Bio-based Epoxy Resins from Biorefinery By-products

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In the transition from petrol to bio-based chemicals, the total utilization of the components from biomass during the biorefinery process can be regarded as the key to its success. Currently, the lignin obtained from the biomass during the pulping of wood is burned; however, this component has the potential to be an alternative to petroleum for producing aromatic feedstocks. Additionally, glycerol is a by-product of biodiesel production. In this work, epoxy resins were synthesized from these two components in an environmentally compatible process using water as the reaction medium (as opposed to organic solvents). Base-catalyzed depolymerized lignin, the only depolymerized lignin available at a multi-kilogram-scale, was chosen as the lignin source. This depolymerized lignin acts as the curing agent for glycerol, which results in entirely bio-based resins. Depolymerized lignin imparts rigidity to the resins, and the glass transition temperature (T_g) increased as the lignin content of the resin increased. Thermogravimetric analysis (TGA) data showed that the resins had a relatively high thermal stability with the onset of thermal degradation starting at 281 °C.

Keywords: Depolymerized lignin; Epoxy resin; Bio-based epoxy; Glycerol; Biorefinery By-products

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INTRODUCTION

Epoxy thermosets are high-performance resins that possess excellent mechanical properties, resistances to chemical degradations, good electrical properties, and low moisture absorption. Currently, most epoxy resins are derived from non-renewable feedstocks. The main source for epoxy is the diglycidyl ether of bisphenol A (BADGE), which is industrially produced by reacting epichlorohydrin with bisphenol A (BPA) (Fig. 1); this compound is present in more than 90% of epoxy polymers due to its good thermal properties that are conferred by its aromatic structure (Auvergne *et al.* 2014). However, BPA is under great regulatory pressure due to its ability to disrupt endocrine processes (Michałowicz 2014). Hence, there is a strong incentive to find a replacement for BPA. Moreover, there are environmental concerns related to the use of dwindling fossil fuels that are pressuring the chemical industry to move towards the use of renewable resources. Consequently, research related to bio-based thermosetting epoxies has attracted increased attention in the past few years (Auvergne *et al.* 2014; Ng *et al.* 2017). Besides the epoxy monomer, the hardening or curing agent is the other main component of an epoxy thermoset resin. As in the case of the epoxy monomers, the curing agents (such as polyamines or anhydrides) are currently derived from petroleum. Moreover, many of these are toxic before being cured (Baroncini *et al.* 2016).

There are only a few natural sources with aromatic structures that are suitable for replacing BPA, which include cardanol, tannic acid, and lignin (Baroncini *et al.* 2016; Ng *et al.* 2017). Lignin is the most abundant aromatic biopolymer found in nature and is the second most abundant biopolymer after cellulose. The pulp and paper industry uses the kraft process (NaOH and Na_2S) to cleave the bonds between the three main polymers found in lignocellulosic materials (*e.g.*, wood): hemicelluloses, cellulose, and lignin. Kraft pulping is the dominant process used in chemical pulp production; dissolved kraft lignin is a by-product of the process that is used as a fuel in the recovery boilers to produce steam, which is used to produce electrical power for the mills. This recovery process also regenerates the Na_2S when the dissolved kraft lignin is burned. Only a tiny fraction (2%) is not burned, but it is still used for low-value products such as dispersants or binders. Only recently has there been renewed interest in lignin valorisation (Rinaldi *et al.* 2016), especially with regards to the integrated biorefinery (Ragauskas *et al.* 2014).

