Preparation of aerogels from wheat straw lignin by cross-linking with oligo(alkylene glycol)-α,ω-diglycidyl ethers

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A B S T R A C T

Lignin is one of the most abundant by-products of pulp and paper manufacturing and second-generation biorefineries. Presently it is mainly used for energy production, but it is evident that higher added-value utilization options would be beneficial. One possible process is to use lignin as building block for chemical synthesis. In this work, lignin was used as a raw material for the production of aerogels as special class of porous materials. Lignin obtained from Liquid Hot Water (LHW) pretreatment of wheat straw has been cross-linked with oligo(ethylene glycol)- and oligo(propylene glycol)-α,ω-diglycidyl ethers of varying length, aiming at the preparation of lignin-based hydrogels and their conversion to aerogels. The effect of cross-linking conditions, such as lignin concentration, cross-linker-to-lignin ratio, gelation temperature and solvent exchange conditions, on the textural properties of the resulting aerogels were studied. The obtained aerogels had a surface area of up to 120 m² g⁻¹, bulk density as low as 0.15 g cm⁻³ and a thermal conductivity of about 50 mW m⁻¹ K⁻¹.

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1. Introduction

Isolation and utilization of lignin as one of the major constituents of lignocellulosic biomass is increasingly moving into the limelight of second-generation and third-generation biorefinery approaches [1]. While lignins have been mainly used for energy generation, there is broad consent that its controlled depolymerization to fine chemicals or its processing to innovative materials is a future-oriented measure to improve the overall performance of respective biomass processing units.

Along with the increasing interest of PF resin producers in partially substituting phenol for the renewable and cheaper phenolic resource lignin, cross-linking of lignin as an approach to lignin aerogels has recently become a hot topic in material research. Aerogels are cellular solids that feature very low density, high specific surface area and consist of a coherent open-porous network of loosely packed, bonded particles or fibers whose voids are filled with gas [2]. Besides inorganic precursors like alkoxysilanes, biopolymers, such as cellulose, hemicellulose, lignin, starch, alginate, or pectin are of increasing interest in aerogel research due to the intriguing properties of the obtained materials [3,4]. Their particular properties render them attractive materials for a multitude of applications including insulation, filtration, adsorption, catalysis, or slow-release [5,6].

Following classical Lederer–Manasse chemistry, ligneous aerogels have been prepared by cross-linking a mixture of enzymatically isolated lignin and resorcinol with formaldehyde in aqueous sodium hydroxide at room temperature, subsequent solvent exchange to ethanol and extraction of this solvent with supercritical carbon dioxide (scCO₂, 201 °C, 10 MPa; [7,8]). Highly porous lignin–tannin composite aerogels featuring porosities of 70–85% have been synthesized in a similar way [9]. The most significant progress in the field of ligneous phenol–formaldehyde resin (PF)-type aerogels have been recently made by the same authors [10] who succeeded to substitute up to 80% of phenol by a LignoBoost softwood Kraft lignin. The aerogels obtained at such high lignin contents had a bulk density of about 220 mg cm⁻³, porosity of 83%, BET surface areas of 330 m² g⁻¹, and a thermal conductivity of 44 mW m⁻¹ K⁻¹. Apart from formaldehyde, also dialdehydes, such as glyoxal or glutaraldehyde, afford lignin gels, as exemplarily demonstrated for pine Kraft lignin [11].

To the best of our knowledge, the preparation of aerogels with lignin as the only principal phenolic constituent has not been reported. Substitution of more than 80% of phenol by lignin in resole-type condensation reactions was demonstrated not to afford gels [10]. Similarly, gel formation from wheat straw soda lignin by thermal condensation in hot 1-butyl-3-methylimidazolium...
chloride (BMIM-Cl) at 130 °C and subsequent coagulation with ethanol was not successful, even though ligneneous gels could be obtained when milled spruce wood meal was used or if sufficient amounts of cellulose and/or birch xylan had been co-dissolved with the lignin [12].

Oligo(ethylene glycol)-x,0-diglycidyl ethers have been demonstrated to be promising, alternative cross-linking agents that can afford highly swellable lignin hydrogels of high water adsorbing capacity [13]. Similar to the electrophilic addition of formaldehyde to phenol in conventional resol formation, lignin is first dissolved in concentrated sodium hydroxide which causes formation of phenolates. However, different from PF resin chemistry, the latter acts as nucleophiles attacking the terminal epoxide moieties of the subsequently added cross-linking agent at the non-substituted methylene ring position. Due to the very high Baeyer ring tension a d-drying step [33] before as stationary phase in size exclusion chromatography applications [17].

