

RSC Advances



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ARTICLE

Processing of lignin in urea/zinc chloride deep-eutectic solvent and its use as filler in a phenol-formaldehyde resin

Cite this: DOI: 10.1039/x0xx00000x

H. Lian,^a S. Hong,^a A. Carranza,^b J. D. Mota-Morales,^{*c} and J. A. Pojman ^{*b}

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

The main goal of our research deals with a new greener and more efficient lignin modification method to optimize its structural performance as phenol-formaldehyde resin filler. Through the appropriate increase in the phenolic hydroxyl content, an added value as a raw material was intended. For that, a series of mixtures of zinc chloride/urea with different molar ratios was prepared to obtain deep-eutectic solvents (DESs). Two heating methods (oil bath and microwave heating) were compared and optimized. Microwave helps reducing the preparation time but to the detriment of temperature control. On the other hand, heating with an oil bath provided better temperature control and homogeneity of the mixture. The preferable molar ratio of ZnCl₂/urea was 3:10 ($T_g = -26.3$ °C). The structural changes of the pretreated lignin samples were investigated by Fourier transformed infrared and X-ray photoelectron spectroscopies, scanning electron microscopy, induced coupled plasma and X-ray diffraction. Thermogravimetric analysis demonstrated significant differences in the thermal behavior of the recovered lignin as a result of DES treatment. The weight of lignin recovered was 4 times that of original lignin, indicating that the structure of lignin was transformed through the integration of Zn. The integration of Zn enhanced the thermal stability and enhanced lignin's reactivity towards phenol-formaldehyde resin formation. Phenol-formaldehyde resin containing the recovered lignin exhibited lower thermocuring temperatures and better thermostability than those without filler. To the best of our knowledge, this is the first report on the investigation of the structural transformations of lignin through its dissolution in urea/ZnCl₂ DES and subsequent use as filler for phenol formaldehyde resin synthesis.

Introduction

Lignin is one of the three main constituents of plants. After cellulose, it is the second most abundant biopolymer in the world. It is estimated that the amount of lignin on the earth is about 300 Gt, which make it a large renewable feedstock.¹ In the pulp of paper industries, lignin is produced extensively as a byproduct. For instance, ca. 1.5 tons of black liquor solid is discharged per ton of paper pulp produced, which is blamed for serious environmental pollution such as water contamination. Lignin is not utilized significantly because of its relatively unreactive natural structure. It is estimated that 1.5 to 1.8 million tons of lignin are produced annually from wood globally, and most of it is used as fuel and less than 1% of lignin is a feedstock for the chemical industry.² Therefore it is of great significance to strengthen the research on modification and application of lignin.³

The major chemical functional groups in lignin include hydroxyl, methoxyl, carbonyl and carboxyl groups in various amounts and proportions for various types of industrial lignin. One of the main drawbacks in the use of lignin is its low and chemically inactive hydroxyl content. In addition, its solubility in common solvents is poor, which restricts its use and reduces its practical value.

Several modification methods of lignin have been reported. Those include sulfonation, graft copolymerization, condensation, crosslinking between lignin and acrylamide, acrylic acid and polyhydric monomer ammoxidation and oxidation in dilute nitric acid.⁴ These methods are mostly confined to laboratory research, just a very few have been scaled up to industrial production. For example, high-pressure, high temperatures during long periods of time or high acidic conditions are necessary.

Within the frame of green chemistry, deep eutectic solvents recently emerged as an environmentally friendly solvent alternative. The term deep-eutectic solvent (DES) was coined by Abbott and co-workers in 2003.⁵ A DES is composed of two or more components that are capable of self-association through hydrogen bonding to form a mixture with a melting point lower than that of each individual component.⁶ DESs are usually liquids at temperatures lower than 100 °C. Although DESs exhibit almost identical physicochemical properties to traditional ionic liquids, they do offer advantages due to their lower cost and environmentally friendlier nature.⁷ Besides, the purity of a DES only depends on the purity of their components and requires no complicated synthesis. Owing to these advantages, DESs are a growing interest in many fields of research e.g., catalysis, organic syntheses, dissolution media, extraction processes, electrochemistry and material chemistry.⁸ Regarding biomass processing, DESs have been used as extraction as well as dissolution media for certain biopolymers including suberin (from cork), chitin, cellulose, starch and lignin.⁹ Further, the suitability of some DESs for the catalytic conversion of these renewable raw materials has been reported.¹⁰ Cellulose is the most studied biopolymer; reports include its dissolution and derivatization in basic choline chloride-based DES,¹¹ its solubilization and decrystallization in choline acetate/tributylmethylammonium chloride mixtures,¹² and its solubilization in DESs containing amino acids, choline and betaine.¹³ The first attempt to fractionate biomass in lignin and other lignocellulosic compounds by means of DESs was reported by Francisco and co-workers. In that work 26 mixtures comprising DES with different polarities were screened for the selective dissolution of lignin, among cellulose and starch, and for delignification of wheat straw.¹³

The adhesive properties of lignin should be similar to synthetic polyphenols, i.e. phenol-formaldehyde resins (PF).¹⁴ Phenol-formaldehyde resins are thermosets that result from the reaction of phenol with aldehydes in the presence of an alkali or an acid catalyst. In this sense, under the appropriate chemical transformation, lignin has the potential of being a renewable raw material for PF thermosets.¹⁵ Taking into account that aqueous solutions of zinc (II) salts promote solubilization of biopolymers (e.g. cellulose)^{16, 17} and that zinc (II) salts also can catalyze the polymerization of phenol-formaldehyde resin (PF),¹⁸⁻²⁰ its expected that Zn-based DESs²¹ could provide a greener platform for the transformation of lignin in order to function as favorable filler for PF.

