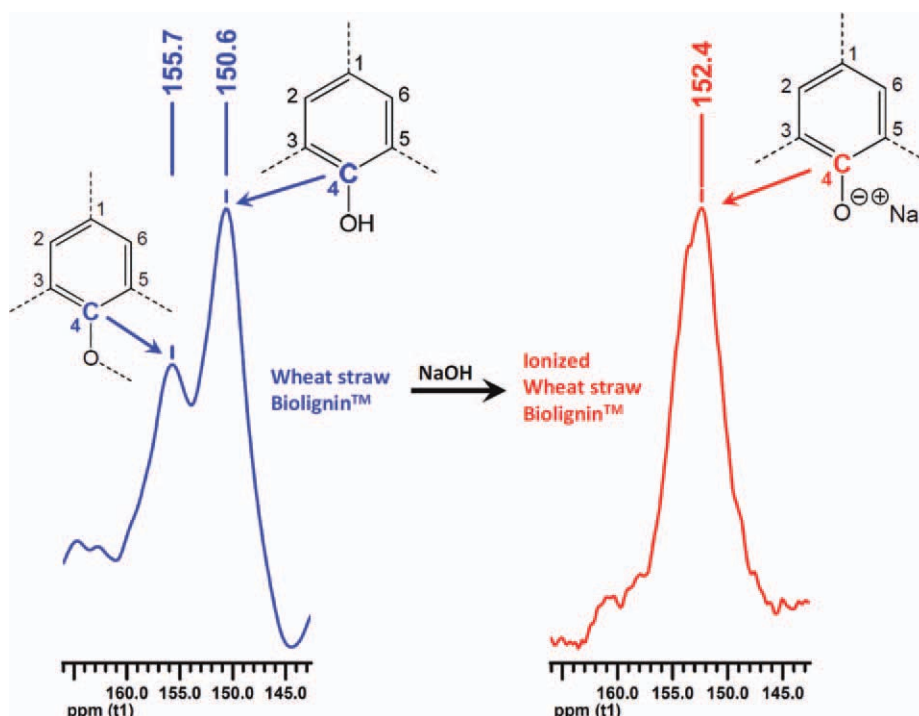
Figure 1. Solid-state ^{13}C NMR spectra of original and ionized wheat straw Biolignin^{TM} in the region of 145–165 ppm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

chloride. The organic phase is dried over MgSO$_4$. Organic solvent is evaporated under reduced pressure to give a clear oil which, after analysis, is determined to be hydrolyzed PEGDGE.

Biolignin^{TM} Based Epoxy Resin Synthesis

Twenty grams of dried wheat straw Biolignin^{TM} is dispersed in 130 g of water with an IKA (Staufen, Germany) Ultra-Turrax T18 disperser at 13,000 rpm for 2 min. Under vigorous mechanical stirring, 8 g of a sodium hydroxide aqueous solution (10.7 mol·L^{-1}) is quickly added to obtain a Biolignin^{TM} solution with a pH > 12. The mixture is transferred into a 500 mL reactor equipped with a mechanical stirring, a reflux condenser, a funnel, and a thermometer. The mixture is heated to 60°C under a moderate stirring. Through the funnel, 20 g of PEGDGE is slowly added at a mass ratio of 1 : 1 with respect to the Biolignin^{TM} at this step, and stirring is kept at 60°C during 2 h. The mixture is poured into rectangular silicon molds (25 × 50 × 11 mm^3) and oven dried at 50°C during 48 h to yield a black resin, which, after analysis, is determined to be Biolignin^{TM}-PEGDGE epoxy resin.

The same experimental procedures were used to obtain Biolignin^{TM}-PEGDGE epoxy resins with ratio 1 : 2, 1 : 4, and 1 : 6 except that 40 g (ratio 1 : 2), 80 g (ratio 1 : 4), and 120 g (ratio 1 : 6) of PEGDGE were added.

Gel Time Determination of Biolignin^{TM}-PEGDGE Epoxy Resins

Gel time was determined through physical observation. Start time was engaged when PEGDGE was added into the Biolignin^{TM} solution (pH > 12). Gel time was determined when the mixture formed a solid mass.

Swelling Test of Biolignin^{TM}-PEGDGE Epoxy Resins

Five grams of Biolignin^{TM}-PEGDGE epoxy resin 1 : 1 sample is crushed and immersed in 10 mL of distilled water (pH = 7) during 2 months at room temperature. The mixture is filtered over a Buchner funnel.

Methylene chloride (15 mL) is added to the filtrate and the mixture is transferred in a separating funnel. The organic phase is collected, dried under MgSO$_4$, and evaporated under reduced pressure. A clear oil is obtained, and after infrared analysis, the product is corresponding to hydrolyzed PEGDGE.

The same experimental procedures were used to analyze Biolignin^{TM}-PEGDGE epoxy resins with ratio 1 : 2, 1 : 4, and 1 : 6.

Curing of a Bisphenol-A Epoxy Resin with TriEthylene Hexa-Amine (TETA)

Diglycidylether of bisphenol-A (DGEBA) and TETA (60% grade) were purchased from Sigma-Aldrich. The epoxy resin has a polymerization degree of $n = 1$. In a 50 mL flask, the epoxy resin is mixed with TETA at room temperature with a 1 : 1 molar ratio of epoxy : amine. The mixture is added into rectangular silicon molds (25 × 50 × 11 mm^3) and oven dried at 50°C for 48 h to give a colorless and solid epoxy-amine resin.

