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Room temperature depolymerization of lignin using a protic and metal based ionic liquid system: an efficient method of catalytic conversion and value addition†

Mohit J. Mehta,[a] Akshay Kulshrestha,[a,b] Shweta Sharma[c] and Arvind Kumar ⭐[a,b]

Lignin is one of the most abundant biopolymer which can be utilized to synthesize various chemicals *via* its depolymerization. However, depolymerization of lignin generally occurs under very harsh conditions. Herein, we report the efficient depolymerization of lignin *via* dissolution in a mixed ionic liquid system: ethyl ammonium nitrate (EAN) + prolinium tetrachloromanganate(II) [Pro]$_2$[MnCl$_4$] at 35 °C and under atmospheric pressure conditions. The high dissolution of lignin in ethyl ammonium nitrate provided a large number of H-bonding sites leading to the cracking of lignin and subsequent oxidative conversion by [Pro]$_2$[MnCl$_4$] *via* the formation of metal-oxo bonding between Mn and lignin molecules. The extracted yield of vanillin was found to be 18–20% on lignin weight basis *via* GC-MS analysis. The depolymerization of lignin was confirmed by SEM, FT-IR and PXRD analysis. Since lignin contains UV-absorbing functional groups, the regenerated biomass after the recovery of the depolymerized products was further utilized to synthesize a UV-shielding material. The constructed films from such a material exhibited a high SPF value of 22 and were found to be very effective by limiting the UV degradation of rhodamine B thus making the lignin valorization process economically viable and environmentally sustainable.

Introduction

Lignin is the second most abundant biopolymer in the world. Additionally, lignin is used as an additive to plastics for the synthesis of biofuels and the construction of bioactive compounds.[1–6] Since lignin is readily available in the environment, it can be a potential source of aromatic compounds for our future needs. Even though the applicability of lignin is widely known, most of the lignin is mainly burned in the atmosphere for energy purposes and a very small amount of lignin is being used as a source of aromatic compounds.[7] The limited utilization of lignin is due to its chemical structure, in which the C–C and C–O–C linkages are very strong. However, lignin can be depolymerized at higher temperature and pressure.[8] There are several reports available on the depolymerization of lignin into several aromatic compounds such as phenols, catechols and acids.[9,10] Several methods are being employed for the depolymerization of lignin such as catalysis (3 MPa H$_2$ pressure and 100 °C),[11] hydrogenolysis (5–7 MPa H$_2$ pressure, 180 °C),[12] using super- and sub-critical solvents (400 °C),[13,14] hydrolysis (375 °C, 22 MPa pressure),[15] and pyrolysis.[14] Since these traditional depolymerization processes of lignin depolymerization are energy intensive and utilize environmentally hazardous organic solvents, a green and economical method for lignin depolymerization is required.

Utilization of ionic liquids (ILs) for the processing of lignocellulosic biomass has been well reported.[16] ILs can also act as potential solvents as well as catalysts for the dissolution and depolymerization of various biopolymers. Therefore, a judicious combination of an IL having high solvating ability and low viscosity with an IL having good catalytic ability can serve the purpose. In the past, Das *et al.* utilized [C$_2$C$_1$Im][OAc] for the pretreatment of lignin prior to the catalytic depolymerization of lignin using H$_2$O$_2$ in the presence of a metal catalyst.[17,18] In the same manner, [HSO$_4$]-based ILs have been utilized by Prado *et al.* as pretreatment media for the oxidative depolymerization of lignin.[19] Tolesa *et al.* have used aqueous solutions of ammonium-based ILs for the depolymerization of lignin at 90 °C.[20] We have summarized the ionic liquid-based lignin depolymerization in Table 1.