The main goal of our research is to optimize the method by which the lignin is dissolved and modified in a Zn-based DES. The heating process for dissolution, the reaction temperature and the mole ratio of zinc chloride to urea were all optimized on the basis of economy and time. Finally, the structural and thermal features of recovered lignin (after precipitation in water) were compared with those of the original lignin in order to get insights on the transformations that take place during dissolution. To the best of our knowledge, this is the first report on the investigation of the structural transformation of lignin

under urea/ZnCl₂ DES that yields a material useful as filler for PF synthesis.

Experimental

All chemical reagents used were of analytical grade or best available. All chemicals were used as received without further purification. Lignin was purchased from ALM India Protobind 2400 and was dried for 5 h at 60 °C. The moisture content of lignin was 2.56 %. The PF resin with 45.6% solids and viscosity of 116 mPa·s was obtained from Dynea Nanjing.

Preparation of DES

Zinc chloride and urea were mixed in different proportions and heated in a microwave or oil bath (at 80 °C, 90 °C or 100 °C), until transparent homogenous liquids were obtained.

Dissolution of lignin in DES

1 %, 2 % and 3 % wt. of lignin (0.15 g, 0.3 g and 0.45 g) was slowly added to 15 g of DES, with slight stirring. The mixture was then placed into an oil bath at given temperatures (80 °C, 90 °C or 100 °C) for different times without stirring. After the dissolution, lignin was recovered by addition of distilled water (a non-solvent for lignin) and subsequent centrifugation. Recovered lignin was allowed to dry at room temperature.

Modified PF resin by lignin

100 g PF resin and 30 g pristine lignin (lignin) or recovered lignin from DES (relicignin), were added to a 250 ml Erlenmeyer flask equipped with stirrer. The flask containing the filler (lignin or relicignin) and the PF resin was stirred on room temperature until blended.

Differential scanning calorimetry (DSC)

DSC was performed with a TA Instruments Model DSC Q-100 system under a nitrogen atmosphere. The measurements were made with 20-30 mg samples in hermetic pans. For DESs, the heating rate was 3 °C min⁻¹, over a temperature range of -50 °C to 50 °C. DSC scans showed the glass transition temperature (T_g) of DES. The glass transition was determined at the midpoint of the transition of the heat capacity (C_p). For lignin, relicignin, phenol-formaldehyde resin (PF), phenol-formaldehyde resin containing lignin (LPF), and phenol-formaldehyde resin containing recovered lignin (RLPF), the temperature program was 10 °C min⁻¹ from 25 °C to 600 °C in N₂ atmosphere, and the onset of the peak temperatures were registered.

TG and DTG Analysis

The thermal stabilities of the DESs, lignin and relicignin, were studied with a thermogravimetric analyzer (TA, 2950 TGA HR V6.1A, standard TGA aluminium pans) from room temperature to 600 °C. The heating rate was 10 °C min⁻¹ under nitrogen environment. The measurements were made using 6-10 mg of sample.

FTIR spectra

FTIR spectra were collected on a Perkin-Elmer spectrophotometer using an ATR accessory in the range 4000-600 cm^{-1} at room temperature, resolution was set to 4 cm^{-1} , and the spectra shown were an average of 16 scans.

SEM Analysis

Scanning electron microscopy (SEM) was used to provide information on the particle size and the surface of lignin and relignin. The model of the SEM is FEI Quanta 200. Samples were gold-coated prior analysis.

XPS analysis

XPS spectra were obtained with a Kratos Axis 165 XPS/AES, operated with a Monochromatic Al K α (1486.6 eV) source with an emission current of 10 mA at 15 kV. Samples were loaded with double-sided carbon tape. A thin layer of powder was applied to one side of the carbon tape, which was attached to the sample-loading bar. Samples were analyzed in a high vacuum chamber with a pressure of 6×10^{-9} Pa. A quick survey scan at the pass energy of 40 eV and high resolution elemental scans at pass energy of 160 eV were performed on each sample. The elemental scans were used to quantitatively analyze the composition of the samples.

XRD and ICP-MS analysis

X-ray diffraction for powder was performed in relignin and lignin in a Panalytical Empereyan model with a PIXcel3D multipurpose mounting system. Relignin was digested with peroxide-acid treatment and the product was then dissolved in a 2% nitric acid solution and analysed using laser ablation ICP-MS ICP-Q model with a LSX-213 laser ablation system through a standard addition method with a 200.8 cal-2 ADH Standard (20 $\mu\text{g mL}^{-1}$).

Sunshine Gel Time (SGT) of PF resin – Short Wire Method

SGT test is based on a method obtained from Ralph Wilson Plastics, formerly known as PTM-5. Briefly, 6.1 g of sample including PF resin, lignin with PF resin (LPF), and relignin with PF resin (RLPF), respectively, were placed in an 18 x 150 mm test tube (without catalyst). The tube was placed in an oil bath and the time for the resin to gel was determined at 130 ± 0.5 °C.