Following a hydrothermal pretreatment of biomass with Liquid Hot Water (LHW process) at 200 °C and 5 MPa, the remaining solid fraction is subject to an enzymatic hydrolysis step (50 °C, pH 5, Novozymes CTEc2®) that converts the majority of polysaccharides into water-soluble products leaving behind the water-insoluble (pH < 7) AS lignin [18,19].

The cross-linking agents ethylene glycol diglycidyl ether (EGDE), oligo(ethylene glycol)-x,0-diglycidyl ether (PEGDE, n ≈ 8), and the oligo(propylene-1,2-glycol)-x,0-diglycidyl ethers PPGDE 380 (n = 4.3) and PPGDE 640 (n ≈ 8.8) were purchased from Sigma Aldrich (St. Louis, MO, USA).

Ethanol (99%, 1% MEK) and acetone (99%) were purchased from H. Möller GmbH & Co. KG (Steinfurt, Germany) and used as received. NaOH (>99%) was purchased from Carl Roth GmbH & Co. KG (Karlsruhe, Germany). Deionized water was used for the preparation of all aqueous solutions.

2.2. Methods

2.2.1. Lignin composition analysis

Dry matter content of AS lignin was determined by drying a known amount at 105 °C until constant weight. Klasson lignin and ash content analyses were accomplished at the Analytical Laboratory at Hamburg University of Technology. Elemental analysis was performed at the Microanalytical Lab of the University of Natural Resources and Life Sciences, Vienna. Quantification of free phenolic groups and their assignment to the main lignin building blocks, i.e., p-hydroxyphenyl (P-), guaiacyl (G-), and syringyl (S) units, was based on a 31P NMR method described elsewhere [21]. 4,4,5,5-Tetramethyl-2-chloro-1,3,2-dioxaphospholane and cyclohexanol were used as derivatization reagent and internal standard, respectively. 31P NMR was performed on a BrukerAvance II 400 spectrometer equipped with a 5 mm broadband probe head (Bruker Corporation, MA, USA).

2.2.2. Lignin crosslinking and gelation

Different amounts of AS lignin (5–12.5 g) were dissolved under continuous stirring in 50 ml of aqueous sodium hydroxide (0.1–3.3 M). After an activation time of 24 h the respective oligo(alkylglycol)-x,0-diglycidyl ethers varying by type and number of repeating units were added at a concentration of 0.1–3 mmol g⁻¹ dry lignin dissolved in aqueous sodium hydroxide. The solutions were stirred for another 25–45 min and transferred to cylindrical moulds for gelation. Different process parameters were varied: lignin concentration, type of cross-linker, cross-linker-to-lignin ratio, concentration of sodium hydroxide, and gelation temperature.

2.2.3. Solvent exchange and supercritical drying of lignin gels

After a gelation and ripening time of 24 h the formed gels were subject to a solvent exchange, that is, the interstitial water filling the voids of the hydrogel was sequentially replaced by aqueous ethanol or acetone of decreasing water content. Aiming at a full preservation of the gel morphology, the impact of both the increase of the concentration of the organic solvent and the residence time of the gels in the respective solvent/water mixtures was studied. The concentration of the organic solvent in the respective baths was varied as follows: 100% (one-step approach), 30–50–70–100% (five-step approach) or 0–10–30–50–70–100% (seven-step approach), while the residence time of the gels in the baths was either 1 or 24 h. The change in volume caused by the different solvent exchange variants was recorded for each sample. Supercritical CO2 extraction of the resulting lignin organogels was accomplished in a 250 ml autoclave (12 MPa, 40 °C, 4 h). After that the dimensions of the aerogels were recorded to calculate the extent of shrinkage that occurred during the scCO2 drying step alone, next to the overall volume reduction during conversion of lignin hydrogels to aerogels.

2.2.4. Aerogel characterization

2.2.4.1. Porosity, skeletal and bulk density. Skeletal density of the lignin aerogels was determined by helium pycnometry on a Multivolume Pycnometer 1305 (Micromeritics, Georgia, USA). Bulk density
was calculated from the volume of the aerogel samples and their weight after scCO₂ drying. Porosity (\(\varphi\)) was calculated from the bulk and skeletal density according to Eq. (1).

\[
\varphi = 1 - \frac{\rho_{\text{bulk}}}{\rho_{\text{skeletal}}}
\] 

(1)

2.2.4.2. BET-surface area, mesopore size distribution and total pore volume. Calculated from the results (desorption branch) of nitrogen sorption experiments conducted at 77 K on a NOVA 3000e Surface Area Analyzer (Quantachrome Instruments, Boynton Beach, FL, USA). All samples were degassed under vacuum at 70 °C for 24 h prior to the sorption experiments.