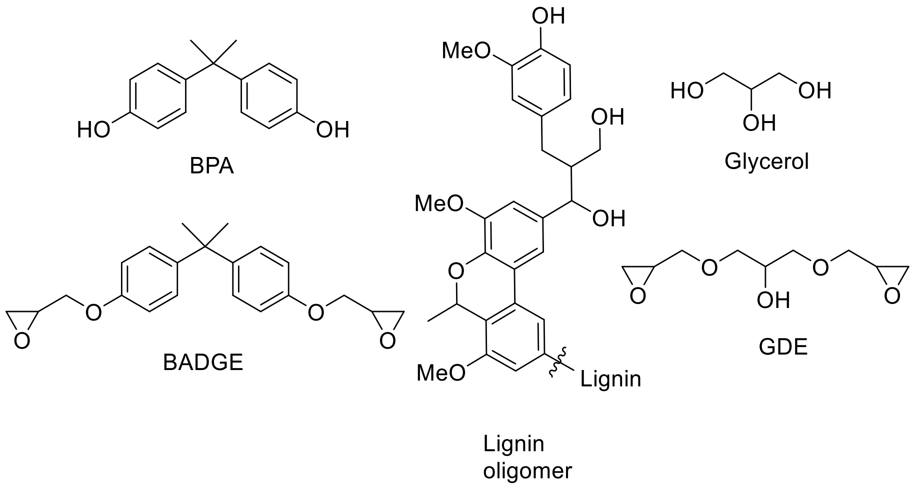

Fig. 1. Petrol-derived BADGE and its bio-renewable replacement obtained from lignin oligomers and GDE

The goal of this paper is to produce bio-based epoxy resins with the products obtained from the biorefinery. More specifically, this paper examines valorising two major biorefinery by-products, namely kraft lignin (from the pulp and paper industry) and glycerol (from biodiesel production). The latter accounts for approximately 10% weight of the produced biodiesel. An increased use of biofuels has created a surplus of glycerol, which calls for its utilization in value-added chemicals (Yang *et al.* 2012). Glycerol diglycidyl ether (GDE) can be synthesized through the reaction of glycerol with epichlorohydrin, which itself can be derived from glycerol as well. Solvay has developed this technology and is commercially selling the bio-based epichlorohydrin as Epicerol$^{©}$. The GDE has been used to manufacture bio-based epoxy resins (Takada *et al.* 2009; Shibata and Nakai 2010) from lignin. A resin derived from GDE and kraft lignin was recently reported to function as an alternative to formaldehyde-based wood adhesives (Li *et al.* 2018). Kraft lignin has also been used before in combination with pyrogallol (Engelmann and Ganster 2013). In another report, epoxy resins are made by reacting lignosulfonates and succinic anhydride along with glycerol or ethylene glycol (Ismail *et al.* 2010).

The use of these technical lignins can result in poor compatibility and reduced performance of epoxy polymers (Lora 2016; Xu and Ferdosian 2017). In contrast, a more defined lignin fraction from lignin depolymerization may improve the properties of the resulting epoxy polymers. Currently, base-catalyzed depolymerization is the only treatment process that can yield lignin oligomers at a multi-kilogram scale. Therefore, this depolymerized lignin was chosen as the starting material as it is closer to industrial implementation and to future availability (Rößiger *et al.* 2017; Rößiger *et al.* 2018). The goal of this research was to develop fully bio-based epoxy resins that are environmentally sustainable. Organic solvents are one of the biggest sources of toxicity and highest cost in epoxy manufacture. Consequently, the reduction in their use is among the principles of green chemistry (Welton 2015). Thus, this research completely avoided the use of organic solvents and opted to use water as the only reaction medium. Furthermore, in accordance with green chemistry principles, epoxy polymer synthesis was conducted in the most direct way (*i.e.*, avoiding derivatization pathways). It is recognized that the lignin product from the base-catalyzed depolymerisation process is already in its ionized form (pH = 12) and is in its higher reactivity state. Hence, the direct use of this depolymerized lignin would avoid the need of its neutralization and subsequent ionization in alkaline medium.

EXPERIMENTAL

Materials

Base-catalyzed depolymerized (BCD) lignin (M_w 100 to 10,000) was obtained from the Fraunhofer Center for Chemical-Biotechnological Processes (Leuna, Germany). Glycerol diglycidyl ether (GDE) was purchased from Sigma Aldrich (Overijse, Belgium).