RESULTS AND DISCUSSION

Solubility of lignin has been highly studied in the field of lignin-based epoxy resins.[3–8] In our case, a complete dissolution of wheat straw Biolignin^{TM} occurs in a concentrated NaOH solution (10.7 mol L^{-1}). In this context, we decided to study the structure of this Biolignin^{TM} in the form of a sodium salt.
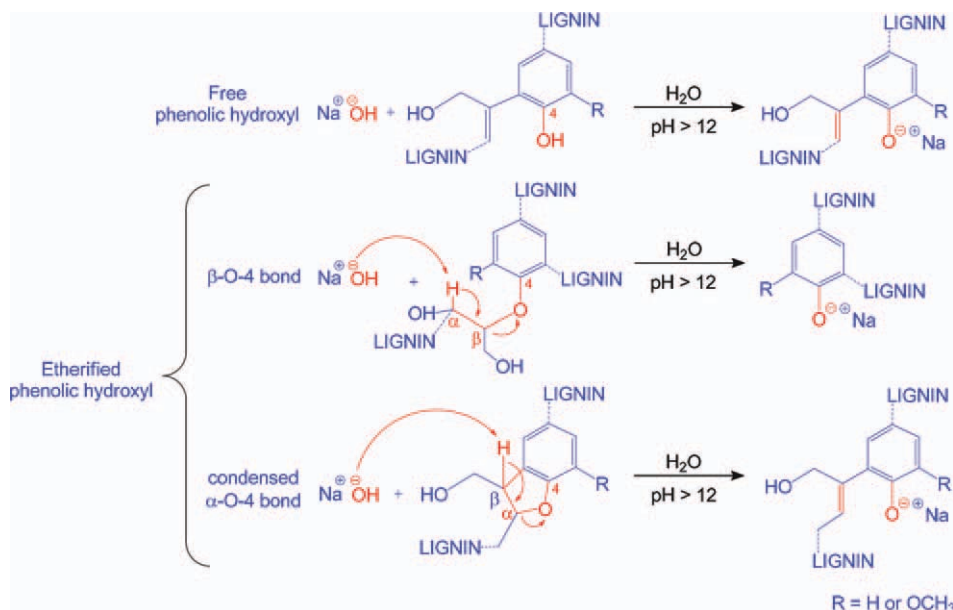
Figure 2. Ionization mechanism of Biolignin™ in NaOH solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Solid-State ^{13}C NMR Analysis of Wheat Straw Biolignin™ under the Form of Sodium Salt

Wheat straw Biolignin™ was dissolved at pH > 12, and the dried product was determined to be ionized Biolignin™. Analysis were performed by solid-state ^{13}C NMR (Figure 1).

In Figure 1, the most interesting information related to this article is observed over the aromatic hydroxyl zone of the spectra between 145 ppm and 165 ppm. Signals at 155.7 ppm and 150.6 ppm are attributed to the C_4 of phenylpropane unit attached to etherified and free phenolic hydroxyl groups in Biolignin™ structure, respectively. The solid-state ^{13}C NMR spectrum of ionized Biolignin™ (red curve) shows a unique signal at 152.4 ppm, which is attributed to the C_4 of sodium phenate groups. In fact, the delocalization of the negative charge over the aromatic ring of a phenate structure, and more precisely over the delocalized π electrons cloud, induces a higher electron density inside the ring. Thus, this phenomenon forms a higher paramagnetic current that contributes to a deshielding over the aromatic C_4 of phenylpropane units. In accordance with these observations, dissolution of wheat straw Biolignin™ in NaOH solution leads to the transformation of free and also etherified phenolic hydroxyls into sodium phenate groups (Figure 2).

We determined in a previous work[16] the amount of free phenolic hydroxyl groups in wheat straw Biolignin™. The biopolymer

is completely dissolved in a NaOH solution when a minimum molar ratio of 1 : 1.5 (phenolic group : NaOH) is used. The 0.5 molar excess of NaOH is probably necessary to convert the etherified phenolic hydroxyl groups into sodium phenate groups and to partially saponify formyl and acetyl groups,[16] but they cannot be quantified separately from the free phenolic hydroxyl groups.

Analysis of Hydrolyzed PEGDGE under Basic Aqueous Medium

The alkaline hydrolysis of an oxirane ring corresponds to the nucleophilic attack of the hydroxide anion to the less hindered carbon in accordance with a S_N2 nucleophilic substitution. Regarding our experimental conditions, the oxirane ring opening of PEGDGE leads to an intermediate sodium alkoxide group that would react through two competitive reactions:

1. Conversion into hydroxyl group under aqueous medium
2. Nucleophilic attack on the oxirane ring of another PEGDGE molecule that could lead to a chain-growth polymerization

PEGDGE and its hydrolyzed form were analyzed by GPC (Table I).

Molecular weights of hydrolyzed PEGDGE are almost two times higher than PEGDGE and the difference between their PDI is low. Those results highlight the two competitive reactions and would explain that, during alkaline hydrolysis, PEGDGE went through a low chain-growth polymerization and a hydrolysis of the ended oxirane rings (Figure 3).
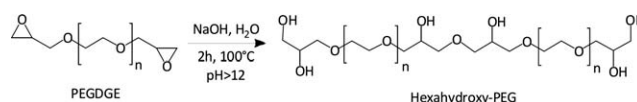
Table I. Gel Permeation Chromatography Results of PEGDGE and Hexahydroxy-PEG

	M_n (g/mol)	M_w (g/mol)	Polydispersity index (PDI)
PEGDGE	546	765	1.40
Hydrolyzed PEGDGE	1010	1550	1.53

Figure 3. Alkaline hydrolysis of PEGDGE.