3. Results and discussion

3.1. Lignin composition

The Klason lignin content of AS lignins can be regarded as a criterion for both the effectiveness of hemicellulose removal during hydrothermal biomass pretreatment and cellulose degradation by subsequent enzymatic hydrolysis. Common values for AS lignin range from 60 to 80 w% while the Klason lignin content of the parent material, that is wheat straw, ranges from around 20 to 25 w% [18–20]. The isolated AS lignin used in this work had a Klason lignin content of 74.6 w%. The remaining fraction of 25.4 w% consisted mainly of carbohydrates supposedly covalently linked to lignin and resisting enzymatic degradation (Novozymes CTec2™), and a smaller amount of inorganics as reflected by the ash content of 3.7 w% which is typical for straw samples [22,23]. The nitrogen content of 2.1 w% as determined by elemental analysis furthermore evidences the presence of smaller amounts of proteins which are assumed to originate at least partly from the enzyme added.

Quantitative 31P NMR studies of AS lignin samples after derivatization with 2,2,3,3-tetramethyl-2-chloro-1,3,2-dioxrophospholane revealed a total amount of 1.84 mmol g⁻¹ (3.1 w%) of free phenolic groups which is similar to the values of milled wheat straw lignin (1.53 mmol g⁻¹) as published elsewhere [24].

31P NMR furthermore confirmed that the LHW process and subsequent enzymatic treatment preserves the H:G:S-type of the parent wheat straw lignin [25] as the obtained AS lignin contains significant amounts of each of the principal p-hydroxyphenyl (P)-, guaiacyl (G)-, and syringyl (S) building blocks (Fig. S1, Supporting information). The calculated H:G:S ratio of 12:40:48 is in good agreement with that published previously for a wheat straw dioxane lignin (9:45:46) analyzed by 1H and 13C NMR spectroscopy [26].

3.2. Lignin crosslinking and gel formation

The critical values for gel formation in terms of lignin to crosslinker ratio, type and number of repeating unit of the studied crosslinkers, lignin content of the alkaline reaction mixture, temperature, and initial pH for lignin dissolution are shown in Table 1.

3.2.1. Lignin content

Gel formation from wheat straw AS lignin by crosslinking with oligo(alkylene glycol)-diglycidyl ethers occurred only if the lignin content in aqueous alkaline solution was at least 10% (w/v). However, only the studied PPGDE crosslinkers of different number of constitutional repeating units (CRU) formed a gel under these conditions while EGDE and PEGDE required a higher stock concentration of \(\geq 20\%\) (w/v). Lignin contents below these respective values caused only an increase in viscosity, and even long reaction times at elevated temperature did not afford gels. This is in accordance with a previous study which demonstrated that lignin–PEGDE gels are only formed at high lignin contents of 25–50% (w/v), depending on the type of lignin used [13]. A similar reaction behavior was reported for birch acetic acid lignin and oligo(ethylene glycol)-\(\alpha\),\(\omega\)-diglycidyl ethers of different number of CRU. In this case, gels were formed only at lignin contents beyond 33% (w/v) [14,15].

The high stock consistency of lignin necessary for crosslinking is assumed to be due to the comparatively low content of reactive phenolic groups and the steric hindrance of the lignin macromolecules which prevent the bi-functional crosslinker from establishing intermolecular links. Lignin pre-activation by Fenton-type oxidation which is capable of introducing more hydroxyl moieties available for crosslinking is an alternative approach to successful gel formation at lower lignin concentration.

3.2.2. Crosslinker to lignin ratio (Crl:L ratio)

Gel formation is a function of crosslinking density, defined as the number of crosslinks established between individual macromolecules. Within the respective ranges of all parameters studied in this work, a crosslinker to lignin ratio of 0.5–2.0 mmol g⁻¹ lignin was demonstrated to be sufficient for gel formation. This is in good agreement with previously published data. While an amount of 0.55 mmol PEGDE (n = 13) g⁻¹ lignin was demonstrated to be sufficient to form a gel from a solution of 33% (w/v) of birch acetic acid lignin in sodium hydroxide solution [15], cross-linker concentrations \(\geq 2\) mmol g⁻¹ were required for the pine Kraft lignin Indulin AT™ and the autohydrolysis bagasse lignin Sucrolin™ [13].