ᵃSalt and Marine Chemicals Division, CSIR-Central Salt and Marine Chemicals Research Institute, Council of Scientific and Industrial Research, G. B. Marg, Bhavnagar, 364002 Gujarat, India. E-mail: arvind@csmcri.res.in, arvind@csmcri.org
ᵇAcademy of Scientific and Innovative Research (AcSIR), Ghaziabad-201002, India
ᶜDepartment of Chemistry, Dr. B R Ambedkar National Institute of Technology, Jalandhar, India-144011
†Electronic supplementary information (ESI) available. See DOI: 10.1039/d0gc03463k

Table 1 Reported methods for lignin depolymerization by using ionic liquids

Type	Ionic liquid	T (°C)	Time (h)	Depolymerized product	Ref.
Alkali lignin	[DIPEA][Ac], [DIPEA][B]	100–170	0.5–15	Various alkanes	27
Enzymatic lignin	[Bmim][Cl]	150	3	Not extracted	28
Oak wood lignin	[HMIM][Cl]	110–150	3–5	Not quantified	29
Organosolv lignin, Klason lignin	[Emim], [Bmim][MeSO$_4$], [Emim]	180	6	Lignin fragments (90% depolymerization)	30
Alkali lignin	EAN + [Pro]$_2$[MnCl$_4$]	35	4	Vanillin (18–20%) (depolymerization 88%)	This work

Lignin can be degraded into various products such as vanillin, syringaldehyde, vanillic acid, propanolcatechol, ethylguaiacol, ethylphenol, and various other compounds based on the depolymerization methods.[21] One of the noteworthy compounds is vanillin. Vanillin has numerous advantages as a bifunctional safe aromatic compound. The less reactive methoxy group rather than the aldehyde and phenol groups provides two reactive functions which can be chemically modified which makes lignin a very important building block for thermoplastic polymers.[22] Vanillin can be used as an alternative for bisphenol in the synthesis of epoxy polymers.[23] Similarly, vanillin can also be used in the synthesis of polycarbonates,[24] a base material to synthesize polymers with good thermal properties[25] as an alternative for petro-based terephthalic acid and as a crosslinker[26] in vinyl ester formulations.

Vanillin is also being used as a precursor for the synthesis of fine pharmaceuticals.[31] Due to the multi-fold applications of vanillin as discussed above, we have devised a strategy to depolymerize lignin into vanillin by utilizing the combination of a protic IL and an amino acid metal based IL in a sustainable manner.

We have successfully depolymerized lignin into vanillin using a mixed IL system consisting of ethyl ammonium nitrate (EAN) + [Pro]$_2$[MnCl$_4$] wherein EAN assists in higher dissolution of lignin while the Mn-based IL catalyzes the reaction leading to the enhancement of the product yield. The entire depolymerization process has been perfected in terms of reaction time and yield. The astonishing aspect of this process is that lignin has been depolymerized at 35 °C which is the lowest reported temperature for lignin depolymerization in any media. The depolymerized products and prepared films have been thoroughly characterized by using various physicochemical techniques.

Experimental section

Materials

Ethylamine (>70%) and proline (>99%) were purchased from Spectrochem India. 1-Butyl-3-methyl imidazolium chloride ([C$_4$mim]Cl) (>98%), manganese chloride tetrahydrate (>98%), and nitric acid (>65%) were procured from Sigma-Aldrich. Alkaline lignin was procured from TCI, Japan. The solvent ethyl acetate (99%) and hexane (99%) were purchased from Fisher Scientific India. All the chemicals were used as received unless stated otherwise.

Synthesis of ionic liquids

Ethyl ammonium nitrate (EAN). EAN was synthesized as per our earlier work.[4] In brief, an aqueous solution of ethylamine (>70%) was taken in a round bottom flask and placed in an ice bath to maintain the temperature at <5 °C. An equimolar solution of nitric acid (>65%) was added dropwise to the round bottom flask containing ethylamine. The reaction mixture was stirred at room temperature for 24 h. The resultant EAN was dried under vacuum using a rotary evaporator and stored in a vacuum desiccator contain P$_2$O$_5$ as the desiccant. The purity of the synthesized EAN was confirmed by ^{1}H NMR (ESI).

1-Butyl-3-methyl imidazolium tetrachloromanganate(II) [(Bmim)$_2$(MnCl$_4$)]. 1-Butyl-3-methyl imidazolium chloride and manganese chloride tetrahydrate were taken in a ratio of 2 : 1 respectively and dissolved in methanol as the solvent. The reaction mixture was refluxed for 24 h for the synthesis of the IL. The synthesized IL was dried under vacuum using a rotary evaporator and stored in a vacuum desiccator containing P$_2$O$_5$ as the desiccant. The purity of the synthesized IL was confirmed by Raman and UV spectroscopy (ESI – Fig. S1†).