Table II. Gel Time and Physical Aspect of Biolignin™-PEGDGE Epoxy Resins

Mass ratio Biolignin™ : PEGDGE	Gel time	Physical aspect of oven-dried resins
1 : 1	120 min	Black resin, flexible, and resistant
1 : 2	210 min	Black resin, flexible, and brittle
1 : 4	400 min	Black elastic resin and breakable
1 : 6	700 min	Black sticky elastic and breakable

Judging by the structure of the hydrolyzed product of PEGDGE composed of six hydroxyls groups within chains of PolyEthylene Glycol (PEG), we will name it hexahydroxy-PEG in the following studies.

Synthesis and Structural Analysis of Wheat Straw Biolignin™-PEGDGE Epoxy Resins

Synthesis of Biolignin™ based epoxy resins was carried out using various mass ratios of Biolignin™ : PEGDGE, ranging from 1 : 1 to 1 : 6, and gelling occurred in all cases. The gel time was the longest at 60°C and depended on the amount of PEGDGE used (Table II).

Gelling is a physicochemical process observed when the viscosity of the mixture increases progressively until the formation of an infinite polymer network. At this point, the product has an infinite molecular weight and becomes completely insoluble. This is mostly the case observed in the curing process of epoxy resins. The same phenomenon is observed during the synthesis of Biolignin™-PEGDGE epoxy resins, and thus, confirms the chemical reaction between the two products.

Stiffness of Biolignin™-PEGDGE epoxy resins depends on Biolignin™ : PEGDGE mass ratio. We proceeded to their acetylation to improve their solubility in organic solvent. Biolignin™-PEGDGE epoxy resins and their acetylated forms, at mass ratios 1 : 1 to 1 : 6 (Biolignin™ : PEGDGE), were analyzed by ATR-FTIR. All spectra had the same shape, so we chose the spectrum of Biolignin™-PEGDGE epoxy resin of 1 : 1 ratio as a representative of all epoxy resins obtained in Table I (Figure 4).

Regarding the Biolignin™-PEGDGE epoxy resin spectrum (blue curve), the large band observed in the region of 3400 cm^{-1} is attributed to the υO—H of hydroxyl groups (free and H-bonded). Band observed at 1578 cm^{-1} is attributed to a υC=O carboxylate of Biolignin™. The band observed at 1086 cm^{-1} in both spectra is attributed to the υC—O aliphatic ether of PEGDGE ether chains.

IR spectrum of acetylated Biolignin™-PEGDGE epoxy resin (red curve) shows a υO—H band (free and H-bonded) around 3400 cm^{-1}. The band observed at 1738 cm^{-1} is attributed to the υC=O ester band. The band at 1224 cm^{-1} is attributed to a υC—O aromatic ester. Those observations are interesting in many aspects. The acetylation of Biolignin™-PEGDGE epoxy resin is partial since we observe the υO—H of hydroxyl and the υC=O of ester bands. This would explain why the product is insoluble in this form. Moreover, the υC—O aromatic ester is a proof that there are still sodium phenate groups in Biolignin™-PEGDGE epoxy resins. This implies that the reaction would not consume all phenolic hydroxyls whatever the mass ratio used.

We proceeded to the structural analysis of Biolignin™-PEGDGE epoxy resin 1 : 1 by solid-state ^{13}C NMR (Figure 5).

The signal observed at 27.9 ppm is attributed to a CH_3 linked to a carbonyl $C=O$ (ester and/or carboxylate) which is observed at 173.7 ppm. Indeed, during ionization of Biolignin™, some ester groups[16] (formyl and acetyl) may have been saponified, but it was not possible to evaluate the amount of sodium formiate and acetate formed. The signal at 57.7 ppm is attributed to the CH_3—O methoxy and C—O ester groups. The most intense signal at 72.4 ppm is attributed to the —$(CH_2$—O$)_n$— ether chains of PEGDGE and aliphatic hydroxyl CH_2—OH. Signals of aromatic carbons are observed in the region between 100 and 160 ppm. The signals at 183.2 ppm and 212.2 ppm are, respectively, attributed to a $C=O$ carbonyl of a sodium carboxylate (main structure of Biolignin™) and a ketone function. The signal observed at 152.2 ppm corresponds to the C_4 of sodium phenate groups observed in Figure 1, which is in correlation with the υC—O aromatic ester band observed in the IR spectrum of acetylated resin (Figure 4). The signal at 155.3 ppm is attributed to a C_4 aromatic ether bond. These last
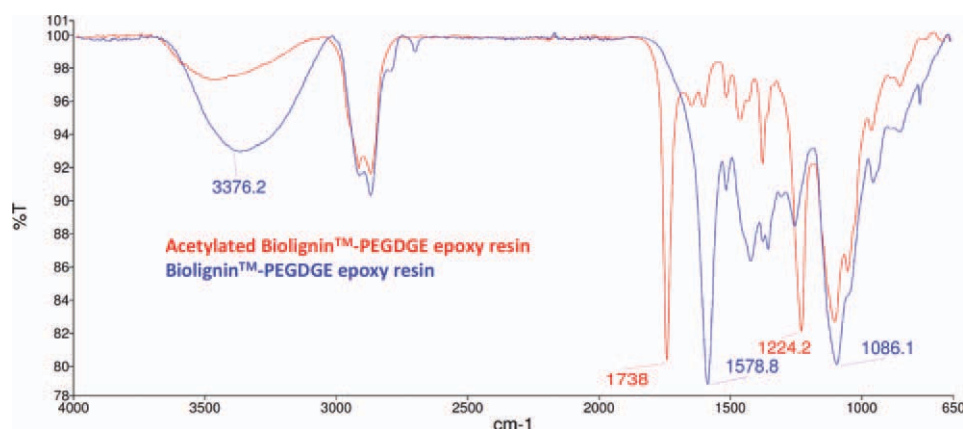