3.2.3. Type of the crosslinking reagents

Both the type of crosslinker and the number of repeating units were factors that impact gel formation. At comparable number (\(n \approx 9\)) of constitutional repeating units (CRU) the less polar and hydrophilic PPGDE 640 afforded gel formation already at half the crosslinker concentration (0.5 mmol g⁻¹) required for the more hydrophilic PEGDE (1.0 mmol g⁻¹) under otherwise identical conditions. On the other hand, the minimal crosslinker concentrations required for gelation decreased with increasing number of repeating units. While 2 mmol g⁻¹ lignin was needed for EGDE (n = 1), only a concentration of 1 mmol g⁻¹ lignin was required for PEGDE (n = 9.0). Similarly, the minimum crosslinker concentration decreased significantly from 2 to 0.5 mmol g⁻¹ lignin for PPGDE when doubling the CRU number from n = 4.3 to 8.8. This is highly likely due to the better ability of the respective longer-chain homologous compounds for connecting hydroxyl groups of different lignin molecules. At higher spacer lengths the influence of gel formation seems to level out as the minimum PEGDE concentration that allowed for gel formation was 0.55 mmol g⁻¹ birch acetic acid lignin no matter if the number of repeating units was n = 13 or 22 [15].

3.2.4. Gelation temperature

Oligo(alkylene glycol)-\(\alpha\),\(\omega\)-diglycidyl ethers with longer, flexible backbones require shorter time periods until gelation set in.

### Table 1

<table>
<thead>
<tr>
<th>Crosslinker</th>
<th>NaOH conc. (M)</th>
<th>Lignin conc. (Sw/v)</th>
<th>Crl:L ratio (mmol g⁻¹)</th>
<th>T (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EGDE</td>
<td>3.3</td>
<td>20</td>
<td>2</td>
<td>RT</td>
</tr>
<tr>
<td>PEGDE</td>
<td>3.3</td>
<td>20</td>
<td>1</td>
<td>RT</td>
</tr>
<tr>
<td>EGDE</td>
<td>3.3</td>
<td>20</td>
<td>1</td>
<td>60</td>
</tr>
<tr>
<td>PEGDE</td>
<td>3.3</td>
<td>20</td>
<td>0.5</td>
<td>60</td>
</tr>
<tr>
<td>EGDE</td>
<td>0.1</td>
<td>20</td>
<td>2</td>
<td>RT</td>
</tr>
<tr>
<td>PPGDE640</td>
<td>1</td>
<td>20</td>
<td>2</td>
<td>RT</td>
</tr>
<tr>
<td>PPGDE380</td>
<td>3.3</td>
<td>10</td>
<td>0.5</td>
<td>RT</td>
</tr>
<tr>
<td>PPGDE640</td>
<td>3.3</td>
<td>10</td>
<td>0.5</td>
<td>RT</td>
</tr>
</tbody>
</table>
This was exemplarily demonstrated for the ethylene glycol-based diglycidyl ethers EGDE (\(n = 1\)) and PEGDE (\(n \approx 9\)). While the monomeric EGDE had a gelation onset time of about 120 min at room temperature, cross-linking of the oligomeric PEGDE was considerably faster (80 min) under these conditions (Fig. 1). These differences in gelation onset time (\(\Delta t_{\text{onset}}\)) became smaller when rising the temperature as the reaction rates increased. Thus, \(\Delta t_{\text{onset}}\) (EGDE–PEGDE) dropped from about 40 to 18 °C when crosslinking was performed at 40 °C instead of room temperature and became negligibly small at 60 °C. Simultaneously, the gelation onset time decreased exponentially from 120 min (25 °C) to 10 min (60 °C) for EGDE at a cross-linker to lignin ratio of 2 mmol g\(^{-1}\).

The better accessibility of hydroxyl groups belonging to two different lignin molecules by the epoxy moieties of higher oligo(alkylene glycol)-\(x\),\(x\)-diglycidyl ether homologues did not only reduce the gelation onset times but also the minimum amount of crosslinker needed for gel formation. While crosslinking with EGDE at 25 °C was only successful when using a crosslinker to lignin ratio of 2 mmol g\(^{-1}\), only half that amount was required for PEGDE. At 60 °C smaller amounts of crosslinkers are generally needed for gel formation, however the critical amount of PEGDE (0.5 mmol g\(^{-1}\) lignin) was lower than that of EGDE (1.0 mmol g\(^{-1}\)) too.