Prolinium tetrachloromanganate(II) ([Pro]$_2$[MnCl$_4$]). [Pro]$_2$[MnCl$_4$] was synthesized using the synthesis of MnCl$_4$ and proline HCl in a two-step reaction. In the first step, proline was dissolved in water and aq. HCl solution was added dropwise until the pH of the reaction mixture reached 1.5. The resultant proline was dried under vacuum using a rotary evaporator and used for the second step. In the second step, proline HCl and MnCl$_2$·4H$_2$O were taken in a RBF in a 2 : 1 molar ratio, using methanol as a solvent. The reaction mixture was refluxed for 24 h. After the completion of the reaction, methanol was evaporated using a rotary evaporator. The synthesized IL was stored in a vacuum desiccator using P$_2$O$_5$ as the desiccant. The synthesized IL was characterized by Raman and UV spectroscopy (ESI – Fig. S2 and S3†).

Dissolution of lignin in IL/DSILs, separation of the product and regeneration of IL/DSILs

In our previous work, we have shown that EAN, due to the H-bonding sites and low viscosity, can act as a potential solvent for biopolymer dissolution.[4] Hence, we utilized EAN as a solvent and Mn-based ILs as a depolymerization and catalytic IL. Different mole fractions of the mixed IL system were screened in the quest for the highest vanillin yield.

In a typical experiment, 5 wt% lignin was added into the mixed IL system and stirred at 35 °C for different time periods.

The processing parameters were perfected for the highest vanillin yield. After the predefined processing time, 2 ml ethyl acetate was added to the reaction vial and mixed thoroughly using a vortex shaker for 5 min, which resulted in the complete dissolution of vanillin into ethyl acetate. The vial was then centrifuged at 4500 rpm for 10 min for phase separation of the IL and organic solvent. The upper ethyl acetate phase was withdrawn, and GC-MS analysis was carried out for product identification and yield determination.

The unreacted dissolved lignin was regenerated by using IPA as the antisolvent. The mixed ILs were recycled up to 5 times and their purity was checked with NMR. The regenerated unreacted lignin was dried and utilized to prepare UV-shielding films as mentioned in a subsequent section.

GC-MS analysis of depolymerized lignin products

The analysis of the extracted vanillin was carried out on a GC-2010 gas chromatograph coupled with a mass spectrometer (GC-MS QP-2010, Shimadzu, Japan). The extracted product solution was analysed by using a gas chromatograph coupled with a mass spectrometer (GC-2010 twinned with GC-MS QP-2010) from Shimadzu (Japan) operating in the electron ionization mode at 70 eV. An RTX-5-fused silica capillary column (30 mV, 0.25 mm, 0.25 mm) was maintained at a flow rate of 1 mL min^{-1} and a precolumn pressure of 49.7 kPa with helium as the carrier gas. The initial oven temperature was 50 °C for the detector and the injector was at 350 °C. The initial temperature was increased to 300 °C at 10 °C min^{-1} and held for 2 min. The MS spectra were identified by comparing them with those from the NIST standard mass spectroscopy library.

Preparation of UV-shielding films

The films were prepared by suspending 0.06 g of the regenerated material in 40 mL solution of 2% w/v chitosan in 1.5% w/v solution of CH_3COOH. The homogeneous solution was then casted on a Petri plate and dried in an oven at 70 °C. The films were conditioned for 2 h prior to analysis.

FT-IR analysis

Measurements were carried out at room temperature by using a Nicolet 6700 ATR-IR spectrometer. To record the spectra, a cell with KRS-5 windows and a Teflon spacer was used; the optical path length was 1 cm. For each spectrum, 40 scans were made with a selected resolution of 2 cm^{-1}.

Powder XRD measurements

PXRD analysis was carried out by using a PANalytical Empyrean (PIXcel 3D detector) system with CuKα radiation ($l = 1.54056$ Å) at a scan rate of 2 min^{-1} and a step size of 0.03.

FE-SEM imaging

The surface morphology of lignin and lignin films was characterized by using a FE scanning electron microscope (JFM 7100 F, Oxford Inc.). The lignin was mounted on a copper stub and sputter-coated with gold.