Figure 4. ATR-FTIR spectra of acetylated and original Biolignin™-PEGDGE epoxy resins. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
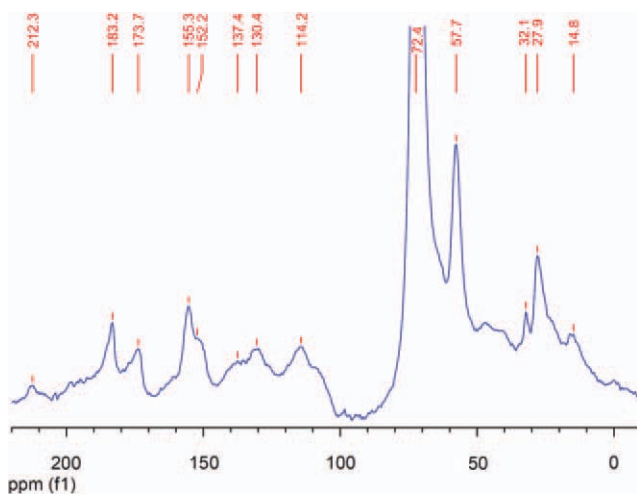
Figure 5. Solid-state ^{13}C NMR spectrum of Biolignin^{TM}-PEGDGE resin (ratio 1 : 1). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

observations confirm that the synthesis of Biolignin^{TM}-PEGDGE epoxy resins involves crosslinking between phenate groups from of Biolignin^{TM} and epoxy groups of PEGDGE.

To study the etherification rate of phenates, the signals of C_4 etherified aromatics (155 ppm) and C_4 phenates (152 ppm) of Biolignin^{TM}-PEGDGE epoxy resins (from ratio 1 : 1 to 1 : 6) were analyzed by solid-state ^{13}C NMR (Figure 6).

Between 140 and 165 ppm, solid-state ^{13}C NMR spectra of Biolignin^{TM}-PEGDGE epoxy resins (ratio 1 : 1 to 1 : 6) do not show a significant difference in signal intensities between etherified C_4 aromatic and ionized C_4 phenates (Figure 6). This observation means that the remaining phenate groups cannot be etherified by PEGDGE, whatever the quantity of epoxide used. It can be explained by the low accessibility of phenates in Biolignin^{TM} due to steric hindrance.

Synthesis Path and Structural Model of Biolignin^{TM}-PEGDGE Epoxy Resin Synthesis

Based on the structural study of ionized Biolignin^{TM} (Figure 2) and the structure of hexahydroxy-PEG (Figure 3), we first propose a synthesis path and a structural model of Biolignin^{TM}-PEGDGE epoxy resin (Figure 7).

In a first step, Biolignin^{TM} is dissolved/ionized in a concentrated NaOH solution (pH > 12). In a second step, after PEGDGE is introduced, two competitive reactions occur during an intermediate step:

1. Partial etherification of Biolignin^{TM} phenates with the epoxy groups of PEGDGE and hydrolysis of the epoxy-end groups (Figure 3) as it was observed by solid-state ^{13}C NMR and FTIR-ATR analysis in Figures 5 and 4.
2. Alkaline hydrolysis of PEGDGE into hexahydroxy-PEG (Figure 3) occurring in the reaction medium.

In the end of reaction, crosslinking of Biolignin^{TM} and PEGDGE forms an infinite network of Biolignin^{TM}-PEGDGE resin that would trap molecules of hexahydroxy-PEG (Figure 7).

The epoxy resins would be softer as the amount of hexahydroxy-PEG is higher (going from ratios 1 : 1 to 1 : 6).

Swelling tests of Biolignin^{TM}-PEGDGE epoxy resins of ratio 1 : 1 to 1 : 6 were conducted in distilled water at room temperature during 2 months to estimate the amount of hexahydroxy-PEG released from the resin samples and thereby to confirm the structure of Biolignin^{TM}-PEGDGE epoxy resins proposed in Figure 7.

Between 0.12% and 0.20% of the total estimated amount of hexahydroxy-PEG was released from the resins depending on the Biolignin^{TM} : PEGDGE ratio (1 : 1 to 1 : 6, respectively). Such a low mass of hexahydroxy-PEG is not in accordance with the structure proposed in Figure 7.

Taking account of the structural study of Biolignin^{TM}-PEGDGE epoxy resins (Figure 5) and PEGDGE under basic aqueous medium (Figure 3), we assume that the crosslinking between Biolignin^{TM} and PEGDGE is a chain-growth polymerization of PEG-like polymer chains between Biolignin^{TM} oligomers that would form in the end an infinite network (Figure 8).