### 3.2.5. Sodium hydroxide concentration

A sodium hydroxide concentration of 3.3 M corresponding to approx. 12 w% has been used for most of the prepared gels as suggested in the literature [15,27]. However, as the respective amount of hydroxyl ions represents a rather large excess compared to the amount of acidic groups of the added lignin, we investigated the impact of reduced NaOH concentrations on gel formation exemplarily using EGDE and PPGDE 640 as cross-linkers. It turned out that at otherwise fixed reaction parameters (lignin content of 20 w%, \(\text{CrI}:\text{ratio}\) of 2 mmol g\(^{-1}\), room temperature) gelation was successful down to a NaOH concentration of 0.1 M (EGDE) and 1.0 (PPGDE), respectively, while further dilution did not afford gels (cf. Table 1).

### 3.2.6. Solvent exchange and supercritical drying

High interconnected porosity and surface area at low bulk density are key features of aerogels. Both the preservation of the solid 3D network structure and the avoidance of shrinking during conversion of hydrogels to aerogels typically require the application of drying techniques that circumvent the formation of an expandable solid phase (freeze-drying) or the occurrence of strong capillary forces. Drying with carbon dioxide under supercritical conditions (scCO\(_2\)) is considered to be one of the most gentle and facile drying techniques. However, due to the poor miscibility of water and carbon dioxide, aquagels are typically subject to a solvent exchange to replace the interstitial water by an organic solvent miscible with CO\(_2\). The choice of the organic solvent and the procedure of how the solvent exchange is accomplished usually demands a great deal of sensitivity as abrupt changes in specific energies occurring on the phase boundaries within the gel are known to be one of the serious reasons for gel shrinkage upon scCO\(_2\) drying.

As both ethanol and acetone used in this study to replace water prior to scCO\(_2\) drying feature a significantly lower surface tension and capacity for hydrogen bonding, the polarity of the interstitial liquid was gradually changed as proposed previously [28]. This has been accomplished by consecutively immersing the gels in a series of baths (\(n = 1–7\)) containing ethanol/water and acetone/water mixtures of decreasing water content, respectively.

Independent on the number of baths, the shrinkage of all gels during solvent exchange was found to be more pronounced for acetone than for ethanol. For gels that were obtained by crosslinking AS lignin with PEGDE at a ratio of 1 mmol PEGDE g\(^{-1}\) lignin for example, the remaining volume after a five-step solvent exchange to ethanol (24 h per step) was 63% while only 46% of the original volume was retained when acetone had been used. This can be explained by both the different solubility parameters and in particular by the different hydrogen bonding capabilities of the used solvents in comparison to water. Hydrogen bonding between the solvent and the oligo(alkylene glycol)\(\times\) crosslinker, the supposedly free primary and secondary OH groups of the lignin side chain, and the residual carbohydrate fraction is assumed to play a considerable role for gel stability. The replacement of water by ethanol or acetone drops the Hildebrand solubility parameter – calculated as square root of the cohesive energy density of a specific solvent – significantly from \(\delta_2 = 48.0\) to \(\delta_2 = 26.2\) (ethanol) and \(\delta_2 = 19.7\) (acetone), respectively. While the Hildebrand solubility value of ethanol is only somewhat higher than for acetone, the contribution of hydrogen bonding (\(\delta_n\) water = 42.3) as one component of the Hansen model for describing solvent–polymer interactions is much higher for ethanol (\(d_h = 19.4\)) compared to acetone (\(d_h = 7.0\)) [29].

Aiming at a gradual adaptation of the polymer–solvent interactions, replacement of the inter-stitial water by organic solvents was accomplished by gradually increasing the concentration of organic solvent in a series of successive solvent exchange baths. However, the increment at which the concentration of the organic solvent had been increased and hence the number of exchange baths turned out to have no significant for EGDE and PEGDE, and only a minor impact on shrinkage for the other cross-linkers or at the utmost. While the differences in shrinkage for one-, three-, and five-step solvent exchange was 1% (volume reduction 19–20%) and 3% (27–30%) for EGDE and PEGDE, respectively, the difference between five and seven steps as tested for the two PPGDE cross-linkers was maximal 10% (PPGDE) with better preservation of the gel’s dimension at lower increment of ethanol concentration.

Similarly, the residence time of the gels in each solvent exchange bath was found to be of minor importance. Prolongation of the residence time from 1 to 24 h for example reduced the extent of shrinkage from 37% to 27% only (ethanol, 5 exchange steps) while no significant difference was observed for acetone under the same conditions.