Results and discussion

Preparation of DES

In order to investigate the optimal parameters for DES formation, various zinc chloride to urea mole ratios were tested. The criteria included the time for the DES's formation, maximum temperature during the process, formation of homogenous liquid and lifetime of the liquid. Two types of heating were also tested; namely, microwave irradiation and oil

bath heating. The results are shown in **Table 1** and **Table 2**. With microwave irradiation, the reaction rate can be increased, but only to the detriment of temperature control and reproducibility. In addition, DESs tend to crystallize after a few days implying the formation of metastable mixtures (**Figure 1**).

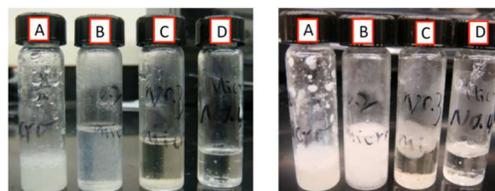


Figure 1. Storage of DES prepared under microwave irradiation after the second day (left) and after the 7th day (right).

Table 1. Properties of DES formation under microwave irradiation.

	Molar ratio (ZnCl ₂ /urea)	Time (s)	Temp. (°C)	Initial/Final appearance	Life time (days)
A	1:10	30	>240	Release of smoke, overflow/ White solid, opaque.	0
B	2:10	20	>210	Release of smoke/ White suspension.	1
C	3:10	25	>230	Release of smoke, overflow/Homogeneous and transparent liquid.	7
D	4:10	30	>240	Release of smoke, overflow/Homogenous and transparent liquid.	7

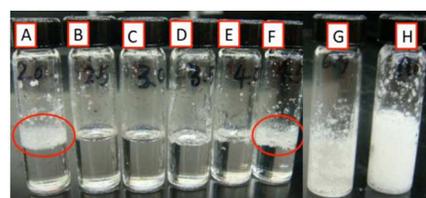


Figure 2. Appearance of DESs prepared by heating in an oil bath.

The time at which the first solid crystal within the liquid was observed, was denoted as the storage lifetime. **Table 2** and **Figure 2** show some features of mixtures of zinc chloride and urea in different molar ratios heated in an oil bath. The evolution of DES formation is directly related with their stability over time, e.g., as the Zn content is lower than 2.5:10 (to urea) the time required for the formation of a liquid is considerable longer than that required for the formation of the liquid consisting of 3:10 (ZnCl₂:urea). Below 2.5:10 it is not possible to obtain a homogeneous liquid, and instead white

crystals remain on top of the liquid formed. On the other hand, as Zn content was further increased above 4:10 (to urea) the mixture becomes again heterogeneous, the preparation time increases and the lifetime of the mixture is reduced significantly.

ATR-FTIR spectroscopy

The FTIR spectrum of DES provided useful information regarding intramolecular interactions between the DES's components. Four mixtures of zinc chloride and urea with different mole ratios were tested (Figure 3).

All of them showed similar spectra, however some differences are noticeable.

Table 2. Properties of DES formed with oil bath heating.

	Molar ratio (ZnCl ₂ /urea)	Time (min)	Temp. (°C)	Initial/Final appearance	Life time (days)
O	1:10	180	100	White solid, opaque.	0
A	2:10	45	100	White solid on the surface.	1h
B	2.5:10	50	100	Homogeneous, transparent liquid.	24h
C	3:10	60	100	Homogeneous, transparent liquid.	>30d
D	3.5:10	75	100	Homogeneous, transparent liquid.	10d
E	4:10	90	100	Homogeneous, transparent liquid.	7d
F	4.5:10	120	100	White solid on the surface.	3d
G	6.7:10	>180	100	White, opaque	0
H	10:10	>180	100	White, opaque	0

For instance, the shoulder around 3200 cm⁻¹ increases its intensity as the relative amount of urea increases, indicating an increase of the N-H bonds. Also the shoulder next to the carbonyl at 1743.6 cm⁻¹ and the peak located at 1494.8 cm⁻¹ both shift to lower wavenumbers as the zinc content increases. By comparing the spectrum of DES ZnCl₂/urea (3:10 molar ratio) with the spectra of its pure components, it is clear that the absorption peak of C=O shifted to lower wavenumber (from 1594 to 1575.8 cm⁻¹) as a result of DES formation. In previous studies,^{22, 23} the role of urea as ligand was found to depend on the type of transition metal ion to which urea coordinates. Considering the resonance structure of urea, H₂N-(C=O)-NH₂, there are two functional groups (carbonyl and amino, -C=O and -NH₂) in its structure capable of forming metal-urea complexes. When the formation of complexes occurs through

oxygen and metal ion, the stretching vibration frequency of carbonyl shifts toward lower wavenumber.

Contrary, when the amino nitrogen is the complexing atom, the carbonyl stretching vibration frequency shifts to higher wavenumber. Metal-O bonding in transition metal salts (including Zn) with urea has been widely reported in literature.²⁴ The coexistence of Zn-O-C=N and Zn-O=C-N resonance structures are possible, therefore the interaction of carbonyl in urea with Zn is responsible for the red shift of carbonyl in DES spectrum, where the majority of the carbonyl oxygen atoms in urea participate in forming coordination complexes.