Methods

Preparation and curing of resins

The GDE was added to the depolymerized lignin solution under vigorous mechanical stirring. The mixture was stirred for 16 h at 30 °C, which allowed the removal of most water while preventing the start of the curing. The viscous solution was poured into Teflon moulds, and the filled moulds were placed in a vacuum oven operating at 850 mbars and 50 °C. The samples were first kept at this temperature (*ca.* 4 h), which allowed the curing to take place and the slow evaporation of remaining water without the formation of cracks in the resins. Resins were post-cured at 100 °C for 2 h, which ensured completion of the curing reaction and removal of remaining water (traces remaining). Different lignin-to-GDE mass ratios (4:1, 2:1, 1:1, 1:2, and 1:4) were prepared. Both 4:1 and 2:1 epoxy resins were very brittle and not subjected to further analyses. The resins with lignin-to-GDE mass ratios of 2:1, 1:1, and 1:2 were viable but still fragile for subjecting them to mechanical testing.

Neutralization of BCD lignin

Dilute HCl (2 to 5 N) was slowly added to the BCD lignin solution in a beaker, which was vigorously stirred until a pH of 1 was reached. The acidified mixture was stirred for an additional hour. Afterwards, the mixture was cooled in an ice bath and filtered using a Büchner funnel that was assisted by vacuum. The retained solid was dispersed with distilled water in a beaker, stirred for 5 min, and filtered using a Büchner funnel. This rinsing was repeated twice. Finally, the solid material was dried in a vacuum oven at 60 °C until fully dried.

Determination of the salt content in BCD lignin

The weight of a non-neutralized dried BCD lignin sample was compared against the dry weight of a neutralized BCD lignin. The 27% weight difference was attributed to inorganic salts that were present in the original BCD lignin.

Thermal analysis

Possible thermal phase transitions in all of the cured resin specimens were investigated using differential scanning calorimetry (DSC). During a DSC experiment, the difference in the amount of heat flow between a sample pan and a reference pan is measured as a function of temperature or time. The DSC measurements were conducted with a Discovery DSC (TA Instruments, New Castle, DE, USA) by subjecting the cured epoxy resins to a heat–cool–heat cycle from -50 to 250 °C at 20 °C/min rate under a nitrogen atmosphere. Normalized heat flows were plotted as a function of temperature, and the plots were analyzed.

Thermal decomposition behaviors of the samples were characterized using thermogravimetric analysis (TGA). During a TGA experiment, the weight loss due to thermal decomposition is continuously monitored during a dynamic temperature scan. The TGA measurements were conducted with a TGA Q5000 (TA Instruments, New Castle, DE, USA). The heat-cured epoxy resins were heated from 40 °C to 600 °C at 20 °C/min during the TGA scan. The data were normalized as a percentage of sample weight loss. The normalized data was then plotted against temperature, and from this plot the first derivative of weight loss as a function of temperature was taken.

Spectroscopic analysis

Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) analyses of the epoxy resins were performed using a Thermo Nicolet Nexus spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) operating at laboratory atmospheric conditions. The measurements were performed in attenuated reflectance (ATR) mode using diamond crystal. The spectral range was 4000 to 500 cm^{-1}. The scans were performed with 4 cm^{-1} scan resolution and 32 scans per sample. Blank scans were subtracted from the sample scans prior to their analysis

RESULTS AND DISCUSSION

Curing Reaction

The recorded ATR-FTIR spectra for BCD lignin, GDE, and epoxy resins (1:1, 1:2, and 1:4 lignin-to-GDE ratios) are presented in Fig. 2. The absorption at 900 cm^{-1} was attributed to the C-O stretch of the epoxide. This absorption peak disappeared in all of the cured resin samples (*i.e.*, dotted region of Fig. 2). The related IR absorption at 845 cm^{-1} was appreciably reduced when the content of lignin was higher in the resin (1:1 *versus* 1:2 and 1:4). However, the amount of this reduction with regards to lignin content was not linear; this observation could be attributed to the presence of water in the system, which could have reacted with the GDE epoxy ring during the curing process (Fig. 3).