The type of crosslinker, however, had a more pronounced impact on shrinkage as occurring during solvent exchange. While aerogels obtained with the rather hydrophilic crosslinking agents EDGE and PEGDE suffered from extensive shrinkage (ca. 50%), the reduction by volume was only half that value (ca. 25%) when using the polypropylene glycol-based crosslinkers PPGDE 380 and 640. This is assumed to be due to the methyl substitution pattern that shields the backbone ether bonds more efficiently from interaction with water molecules than it is the case for EDGE or PEGDE. For the shorter-chain PPGDE crosslinker that is supposed to form a stiffer
network, and optimized solvent exchange conditions (5-step solvent exchange, 24 h intervals between baths) low shrinkage of 5% only was achieved.

Supercritical carbon dioxide (scCO₂) drying is considered to be the method of choice for converting fragile organogels into aerogels as it typically allows a far-reaching preservation of their three-dimensional network structures. However, open-porous, lightweight organogels from polysaccharides seem to be particularly sensitive as significant shrinking during scCO₂ drying has been reported for starch, cellulose, or alginate [28]. The reasons for that can be manifold including the formation of a CO₂ expanded organic phase that is much less polar than the organic solvent itself, capillary stress due to residual solvent or traces of water, insufficient drying time, or inappropriate depressurization rates. Similar to polysaccharide-based materials, the bulk density of all lignin organogels prepared in this study suffered from considerable shrinkage during the scCO₂ drying step, but at different extent and largely depending on the type of crosslinker used. For example, gels that were obtained according to the “standard procedure”, that is, from solutions of 20 w% lignin in 3.3 M aqueous NaOH at 25 °C using a Crl:L ratio of 2 mmol g⁻¹ followed by solvent exchange to ethanol (increment of 20%, residence time 24 h per bath) shrunk in the following order: PPGDE (n = 8.8:40%) > PEGDE (n = 9:34%) > PPGDE (n = 4.3:26%) > EGDE (n = 1:14%). This order reflects the supposedly somewhat higher affinity of CO₂ to PPGDE and the differences regarding spacer length (number of repeating units) between the epoxy moieties.

The volume reduction as observed during solvent exchange and scCO₂ drying summed up for the different variants to an overall shrinkage of 30–60% related to the volume of the samples after casting and crosslinking. For the “standard procedure” (cf. above) the remaining volumes ranged from 51% to 69% with the lowest shrinkage (31% each) obtained for EGDE and PPGDE 380 (n = 4.3). Different from the latter, EGDE affords gels of comparably low shrinkage already at a sodium hydroxide concentration of 1 M.

3.3. Aerogel properties

As a matter of course the bulk density of lignin aerogels (ρbulk) is a function of the lignin concentration (C₇) for a particular type of crosslinker, constant crosslinker to lignin ratio and otherwise identical conditions (Fig. 2). However, as evident from the slope of the C₇–ρbulk correlation, doubling the lignin content from 10 to 20 w% afforded aerogels with bulk densities somewhat lower than expected from the increase of the lignin content in the reaction mixtures. While the bulk density (ρbulk) of aerogels obtained by PPGDE 380 cross-linking was 150 mg cm⁻³ for the conditions given in Table 1 (C₇ = 10%, w/v), a value of 240 mg cm⁻³ was obtained when starting from twice the amount of lignin. This implicates reduced shrinkage for the gels of higher lignin content which is confirmed by the combination of process parameters that afforded the lowest shrinkage during the preparation of aerogels with EGDE and PPGDE 380 as crosslinkers (Table 2).

The number of CRUs of a particular type of crosslinker is another parameter that can be used to control the bulk density of lignin aerogels. At constant crosslinker to lignin ratio (2 mmol g⁻¹ lignin) the respective longer-chain oligo(propylene-1,2-glycol)-α,ω-diglycidyl ether PPGDE 640 afforded aerogels of somewhat lower bulk density for lower lignin concentrations of up to ca. 15% (w/v) as compared to the shorter-chained PPGDE 380. This evidences that by increasing the “spacer length” between terminal glycidyl ether groups the distance between neighboring lignin molecules can increase leading to the formation of larger voids as confirmed by nitrogen sorption experiments at 77 K (see below). At high lignin concentrations the differences between PPGDE 380 and PEGDE 640 level out.