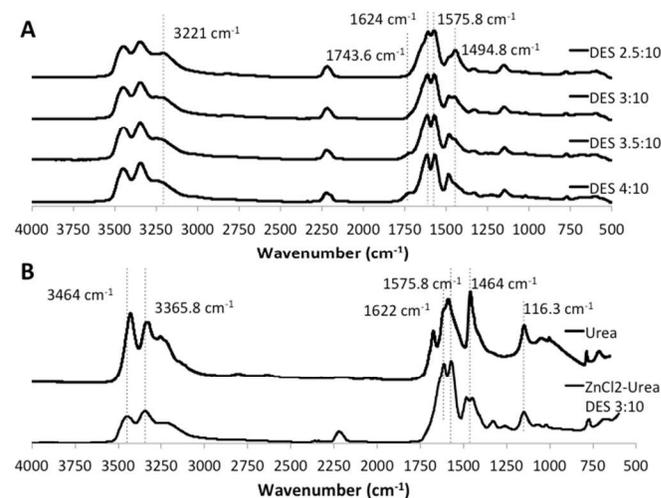


Figure 3. (A) ATR FTIR of DESs varying the ratio ZnCl₂/urea. (B) ATR FTIR of Urea/ZnCl₂ 3:10 and its constituents.

The strong interaction between oxygen in the carbonyl group of urea and zinc weakens the Coulombic attraction between Zn²⁺ and Cl⁻ by increasing the size of the zinc cation and thus lowering the melting point of the mixture to finally result in a eutectic liquid at room temperature. This is in agreement with the view of Dishun Zhao et al.²⁵ that urea, as a ligand, forms coordination compounds with metal salts, specifically with ZnCl₂. They propose that ZnCl₂/urea form a stable coordination compound with formula Zn[OC(NH₂)₂]₃Cl₂, composed entirely of a Zn²⁺ cation coordinated with three oxygen from urea and two chlorine anions. During the reviewing process of this paper Zhang and colleagues²⁶ reported that $[n(\text{urea})/m(\text{ZnCl}_2)]$ deep-eutectic solvents, with $n=1, 2, 3, 4$ and $m=1$, resulted in energy minimum structures through DFT calculations, in contrast when the number of urea molecules rise to 5 and above, thus supporting the experimental findings presented here.

Thermal properties of DES

In order to evaluate the thermal decomposition of the DES, differential scanning calorimetry (DSC) and thermogravimetric analysis (TG) were used.

The melt points of ZnCl₂ and urea are 293 °C and 134 °C respectively, but the glass-liquid transition temperature (T_g) of DESs made of ZnCl₂ and urea in different proportions was

below $-20\text{ }^{\circ}\text{C}$ in all cases. It was observed that there is a correlation between the Zn content in the DES and the T_g exhibited. In **Figure 4A** it can be seen that the larger the Zn content, the T_g appears at higher temperature, although the T_g of $\text{ZnCl}_2/\text{urea}$ DESs in 4:10 and 3.5:10 proportions are the same.

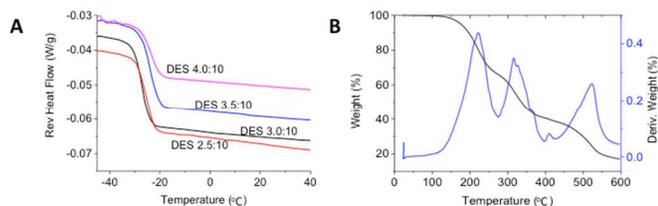


Figure 4. (A) DSC of DES varying the ratio $\text{ZnCl}_2/\text{urea}$. (B) TG-DTG of $\text{ZnCl}_2/\text{urea}$ 3:10.

It is worthy to note that these values differ from those reported by Abbott et al.²¹ and Zhang et al.²⁶ because the latter ones refer to the freezing point (T_f) of the DES. The freezing point was taken as the temperature at which the first solid started forming when the temperature slowly decreased. Hence, the freezing point of $\text{ZnCl}_2/\text{urea}$ DESs in 3.5:10 ratio was $9\text{ }^{\circ}\text{C}$ while its glass transition measured by DSC is $-24.2\text{ }^{\circ}\text{C}$. Large differences between freezing point and the melting point (measured by DSC) have been also reported for DES containing urea and choline chloride, presumably due to the high viscosity of the DESs,²⁷ which seem to be the case here.

The TG of $\text{ZnCl}_2/\text{urea}$ (3:10 molar ratio, **Figure 4B**) showed three main steps during its thermal decomposition. Before $180\text{ }^{\circ}\text{C}$, the weight loss was 0.9% , which is related with the inherent moisture content of ZnCl_2 . The first step occurred about $227\text{ }^{\circ}\text{C}$, the second about $325\text{ }^{\circ}\text{C}$ and last one at $528\text{ }^{\circ}\text{C}$, leaving behind a residue accounting for 19% wt. at $600\text{ }^{\circ}\text{C}$. This is the reason there were some smoke releasing when DES was made using microwave irradiation, i.e., DES's decomposition due to the temperature reached ($200\text{ }^{\circ}\text{C}$ to $220\text{ }^{\circ}\text{C}$).

Lignin dissolution in DES

The solubility of lignin was assessed visually. Lignin was added to the DES carefully with slow stirring. It was found that lower contents of lignin, e.g., 1 and 2 % wt. of DES, had good solubility. Conversely when the amount of lignin was 3 % the viscosity greatly increased making difficult the dissolution process; there were even some insoluble solids on the wall of the vial. Thus, the dissolution of DES containing 2 % of lignin was tested further.