Thus, we suggest a new structural model of Biolignin^{TM}-PEGDGE epoxy resins (Figure 9). It would explain why the
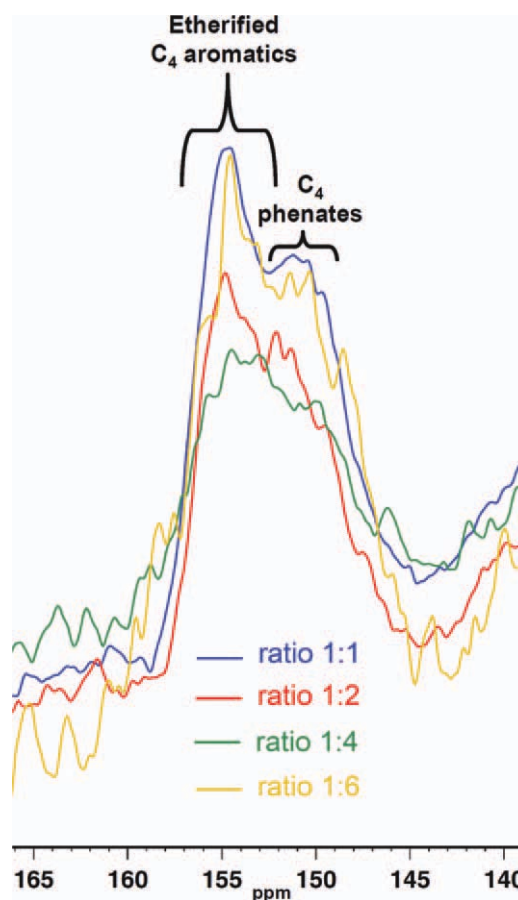

Figure 6. Solid-state ^{13}C NMR spectra of Biolignin^{TM}-PEGDGE epoxy resins (ratio 1 : 1, 1 : 2, 1 : 4, and 1 : 6) in the region of 140–165 ppm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
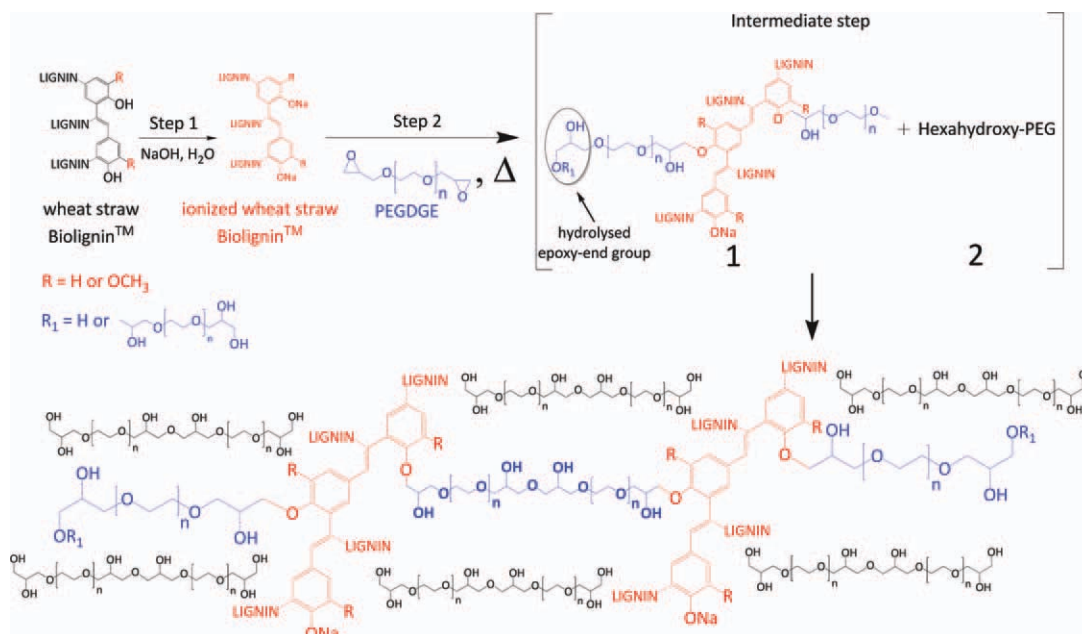
Figure 7. Synthesis path and structural model of Biolignin™-PEGDGE epoxy resins. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Biolignin™-PEGDGE epoxy resin becomes softer as the quantity of PEGDGE used is higher. Considering the very low amount of hexahydroxy-PEG formed during Biolignin™-PEGDGE epoxy resins (from 0.12% to 0.20% with ratio 1 : 1 to 1 : 6), the etherification of phenate groups with PEGDGE is faster than the hydrolysis of the latter. Moreover, the experimental conditions seem to favor a high degree chain growth polymerization of PEGDGE in the presence of Biolignin™. This observation highlights the high reactivity of Biolignin™ toward the diepoxide.

Previous works showed that Kraft lignin was epoxidized by PEGDGE and in the same time cured by an amine[12] in aqueous medium or cured by an anhydride in organic medium.[13] In our case, Biolignin™ crosslinked with PEGDGE in a first step and acted, in a second step, as a curing agent of the obtained epoxy resin. The main difference between these works and the work presented in this article is the reactivity level of Biolignin™ toward PEGDGE. Kraft pulping process is known to modify the structure of lignin because of random coupling reactions of phenolic hydroxyls during process and for the sulfur content in lignin that inhibit its reactivity.[19] On the other side, the structure of organosolv lignin like Biolignin™ is slightly modified and is sulfur-free.[20] In this case, Biolignin™ has more accessible phenolic hydroxyls and they are highly reactive toward epoxy functions unlike Kraft lignin.

Differential Scanning Calorimetry Study of Biolignin™-PEGDGE Epoxy Resins

DSC analysis of Biolignin™-PEGDGE epoxy resins of ratios 1 : 1 and 1 : 2 are shown in Figure 10.

An endothermic transition was observed for both epoxy resins in the temperature range between 150°C and 200°C. After a preheating of these samples at 190°C during 15 min, their DSC analysis were performed from 30°C to 350°C at 5°C min^{-1} and no transition was observed. This would mean that the endothermic transition of epoxy resins of ratios 1 : 1 and 1 : 2 is irreversible (Figure 10). This phenomenon is similar to a postcuring and will be studied in the next part.