Besides their number, the chemical structure of repeating units was demonstrated to have a significant impact on solvent/polymer interactions and thus also on the bulk densities of the aerogels. Replacement of an H atom by a sterically more demanding methyl group in each of the repeating group as it is formally the case when comparing PEGDE and PPGDE 640 (n ≈ 9) turned out to be sufficient to reduce the bulk density of the resulting lignin aerogels from 0.28 to 0.21 g cm⁻³ (1.0 mmol crosslinker per gram of lignin) and from 0.34 to 0.27 g cm⁻³ (2.0 mmol g⁻¹; Fig. 3) even though PPGDE (640 mg mmol⁻¹) has a higher molecular weight average than the used PEGDE (500 mg mmol⁻¹). The methyl substituents apparently shield the neighboring ether oxygen atoms to a certain extent from the interaction with water molecules, reducing the extent of shrinking this way. For both PEGDE and PPGDE 640 the bulk density increased by about 0.06 g cm⁻³ when doubling their amount from 1 to 2 mmol g⁻¹ lignin, which largely corresponds to the mass increment of the crosslinker (Fig. 3).

The average skeletal density of the obtained materials as determined by helium pycnometry was found to be 1.07 g cm⁻³ independent of the type of crosslinker used, while the bulk density varied from 0.2 to 0.4 g cm⁻³. Based on these values the porosity of the lignin aerogels was calculated to range from 75% to 88% (cf. Eq. (1)).

Nitrogen sorption isotherms (77 K) were found to be of type IVb (IUPAC classification) typical for mesoporous materials (Rouquerol et al., 1999) of relatively larger sized pores. The low adsorbed volume (≤25 cm³ g⁻¹) at point B (limit between the monolayer and multilayer adsorption at P/P0 = 0.02) indicated that micropores were largely absent (Fig. 4). Furthermore, the nitrogen sorption experiments revealed that the specific surface area of the samples varied significantly with both the Crl:L ratio and number of CRUs as exemplarily shown for PPGDE 380 and PPGDE 640 (Fig. 5). By
increasing the CrI:L ratio from 0.5 to 1.5 mmol g⁻¹ the surface areas decreased almost linearly from about 120 to 70 m² g⁻¹ (PPGDE 640) and from 80 to 40 m² g⁻¹ (PPGDE 380). Within this range of CrI:L ratios the longer-chained PPGDE 640 crosslinker afforded aerogels of significantly higher surface area and average mesopore size (Fig. 6) compared to PPGDE 380, which is in good agreement with the lower bulk densities of the former. Interestingly, the surface area of aerogels crosslinked with the shorter-chained PPGDE 380 increased considerably at a CrI:L ratio of 2.0 mmol g⁻¹ and surpassed that of PPGDE 640 aerogels which further decreased.

Based on the observation that the increase of PPGDE concentration from 0.5 to 2.0 mmol g⁻¹ lignin was not fully reflected by the gain of bulk density (Fig. 4) and the fact that data analysis (t plot) of the adsorption isotherm strongly indicated the absence of micropores, it is concluded that the decrease in surface area (Fig. 5) is most likely due to a shift of the void size from meso- to macropores (Fig. 7). This assumption is supported by scanning electron micrographs that generally confirm the existence of hierarchical, open-porous morphology (Fig. 8).

Thermo-gravimetric analysis of selected lignin aerogels revealed a very similar response within the temperature range of up to 400 °C largely independent on bulk density, cross-linker to lignin ratio, and type of cross-linker used (Fig. 9). Compared to the parent AS lignin which showed a TGA profile largely typical for isolated lignins [18] but confirming the presence of residual carbohydrates (rather narrow peak in the DTG curve between 300 and 400 °C, lower residual mass at 500 °C; [30]), the maximum weight loss rate shifts by almost 100 °C towards lower temperature for all of the studied lignin aerogels. This behavior of the lignin aerogels possibly emanates from cross-linked fragments as the flexible alkyleneoxy chains are supposed to be the most vulnerable moieties in the cross-linked product leading to earlier degradation in TGA analysis.

One of the most common applications of aerogels is their use for thermal insulation, which is due to their particularly low thermal conductivity. Therefore the obtained lignin aerogels were investigated with regard to their insulation properties using the transient hot wire technique. The latter is a dynamic technique that is based on the measurement of the temperature rise of a linear heat source (hot wire) embedded in the material to be tested. For an infinitely long metallic wire (length/radius ratio > 200) heated at time with a known, constant heat flux per length unit q and immersed in an infinite homogeneous medium (thermal conductivity and diffusivity: λ and α, respectively) with uniform initial temperature, the temperature rise of the wire can be calculated based on the analytical solution of an ideal thermal conductive model assuming a Fourier number ≫ 1 and the absence of convective transfers. By considering the deviations from the ideal model, the thermal