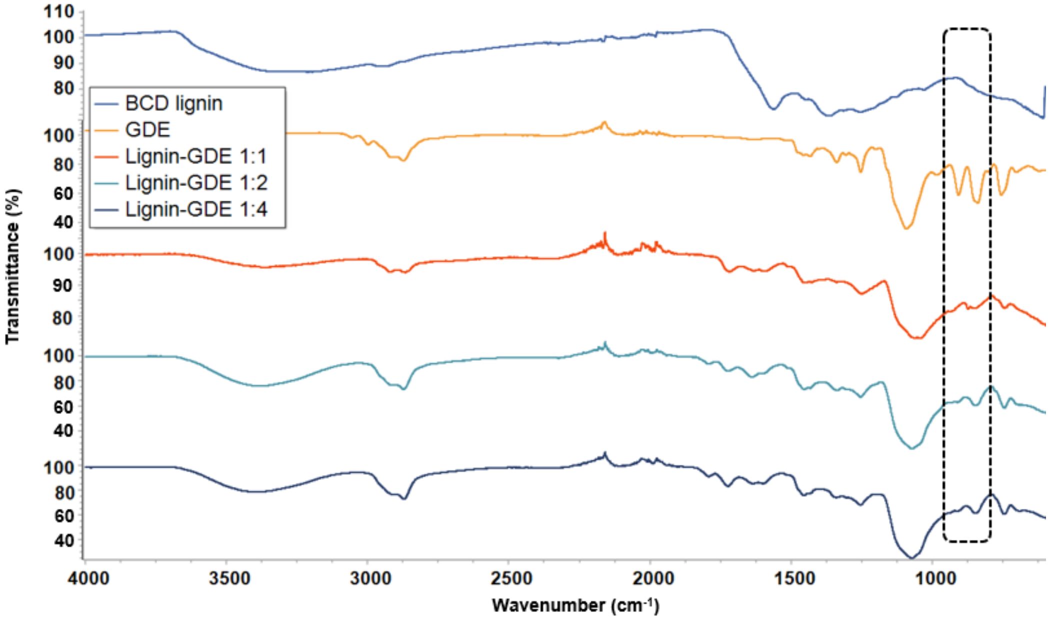

Fig. 2. FTIR spectra of GDE, BCD lignin, and lignin-GDE epoxy resins (1:1, 1:2, and 1:4 lignin-to-GDE ratios)