FTIR analysis of lignin and relignin

From **Figure 5**, it can be seen that the shape and intensity of the peaks in the spectrum of DES compared with the DES containing 2 % wt. of lignin were practically the same. This suggests that lignin was homogeneously dissolved in DES without disturbing the supramolecular features characteristic of $\text{ZnCl}_2/\text{urea}$ DES shows an excellent dissolving capability for lignin because of its ability to form hydrogen bonds and

coordination complexes. This in turns impacts the intermolecular and intramolecular interactions in the lignin network, possibly due to the action of the ionic environment.²⁶ DES.

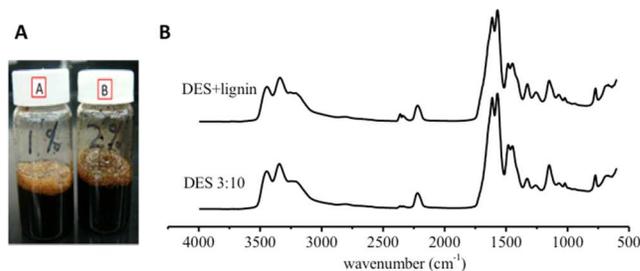


Figure 5. (A) Lignin dissolved in DES. (B) FTIR of DES containing 2 % of lignin.

The dissolved lignin was thoroughly washed with distilled water and recovered by centrifugation. Interestingly, the mass of recovered lignin (denoted as “relignin”) was 4 times that of original lignin, indicating that the structure of lignin was chemically transformed, possibly through the integration of Zn. In order to get insights into the chemical composition of relignin, FTIR, SEM with EDS, XPS, XRD and ICP-MS studies were carried out.

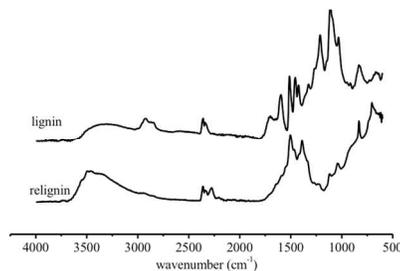


Figure 6. ATR-FTIR spectra of lignin and relignin.

The FTIR spectrum of relignin greatly differed from that of pristine lignin (**Figure 6**). For example, the band that appears at 3300 cm^{-1} is attributed to OH stretching vibrations, caused by the presence of alcohol and phenol hydroxyl groups. This band shifts to high wavenumbers (3439 cm^{-1}), reflecting changes in the hydrogen bonding (either NH and OH) in the lignin polymer network.²⁸ Stretching vibrations at $1715\text{--}1705\text{ cm}^{-1}$ correspond to carbonyl. The bands located at 1419 , 1450 , 1514 and 1604 cm^{-1} indicate the existence of characteristic aromatic rings and C–H bonds in the lignin. The band near 1600 cm^{-1} is caused by the stretching of C–C bond of aromatic benzene rings, while the bands in the region of $1230\text{--}1210\text{ cm}^{-1}$ are caused by aromatic phenyl C–O.²⁹ All these bands diminished in intensity while some others disappeared. This indicates the cleavage of methylene bridges in relignin. Additionally, the C–O stretch assigned to syringyl rings at 1217 cm^{-1} is not present in relignin.

Thermal analysis of lignin

Lignin presents a continuous mass loss throughout the heating process (**Figure 7**). There were three main thermal events

during its decomposition. In the first stage (300–180 °C), the mass loss (ca. 2 %) is mainly attributed to the loss of moisture, bound water and some low molecular weight fractions. Water is also a major degradation product that originates from various types of hydroxyl groups. Pyrolysis of lignin occurs in the second stage, beginning at 180 °C and continuing until 400 °C. This stage exhibits the highest percentage mass loss (about 61 %) and involves fragmentation of inter-unit linkages, releasing monomeric phenol in vapor phase, and the decomposition of some aromatic rings. Decomposition of aromatic ring occurs above 400 °C. Further heating above 400 °C leads to saturation of the aromatic rings, C–C bond cleavage of lignin and release of H₂O, CO₂ and CO. Decomposition of methoxy (–O–CH₃) groups releases methane around 400–600 °C.^{30–32}

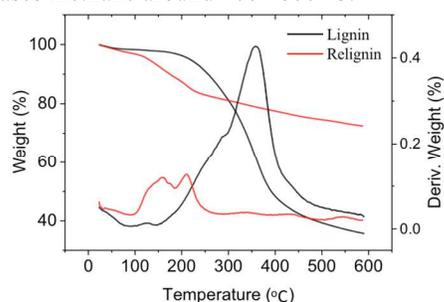


Figure 7. TG and DTG of lignin and relignin.

In the case of relignin, the thermal events were significantly less prominent than in the case of lignin. Relignin showed also three main steps, starting from 30–100 °C, the second between 100 °C and 200 °C and the third in the range of 200–240 °C. The degradation onset of relignin was 110 °C, which occurred earlier than the lignin. Interestingly the total weight loss of relignin at 600 °C was only 12.5 % (compared with 72.6 % for lignin), which means that relignin contained an important amount of inorganic material containing Zn. The high thermal stability of relignin is possibly due to crosslinking with groups containing the –NH–CO– moiety capable of forming irreversible covalent bonds besides to the presence of an important amount of inorganic material.