![Fig. 3. Impact of the crosslinker to lignin ratio on the bulk density of the aerogels (C_{NaOH} = 3.3 M, CrI:L = 2 mmol g⁻¹, RT gelation, 5-step solvent exchange to ethanol, residence time 24 h; n = 3, deviation in density: ± 0.01 g cm⁻³, confidence interval = 95%).](image)

![Fig. 4. Nitrogen sorption isotherms (77 K) of different lignin aerogels.](image)

![Fig. 5. Impact of the CrI:L ratio on the BET surface area of aerogels (3.3 M NaOH, 20% lignin (w/v), RT, five-step EtOH; n = 2, ±10%).](image)

![Fig. 6. Impact of the CrI:L ratio on the average pore size of the obtained aerogels (3.3 M NaOH, 20% lignin, RT, five-step solvent exchange to ethanol; n = 2, ±10%).](image)

![Fig. 7. Pore size distributions for lignin aerogels with different crosslinkers and lignin concentration aerogels (3.3 M NaOH, RT, five-step solvent exchange to ethanol).](image)
conductivity can be calculated according to Eq. (2), where \( \frac{d\epsilon(t)}{d\ln t} \) is a numerical constant deduced from the experimental data and from the linear part of the \( \epsilon(t) = f(\ln t) \) curve, \( R_0 \) the resistance of the wire at \( T_0 \) reference temperature, \( b_0 \) the temperature coefficient of the wire at 22°C, and \( i \) the electrical current [31].

\[
\epsilon = \left( \frac{qR_0b_0i}{4\delta} \right) \left( \frac{d\epsilon(t)}{d\ln t} \right)^{-1}
\]

Fig. 8. SEM images of aerogels obtained by crosslinking of lignin with PPGDE 380 (left: 10 wt% lignin, CrL ratio = 2 mmol g\(^{-1}\); right: 20 wt% lignin, CrL ratio = 1 mmol g\(^{-1}\)). A five-step solvent exchange from water to ethanol was performed for all samples. (Inset: Picture of a self-standing aerogel obtained after scCO\(_2\) drying).

Fig. 9. Thermogravimetric analysis of AS lignin and respective aerogels obtained by crosslinking with PPGDE 380 and PPGDE 640 using different lignin solute concentrations (15 or 20 wt%) and CrL ratios (0.5 or 2 mmol g\(^{-1}\)).

First measurements revealed a thermal conductivity of 50 mW m\(^{-1}\) K\(^{-1}\) for lignin aerogels that had been obtained by crosslinking of AS lignin (20% in 3.3 M NaOH) with EGDE (2 mmol g\(^{-1}\) lignin) at room temperature, followed by a five-step solvent exchange to ethanol and extraction of the solvent with scCO\(_2\) (12 MPa, 40°C, 4 h). Even though this value is still in the upper range of the thermal conductivity scale of common insulation materials (55 to 5 mW m\(^{-1}\) K\(^{-1}\); [32]), the manifold possibilities for controlling the pore features render lignin aerogels promising thermal insulation materials for a wide range of applications.

4. Conclusions

Wheat straw lignin produced by LHW pretreatment of the respective biomass and subsequent enzymatic hydrolysis was demonstrated to be a suitable raw material for the preparation of aerogels. The latter have been obtained by (1) activation of lignin in aqueous sodium hydroxide, (2) addition of oligo(alkylene glycol)-\(\varepsilon\),\(\omega\)-diglycidyl ethers as crosslinkers, (3) casting and gel formation, (4) gradual replacement of water by an organic solvent miscible with carbon dioxide, and (5) conversion of the obtained organogels to aerogels by scCO\(_2\) extraction.

Ethylene glycol diglycidyl ether (EGDE) and oligo(propylene 1,2-glycol)-\(\varepsilon\),\(\omega\)-diglycidyl ether of an average molecular weight of 640 (PEGDE 640; \( n = 8.8 \)) turned out to be the most promising compounds amongst the studied crosslinking agents. Both of them afforded similarly low bulk densities of 150–200 mg cm\(^{-3}\) and high specific surface areas of 115–120 m\(^2\) g\(^{-1}\).

Aerogels obtained by crosslinking of lignin with oligo(oxyalkylene glycol)-\(\varepsilon\),\(\omega\)-diglycidyl ethers are promising materials for thermal insulation as preliminary test using the transient hot-wire technique revealed thermal conductivities of around 50 mW m\(^{-1}\) K\(^{-1}\) which supposedly can further reduced by optimization of the process parameters. As residual amounts of sodium hydroxide have been shown to accelerate degradation of the aerogel, a thorough neutralization step should be therefore implemented prior to the scCO\(_2\) drying step.

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References