The amount of PEGDGE used in Biolignin™-PEGDGE epoxy resin composition seems to have an influence on the intensity of the endothermic peaks areas (Figure 10). Indeed, during synthesis of Biolignin™-PEGDGE epoxy resin, PEG-like polymer chains between Biolignin™ oligomers tend to be longer (Figure 9) as the amount of PEGDGE is higher. Then, the flexibility of the PEG-like polymer chains would have an influence over the thermal behavior of Biolignin™-PEGDGE epoxy resins regarding Biolignin™ : PEGDGE ratio. Following this way, DSC analysis results of Biolignin™-PEGDGE epoxy resins of ratios 1 : 4 and 1 : 6 are shown in Figure 11.

The endothermic transitions observed for Biolignin™-PEGDGE 1 : 4 and 1 : 6 occurs between 160°C and 170°C (Figure 11) and have different shapes than those observed in resins 1 : 1 and 1 : 2 (Figure 10). Considering these results, it seems that the PEG-like polymers chains between Biolignin™ oligomers have an impact over the thermal behavior of Biolignin™-PEGDGE epoxy resins.

Hexahydroxy-PEG is the monomeric unit of the PEG-like polymer chains between Biolignin™ oligomers, so we proceeded to the analysis of the product by DSC (from 30°C to 250°C at 5°C/min, in Figure 12).

An endothermic transition with the same shape as those in Figure 11 is observed for the hexahydroxy-PEG but at a lower temperature (148°C). It seems that the endothermic transitions observed in Biolignin™-PEGDGE epoxy resins 1 : 4 and 1 : 6 (Figure 12) are influenced by the PEG-like polymer chains.
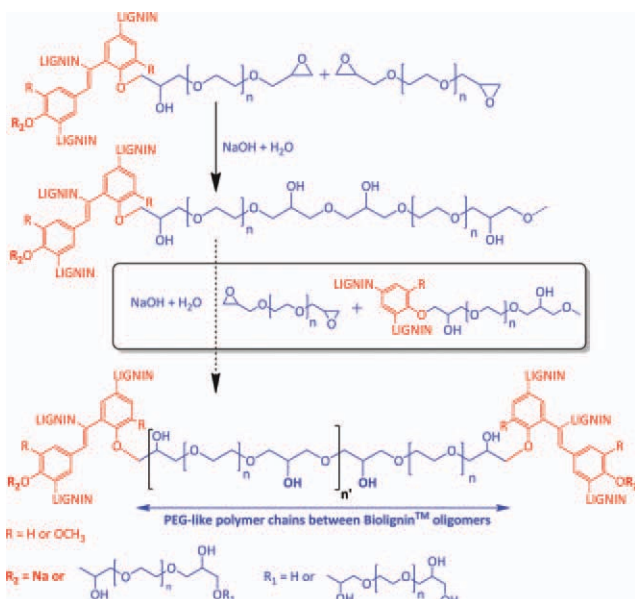
Figure 8. New synthesis path of Biolignin™-PEGDGE epoxy resins based on swelling test results. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

However, when these samples (ratio 1 : 4 and 1 : 6) were preheated at 190°C, during 15 min, and analyzed by DSC (from 30°C to 350°C at 5°C/min), the endothermic transitions were observed at the same temperatures. In this case, postcuring of Biolignin™-PEGDGE epoxy resins with ratio 1 : 4 and 1 : 6 would not occur.

Thermomechanical Study of Biolignin™-PEGDGE Epoxy Resins

To confirm a postcuring reaction of Biolignin™-PEGDGE epoxy resins of ratios 1 : 1 and 1 : 2 (Figure 10), DLTMA analysis
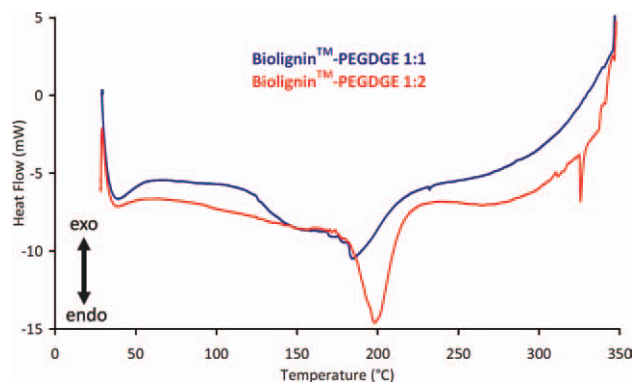

Figure 10. DSC thermograms of Biolignin™-PEGDGE epoxy resins 1 : 1 and 1 : 2. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

was performed on these resins and also on an epoxy-amine resin of bisphenol-A (DGEBA) used as reference. Glass transition temperature (T_g) and Young modulus were determined in dynamic tensile mode (Table III).

We did not performed DLTMA study of Biolignin™-PEGDGE epoxy resins 1 : 4 and 1 : 6 because no postcuring reaction occurred (Figure 11) and their high fragility was not suited for the tensile module device used.