SEM images of lignin and relignin

Scanning electron micrographs of lignin and relignin (**Figure 8**) show differences in the appearance of the lignin's surface compared with the relignin one. The grains of lignin have a hard surface while relignin ones have a smooth form.

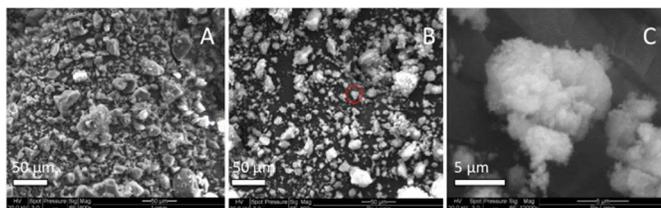


Figure 8. SEM images of lignin (A), relignin (B) and (C) is an enlargement of the region in the red circle in (B).

The average size of the grains of relignin is also smaller than lignin. Both results in the size and surface of relignin are the result of the chemical transformation after dissolution in the DES.

XPS analysis

Oxygen, carbon and a very small amount of nitrogen were observed on the surface of pristine lignin. On the other hand relignin exhibited oxygen and a little less carbon content than lignin; zinc and chlorine were also identified. The high-resolution XPS spectrum, showed a greater fraction of oxygen and Zn, and the existence of a few percentage of chlorine atoms on the surface of relignin after centrifugation, indicating that the DES may act as a catalyst in the oxidation of lignin. This also confirms that C–O in lignin coordinates Zn²⁺ in DES as previously noted by TG.

The content of oxygen atoms on the surface of lignin was compared to carbon atom content, and it was noted that the ratio O/C approximately doubled. After the DES was washed out, the oxygen atom content largely increases to reach about 27.58 % (O/C went from 0.23 to 0.46) (**Table 4**). The ratio of zinc to chloride that remained on the surface of relignin was 4:1, which differs from the original composition of ZnCl₂ in the DES. This confirms the fact that DES was not only acting as solvent but the Zn²⁺ in DES was integrated into lignin structure, possibly through formation of complex chelates with hydroxyl and methoxyl groups in lignin.^{33, 34}

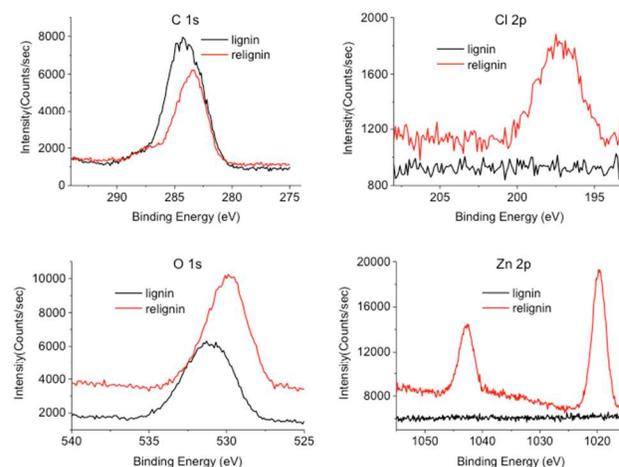


Figure 9. XPS spectra of lignin and relignin.

DES playing multiple roles (e.g. solvent and reactant) in the transformation of biomass has been reported before.²¹ One could therefore conclude that ZnCl₂:urea DES acts as solvent and the bivalent zinc, mostly alone, acted as catalysis and reactant during lignin dissolution (the small amount of Cl⁻ in XPS spectra does not correspond the stoichiometry of ZnCl₂ in DES).

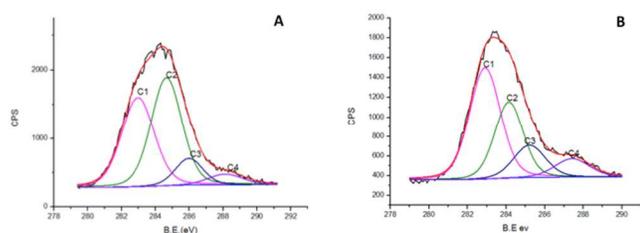


Figure 10. High-resolution XPS spectra of lignin and relignin in the carbon region.

Four types of carbon bonds (denoted C_1 to C_4) in lignin and relignin were identified by XPS.³⁵

C_1 = carbon atoms bonded to other carbon atom or hydrogen atoms (C–C; C–H).

C_2 = carbon atoms bonded to one oxygen atom (C–O, C–O–C).

C_3 = carbon atoms involved in carbonyl groups or bonded to two oxygen atoms (C=O, O–C–O).

C_4 = carbon atoms bonded to carboxyl groups (O–C=O).

A likely scenario is the degradation of β -O-4', β - β' and β -5' linkages so that there is a decrease in the C_1 and C_2 carbons. Therefore the molecular weight is also reduced by fractioning larger structures. The increase of C_3 and C_4 indicates that the O–C–O and C=O bonds increased as result of lignin oxidation. The appearance of new end groups observed by FTIR and XPS are due to the aromatic ring oxidation, open loop, and generated muconic acid and ortho and para-quinones.³⁶

Table 3. Chemical composition of the surface of lignin and relignin measured by XPS.