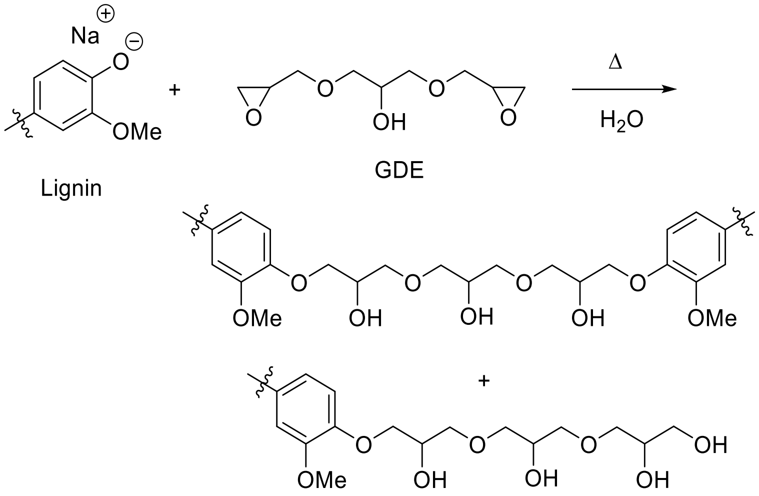

Fig. 3. Resin formation mechanism

Base-catalyzed lignin depolymerization results in an alkaline solution within which the lignin monomers and oligomers are ionized. This phenomenon was observed in the FTIR spectra of the BCD lignin (Fig. 4). Alkali lignin that had been acidified (*i.e.*, neutral lignin) exhibited higher IR absorption intensities for both hydrogen-bonded and free hydroxyl groups (3600 to 3000 cm^{-1} wavenumber range), as well as carboxylic acid group absorptions at 1695 cm^{-1}. The sodium salts of carboxyl groups intensely absorb at 1560 cm^{-1} (Max and Chapados 2004). The BCD lignin is water soluble, but has a high content of inorganic salts (27% by weight). This high salt content in BCD lignin is likely to be the reason for the observed fragility of the resins formed from it.

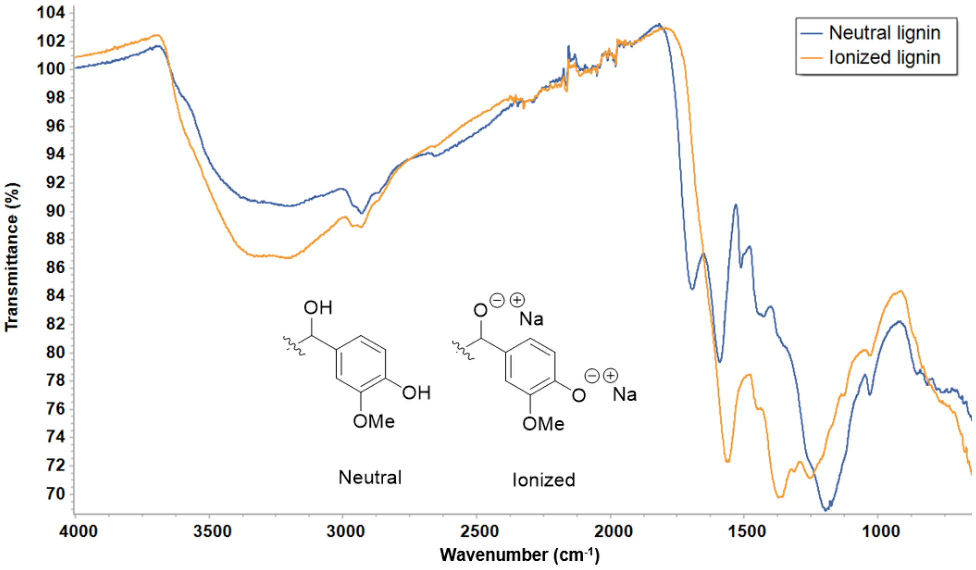

Fig. 4. FTIR spectra of neutralized and ionized BCD lignin

Thermal Analysis

The DSC measurements were recorded for the cured epoxy resins made with lignin-to-DGE ratios of 1:1, 1:2, and 1:4. The thermogram for the 1:2 resin is shown in Fig. 5; the thermograms for the other resins are analogous to the trends shown in this example.