The T_g of Biolignin™-PEGDGE 1 : 1 was determined at 45°C. Young modulus showed that the resin has a higher stiffness before T_g and is softer after T_g. DLTMA analysis was also performed on the reference epoxy resin and compared with that of Biolignin™-PEGDGE 1 : 1. The Young modulus of both samples dropped after their respective T_g, meaning that Biolignin™-PEGDGE 1 : 1 epoxy resin behaves in the same way as a bisphenol-A based epoxy resin.
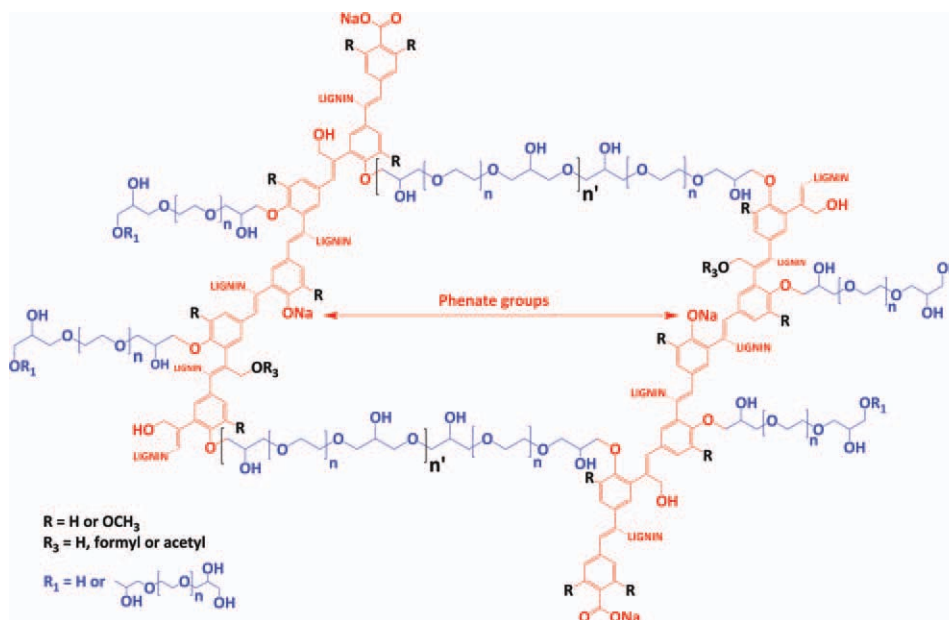

Figure 9. Structural model of Biolignin™-PEGDGE epoxy resins. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
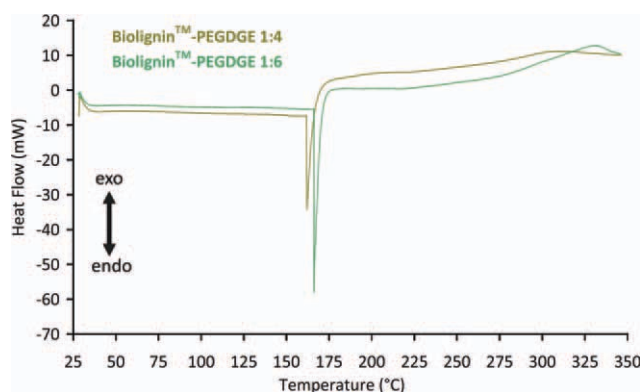
Figure 11. DSC thermograms of Biolignin^{TM}-PEGDGE epoxy resins 1 : 4 and 1 : 6. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Young modulus of Biolignin^{TM}-PEGDGE 1 : 2 is nearly the same at 25°C and 50°C and it was not possible to determine its T_g. This result would mean that up to a ratio of 1 : 1 of Biolignin^{TM} : PEGDGE, the resulting epoxy resin has similar mechanical properties than a Bisphenol-A based epoxy-amine resin.

A preheating at 190°C of Biolignin^{TM}-PEGDGE 1 : 1 and 1 : 2 samples was carried out to study the endothermic and irreversible transition observed as a postcuring reaction (Figure 10). The reference sample was also preheated under the same experimental conditions. DLTMA analysis was performed on these samples (Table IV).

Hardening of Biolignin^{TM}-PEGDGE 1 : 2 epoxy resin did not occur after the preheating process. From this ratio, it seems that the postcuring reaction of the sample had no influence on its mechanical properties that underline the interaction with the PEG-like chain polymer (see "Differential Scanning Calorimetry Study of Biolignin^{TM}-PEGDGE Epoxy Resins" section).

However, the postcuring process of Biolignin^{TM}-PEGDGE 1 : 1 and reference epoxy resins is highlighted by DLTMA analysis because the T_g and Young modulus at 25°C increased, compared with results in Table III, resulting in a hardening of the resins. (By the way, Biolignin–PEGDGE 1 : 1 epoxy resin is harder than the reference epoxy resin at 90°C judging by their
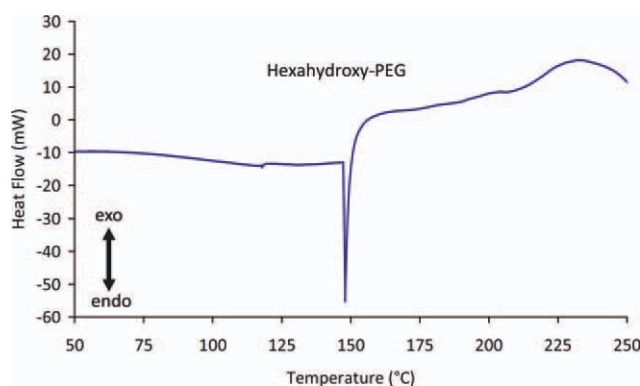

Figure 12. DSC thermogram of hexahydroxy-PEG.