Elements	Atomic conc. (%)		% Weight	
	Lignin	Relignin	Lignin	Relignin
Zn 2p	0	10.3	0	35.22
O 1s	18.97	27.58	23.79	23.08
C 1s	81.03	59.6	76.21	37.4
Cl 2p	0	2.52	0	4.3
O/C ratio	0.23	0.46	0.31	0.62

Table 4. Chemical composition by XPS in the carbon region. (atomic content in lignin and relignin surfaces).

Peak	Position BE(eV)	Bond type	Atomic Conc. (%)	
			Lignin	Relignin
C_1	282-282.5	C–C, C–H	6.09	1.43
C_2	283-284	C–O, C–O–C	90.9	76.79
C_3	285-285.5	O–C–O, C=O	0.42	1.86
C_4	287-289	COO	2.59	19.92

XRD and ICP-MS analysis

By X ray diffraction it is clear that the amorphous (i.e. lack of well defined diffraction peaks, Figure S3) structure of lignin is transformed by the introduction of Zn in relignin. Actually most of the peaks in the diffractogram of relignin adjust to ZnO. On

the other hand, the Zn content measured by ICP-MS analysis in relignin after an acidic digestion rendered a value of 63.1 % wt. of Zn (78.52 % wt. expressed as ZnO). This value corresponds well with the mass gained after precipitation with water and it is also close to the inorganic material remained by TG analysis (77.5 %wt.).

Thermal properties of PF resins

Lignin and relignin (accounting for 30% wt.) were used as fillers in a conventional phenol-formaldehyde resin (PF). Before curing, phenol-formaldehyde containing lignin showed higher viscosity than the PF precursors. The Sunshine gel time of PF, LPF and RLPF are 493 s, 617 s and 309 s at 130 °C respectively. One can see that when relignin was added to PF resin as filler, it cured faster, which is reflected in the gel time (shorter by about 37 % than that of PF resin without filler). This confirms the hypothesis that lignin modified with Zn is able to act as both filler and catalyst in PF polycondensation.^{18, 19} By TG/DTG curves (heating rate of 10 °C min⁻¹), it was found that the degradation, i.e. the thermal stability, of the final resin is affected by the presence of lignin and relignin which is in accordance with the literature on thermal degradation of phenolic resins^{37, 38} and resins filled with lignin.³⁹ After 600 °C a considerable amount of residues as carbonized residues still remained: 35 % in the case of PF, 38 % of LPF and 47 % of RLPF. Therefore RLPF resin shows higher resistance to thermal degradation than LPF resin and the commercial PF resin.

Conclusions

Deep eutectic solvents based on zinc chloride and urea offer a readily green approach for lignocellulosic biomass treatment. DES with the optimum molar ratio ZnCl₂:urea of 3:10 (T_g at -26.3 °C) prepared in oil bath resulted in the best lignin solvation.

Lignin dissolved in DES was precipitated in water having a mass equal to 4 times the original lignin. Through FTIR, XPS, XRD and ICP-MS analysis the introduction of Zn²⁺ in the basic structure of lignin was confirmed. The lignin modification with Zn was accompanied by an increase of the ratio O/C and an enhancement in its thermal stability.

PF resin filled with relignin showed shorter Sunshine gel times than the PF resin alone possibly through a catalytic effect. Interestingly the onset of thermal degradation of RLPF occurred at higher temperatures than those resin with unmodified lignin and without it, showing superior thermal properties.

This work presented the first lignin processing in a DES that enhance its thermal stability and integrates compounds (e.g. ZnO) that are useful as filler for phenol-formaldehyde resin. Although the exact mechanisms occurring during lignin transformation remain unknown, the increase in the oxidized groups in lignin surface and possible presence of ZnO provide some clues. Future studies incorporating Zn derived DES that

will allow an elucidation of the chemical process during lignin dissolution and precipitation are currently on their way.

Acknowledgements

This work was supported by the grants from the National Natural Science Foundation of China (31370567), Natural Science Foundation of Jiangsu Province (BK20131427) and sponsored by a project funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD) and Qing Lan Project. HL would like to acknowledge the hospitality of the LSU Chemistry Department during her stay. Special thanks to Dr. Herrmann and Dr. Amar Karki for kindly allowing the use of their facilities.

Electronic Supplementary Information (ESI) available: Details of DSC, TG/DTG, XRD and ICP-MS results. See DOI: 10.1039/c000000x/

Notes and references

^a College of Wood Science and Technology, Nanjing Forestry University, Nanjing, 210037, China.

^b Department of chemistry, Louisiana State University, Baton Rouge, LA 70820, USA. E-mail: john@pojman.com

^c Cátedras Conacyt at CNYN-UNAM, Ensenada, BC 22860, México. E-mail: mota_josue@hotmail.com; jmota@cnyun.unam.mx