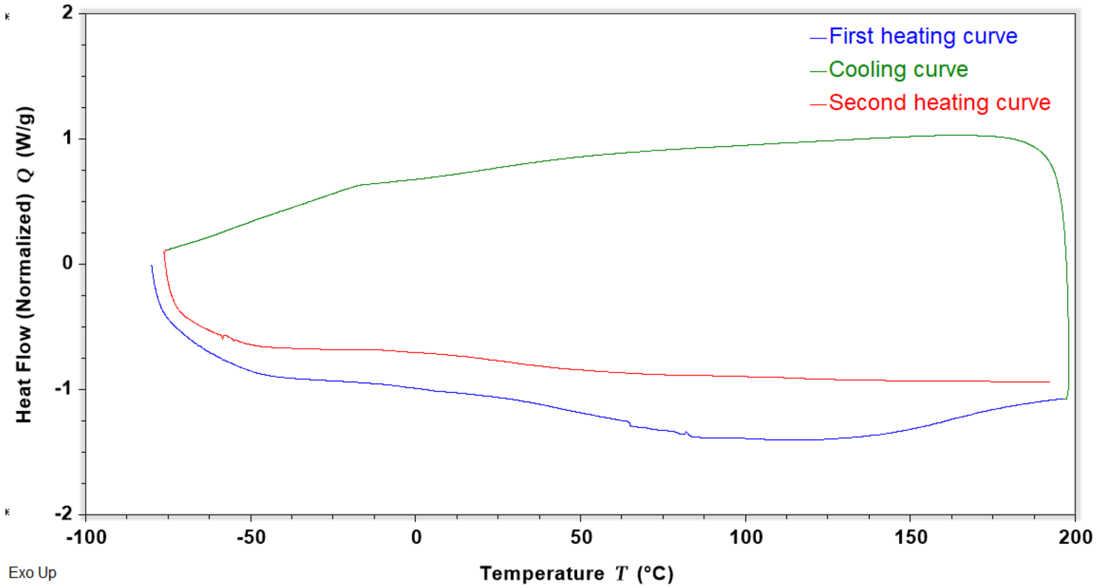

Fig. 5. DSC thermogram of BCD lignin-GDE epoxy (1:2 ratio); thermograms for 1:1 and 1:4 ratio epoxies are analogous to this example

The glass transition (T_g) experienced a shift to a lower temperature from the first to the second heating curve, which suggested that residual water was present in the resin and acted as a plasticiser. Additional support for this assertion can be seen from the thermogram of underivatized BCD lignin, which also had an analogous endothermic peak (Fig. 6). Moreover, the TGA data (Table 3 and Fig. 8) also implied that there was some water in the resin.