Table III. DLTMA Analysis of Epoxy Resins in Dynamic Tensile Mode

Epoxy resin	T_g	Young modulus	
		25°C	50°C
Biolignin^{TM}-PEGDGE 1 : 1	45°C	700 MPa	160 MPa
Biolignin^{TM}-PEGDGE 1 : 2	–	24 MPa	21 MPa
Reference (DGEBA-TETA 1 : 1)	35°C	1000 MPa	51 MPa

Young modulus.). This is why we proceeded to the structural study of the postcured Biolignin^{TM}-PEGDGE 1 : 1 by solid-state ^{13}C NMR.

Solid-State ^{13}C NMR Analysis of Postcured Biolignin^{TM}-PEGDGE 1 : 1

The postcured Biolignin^{TM} based epoxy resin was analyzed by solid-state ^{13}C NMR and compared with same resin before postcuring (Figure 13).

Signals previously attributed in Figure 5 to a **CH$_3$** acetyl/acetate (27.9 ppm), a **C**═O carbonyl ester/carboxylate (173.7 ppm) and a **C**═O carbonyl of a carboxylate within Biolignin^{TM} structure (183.2 ppm) are not observed in the spectrum of the postcured Biolignin^{TM}-PEGDGE 1: 1 (red curve in Figure 13). The signal intensity of the C$_4$ phenate and C$_4$ etherified aromatic hydroxyl groups (155.6 and 151.5 ppm) did not change after preheating. These observations suggest that the postcuring process of Biolignin^{TM}-PEGDGE 1 : 1 epoxy resin initiates at 190°C and involves the carbonyl groups. Indeed, we can associate this reaction with the endothermic transition observed on DSC thermogram (Figure 10) and also with the consequence of a higher stiffness of the epoxy resins analyzed by DLTMA (Table IV). These results lead to consider the Biolignin^{TM}-PEGDGE 1 : 1 epoxy resin as a thermosetting polymer like the bisphenol-A epoxy resins.

CONCLUSIONS

Bisphenol-A and epichlorohydrin were substituted by wheat straw Biolignin^{TM} and PEGDGE, respectively, in the field of epoxy resins synthesis. Before synthesize Biolignin^{TM}-PEGDGE epoxy resins, we proceeded to the study of their chemical behavior under basic aqueous medium separately. Solid-state ^{13}C NMR analysis of ionized Biolignin^{TM} showed that etherified and free phenolic hydroxyls groups were all transformed into phenate groups. GPC analysis of hexahydroxy-PEG revealed that

Table IV. DLTMA Analysis of Epoxy Resins in Tensile Mode after a Preheating at 190°C

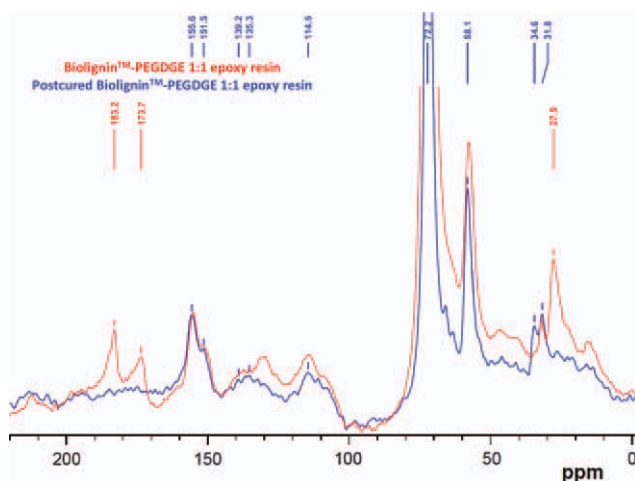| Epoxy resin	T_g	Young modulus	
		25°C	90°C
Biolignin^{TM}-PEGDGE 1 : 1	70°C	3700 MPa	290 MPa
Reference (DGEBA-TETA 1 : 1)	50°C	4100 MPa	22 MPa
Biolignin^{TM}-PEGDGE 1 : 2	–	40 MPa	22 MPa

Figure 13. Solid-state ^{13}C NMR spectrum of Biolignin^{TM}-PEGDGE 1 : 1 and postcured epoxy resin. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

PEGDGE went through a dimerization and hydrolysis of its ended epoxy groups.

ATR-FTIR and solid-state ^{13}C NMR studies of Biolignin^{TM}-PEGDGE epoxy resins showed very interesting informations about their general structure. Indeed, Biolignin^{TM} phenates were not totally etherified by PEGDGE, even when a large excess of the latter was used. The crosslinking of Biolignin^{TM} with PEGDGE formed an infinite network with a residual amount of hexahydroxy-PEG obtained during epoxy resins synthesis. In these experimental conditions, Biolignin^{TM} showed a high reactivity toward PEGDGE which was faster than the formation of hexahydroxy-PEG. In accordance with these structural studies and the swelling tests of the resins, a structural model of Biolignin^{TM}-PEGDGE epoxy resins was proposed. We assumed that Biolignin^{TM} reacted as a polyphenol in the synthesis of epoxy resin but also as a hardener of the PEGDGE epoxy resin.

Thus, thermomechanical properties of Biolignin^{TM}-PEGDGE epoxy resins were performed by DSC and DLTMA. The Biolignin^{TM}-PEGDGE epoxy resin 1 : 1 gave the most promising results. Postcuring of this epoxy resin was confirmed by solid-state ^{13}C NMR analysis and involved carbonyl groups of Biolignin^{TM}. Thermal and mechanical properties of this resin were similar to those of a bisphenol-A epoxy-amine before and after postcuring. This study confirmed the high potential of the biosourced wheat straw Biolignin^{TM} used as a Bisphenol-A substitute and its application in epoxy resin synthesis.

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