- R. Singh, S. Singh, K. D. Trimukhe, K. V. Pandare, K. B. Bastawade, D. V. Gokhale and A. J. Varma, *Carbohydrate Polymers*, 2005, **62**, 57-66.
- A. Tejado, C. Peña, J. Labidi, J. M. Echeverria and I. Mondragon, *Bioresource Technology*, 2007, **98**, 1655-1663.
- X. Pan, X. Zhang, D. Gregg and J. Saddler, *Appl Biochem Biotechnol*, 2004, **115**, 1103-1114.
- M. N. Sathesh Kumar, A. K. Mohanty, L. Erickson and M. Misra, *Journal of Biobased Materials and Bioenergy*, 2009, **3**, 1-24.
- A. P. Abbott, G. Capper, D. L. Davies, R. K. Rasheed and V. Tambyrajah, *Chemical Communications*, 2003, 70-71.
- A. P. Abbott, D. Boothby, G. Capper, D. L. Davies and R. K. Rasheed, *Journal of the American Chemical Society*, 2004, **126**, 9142-9147.
- Q. Zhang, K. De Oliveira Vigier, S. Royer and F. Jerome, *Chemical Society Reviews*, 2012, **41**, 7108-7146.
- D. Carriazo, M. C. Serrano, M. C. Gutierrez, M. L. Ferrer and F. del Monte, *Chemical Society Reviews*, 2012, **41**, 4996-5014.
- P. Domínguez de María, *Journal of Chemical Technology & Biotechnology*, 2014, **89**, 11-18.
- F. Pena-Pereira and J. Namieśnik, *ChemSusChem*, 2014, n/a-n/a.
- A. P. Abbott, T. J. Bell, S. Handa and B. Stoddart, *Green Chemistry*, 2006, **8**, 784-786.
- Q. Zhang, M. Benoit, K. De Oliveira Vigier, J. Barrault and F. Jérôme, *Chemistry – A European Journal*, 2012, **18**, 1043-1046.
- M. Francisco, A. van den Bruinhorst and M. C. Kroon, *Green Chemistry*, 2012, **14**, 2153-2157.
- S. Sahoo, M. Ö. Seydibeyoğlu, A. K. Mohanty and M. Misra, *Biomass and Bioenergy*, 2011, **35**, 4230-4237.
- N. E. E. Mansouri, A. Pizzi and J. Salvado, *Journal of Applied Polymer Science*, 2007, **103**, 1690-1699.
- H. Leipner, S. Fischer, E. Brendler and W. Voigt, *Macromolecular Chemistry and Physics*, 2000, **201**, 2041-2049.
- N. J. Richards and D. G. Williams, *Carbohydrate Research*, 1970, **12**, 409-420.
- J. Huang, M. Xu, Q. Ge, M. Lin, Q. Lin, Y. Chen, J. Chu, L. Dai and Y. Zou, *Journal of Applied Polymer Science*, 2005, **97**, 652-658.
- Y. Lei and Q. Wu, *Journal of Applied Polymer Science*, 2006, **101**, 3886-3894.
- D. A. Fraser, R. W. Hall and A. L. J. Raum, *Journal of Applied Chemistry*, 1957, **7**, 676-689.
- A. P. Abbott, J. C. Barron, K. S. Ryder and D. Wilson, *Chemistry – A European Journal*, 2007, **13**, 6495-6501.
- T. Theophanides and P. D. Harvery, *Coordination Chemistry Reviews*, 1987, **76**, 237-260.
- Z. Yi-Ming, X. Juan, S. Dong-Mei, W. Qing, L. T-Hong and X. Xin-Quan, *Chinese Journal of Applied Chemistry*, 2003, **20**, 305-306.
- R. Custelcean, B. A. Moyer, V. S. Bryantsev and B. P. Hay, *Crystal Growth & Design*, 2006, **6**, 555-563.
- D. Zao, X. Li, B. Liu, Z. Xu and N. Wang, *Fine Chemicals*, 2007, **24**, 632-635.
- Q. Wang, X. Yao, Y. Geng, Q. Zhou, X. Lu and S. Zhang, *Green Chemistry*, 2015.
- H. G. Morrison, C. C. Sun and S. Neervannan, *International Journal of Pharmaceutics*, 2009, **378**, 136-139.
- S. H. Ghaffar and M. Fan, *Biomass and Bioenergy*, 2013, **57**, 264-279.
- Q. Liu, S. Wang, Y. Zheng, Z. Luo and K. Cen, *Journal of Analytical and Applied Pyrolysis*, 2008, **82**, 170-177.
- J. Hu, R. Xiao, D. Shen and H. Zhang, *Bioresource Technology*, 2013, **128**, 633-639.
- D. Shen, J. Hu, R. Xiao, H. Zhang, S. Li and S. Gu, *Bioresource Technology*, 2013, **130**, 449-456.
- J. Ke, D. Singh, X. Yang and S. Chen, *Biomass and Bioenergy*, 2011, **35**, 3617-3626.
- A. Pizzi, *Journal of Applied Polymer Science*, 1979, **24**, 1247-1255.
- A. Pizzi, *Journal of Applied Polymer Science*, 1979, **24**, 1257-1268.
- J. Li, *Wood Spectroscopy*, Science Press, Beijing, China, 2003.
- W. G. Trindade, W. Hoareau, I. A. T. Razera, R. Ruggiero, E. Frollini and A. Castellan, *Macromolecular Materials and Engineering*, 2004, **289**, 728-736.
- A. Y. Malkin, I. Y. Gorbunova and M. L. Kerber, *Polymer Engineering & Science*, 2005, **45**, 95-102.
- J. Wang, M.-P. G. Laborie and M. P. Wolcott, *Thermochimica Acta*, 2005, **439**, 68-73.
- M. V. Alonso, M. Oliet, J. C. Domínguez, E. Rojo and F. Rodríguez, *J Therm Anal Calorim*, 2011, **105**, 349-356.