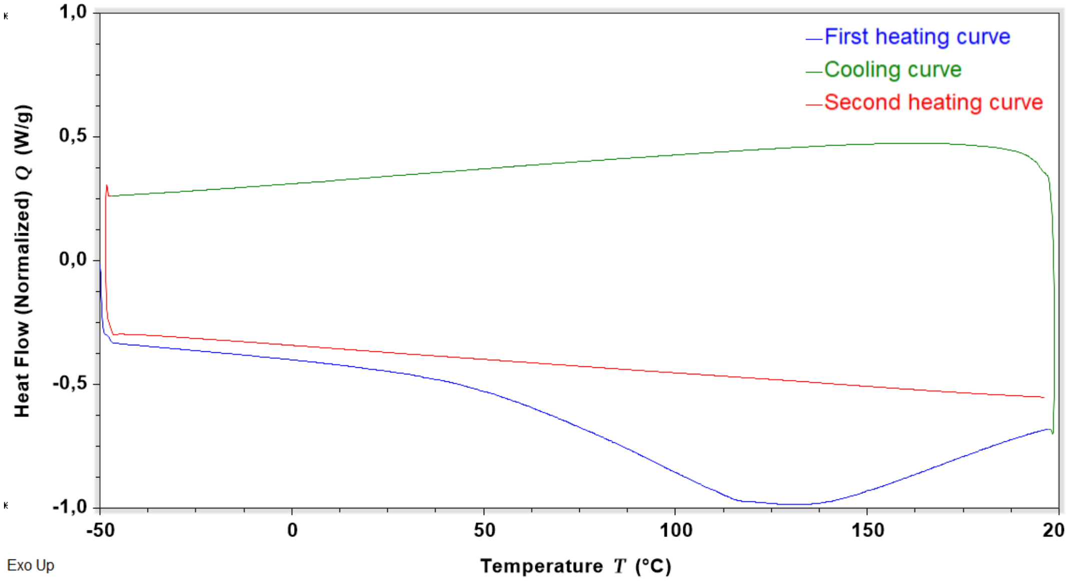

Fig. 6. DSC thermogram of BCD lignin

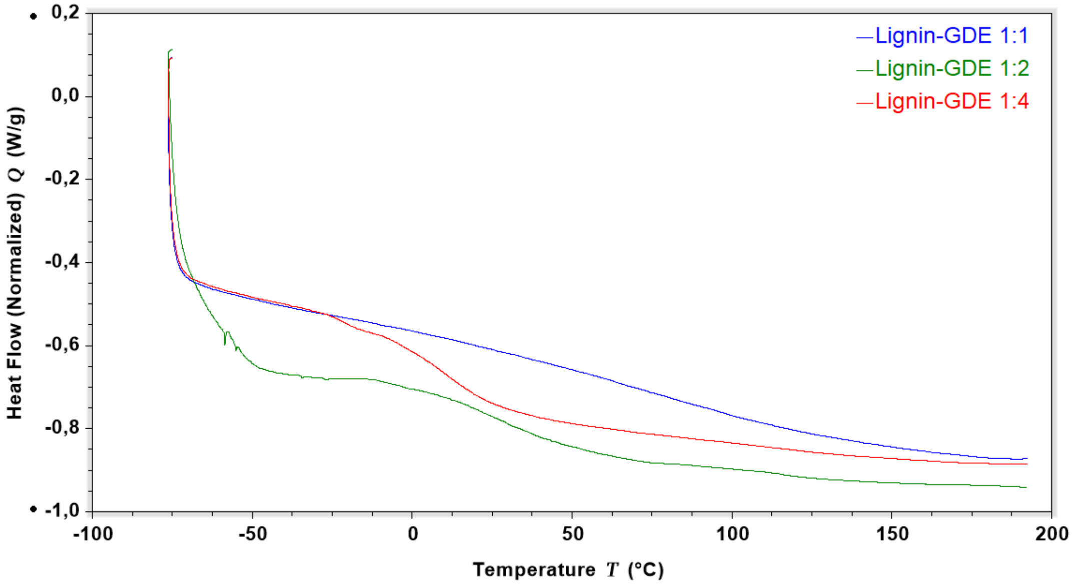

Fig. 7. DSC heating curves (from the second cycle) for lignin-GDE epoxy resins (1:1, 1:2, and 1:4 lignin-to-DGE ratios)

Comparisons of the T_g values from the resins made with different lignin-to-GDE ratios are shown in Fig. 7. As expected, the T_g increased as the lignin content increased. For the 1:1 epoxy resin, the T_g was almost undetectable from the thermogram, but it was calculated to be in the range of 50 °C to 60 °C. The 1:2 epoxy resin had a lower T_g value of 32 °C, whereas the 1:4 epoxy resin had the lowest T_g value of the series (14 °C).

The TGA measurements were recorded to obtain insights regarding the thermal degradation of the resins (Table 1 and Fig. 8). All of the resins had relatively high thermal degradation temperatures. Differential thermal gravimetric (DTG) analysis, which is the first derivative of the TGA curve, indicated that there were three inflection points for all of the resins. The first inflection corresponded to the loss of water. As mentioned earlier, the resins contained trace amounts of water (*ca.* 3% to 3.5% weight loss at 150 °C). It was notable that only 5% weight loss was observed for when all of the resins were heated above 200 °C (Table 1). The 1:2 resin exhibited the highest thermal resistance, which suggested that this ratio afforded the highest cross-linking density. The onset degradation temperatures for all of the resins were similar to one another over a *ca.* Δ20 °C range (281 to 304 °C). The other two inflection points in the DTG curves indicated rapid thermal degradation occurring at *ca.* 420 °C and above 500 °C. This was a thermal property of the epoxy resin itself, as the BCD lignin exhibited a steady decomposition (Fig. 8).

Table 1. TGA Data from Lignin-GDE Epoxy Resins (1:1, 1:2, and 1:4 Ratios)

Sample	5% Weight Loss Temp. (°C)	Degradation Onset Temp. (°C)	Remaining at 600 °C (%Weight)
Lignin-GDE 1:1	211	281	28
Lignin-GDE 1:2	272	304	17
Lignin-GDE 1:4	263	304	9

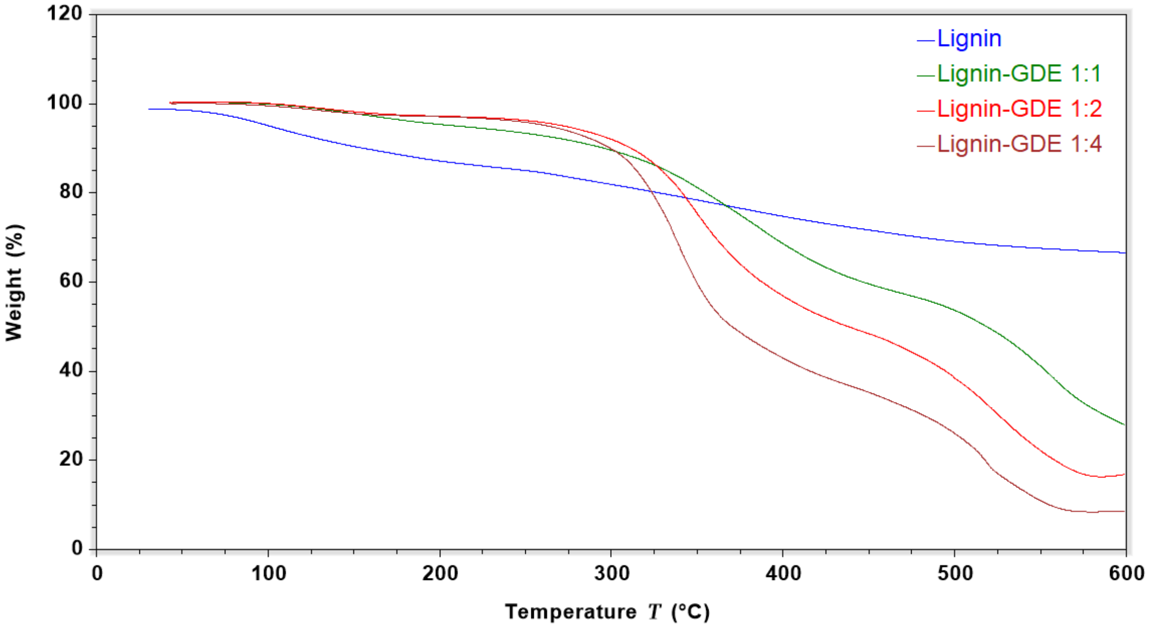

Fig. 8. TGA of BCD lignin and lignin-GDE epoxy resins (1:1, 1:2, and 1:4 ratios)

CONCLUSIONS

1. A series of fully bio-based epoxy resins were synthesized from base-catalyzed depolymerized (BCD) lignin and glycerol diglycidyl ether (GDE), which are by-products from the production of cellulosic pulp and biodiesel, respectively. A direct correlation was observed between the T_g of the resin and the lignin content of the sample. Mass ratios of lignin-to-GDE of 1:1, 1:2, and 1:4 yielded viable resins; however, resins containing higher BCD lignin content resulted in brittle samples.
2. The direct use of BCD lignin for the synthesis of epoxy resin was explored. The synthesis of the bio-based epoxy is attractive from a step-efficiency perspective. The

synthesis only uses water as the reaction medium (as opposed to organic solvents). However, the presence of high levels of inorganic salts with the BCD lignin (27%) negatively affected the mechanical integrities of the resulting resins.

ACKNOWLEDGMENTS

The authors would like to acknowledge the province of Noord-Brabant (The Netherlands) for financial support in the activities at the Shared Research Center Biorizon.

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Article submitted: December 11, 2018; Peer review completed: February 18, 2019; Revised version received and accepted: February 23, 2019; Published: February 28, 2019.
DOI: 10.15376/biores.14.2.3200-3209