Mechanical analysis

Tensile tests (ASTM D882-8) were carried out using a universal testing machine (Zwick Roell, Germany) equipped with a 500 N load cell and at a deformation rate of 10 mm min^{-1}. The tensile strength, elongation at break and Young's modulus were calculated using the provided material testing software, testXpert II. The average thickness of the films was 50 μm ± 10 μm. The analysis was carried out in triplicate and averaged.

UV-shielding performance

UV/Vis spectroscopy was used to determine the opacity of the prepared films. The degradation behaviour of RhB solution in the presence of a photocatalyst (TiO_2) under UV irradiation was analyzed to evaluate the UV-shielding performance of films as per the protocol mentioned by Wang et al.[32] Briefly, 25 mg of TiO_2 and 50 mL of RhB solution (0.01 mM) were mixed for complete dispersion. Prior to irradiation, the suspension was stirred in the dark for 30 min at ambient temperature to reach the adsorption/desorption equilibrium. The prepared film was used to cover the mouth of the beaker before UV irradiation. The distance between the lamp and the film was about 10 cm.
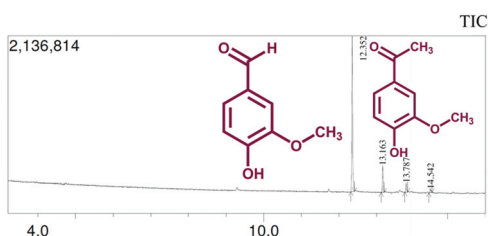
Results and discussion

Extraction of vanillin from lignin using mixed ionic liquids

The dissolution behavior of lignin in EAN + $(Bmim)_2(MnCl_4)$/$[Pro]_2[MnCl_4]$ under different conditions is shown in Table 2. EAN was used as the base solvent as it has the proven capacity to dissolve biopolymers at very high loadings.[4] On the other hand, Mn-based catalysts have shown effective oxidative depolymerization of lignin;[33] hence, we prepared Mn-based ILs $(Bmim)_2(MnCl_4)$/$[Pro]_2[MnCl_4]$ and used them in combination with EAN in various compositions. EAN (entry 1) successfully dissolved and partially depolymerized lignin. The extracted compounds resemble more the complexes of EtOAc (ESI – Fig. S4†). However, after the addition of $[Bmim]_2[MnCl_4]$, the depolymerized products showed an abundance of vanillin (ESI – Fig. S5†). Since the [Bmim] cation is comparatively toxic, we replaced it with the natural amino acid proline. The insertion of the prolinium cation increased the available H-bonding sites and increased the overall depolymerization products (ESI – Fig. S6†). Furthermore, the increase of the $[Pro]_2[MnCl_4]$ concentration to 0.4 g from 0.2 g increased the abundance of vanillin (ESI – Fig. S7†).

Further increase in the $[Pro]_2[MnCl_4]$ concentration made the processing of lignin difficult (data not shown). Therefore, we optimized the EAN : $[Pro]_2[MnCl_4]$ ratio as 0.96 : 0.04. The processing time for 2 h, 4 h and 6 h was tested for achieving maximum depolymerization in the minimum processing time (ESI – Fig. S8 and S9†). The highest yield of vanillin was found in the system of EAN + $[Pro]_2[MnCl_4]$ (9.6 g + 0.4 g) (entry 6). In order to achieve higher efficiency, lignin up to 20 wt% was dissolved under the optimized conditions of EAN + $[Pro]_2[MnCl_4]$ (9.56 g + 0.54 g) (Fig. 1).

Table 2 GC-MS analysis and optimization of the extracted product from the IL/DSIL system at room temperature
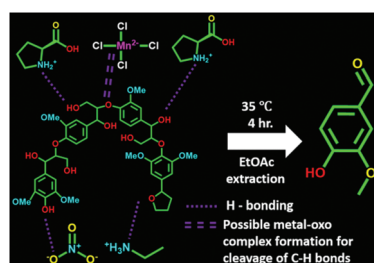
S. no.	ILs/mixed ILs (%)	Lignin (%)	R_t (min)	t (h)	Depolymerization (%)	Extracted compound
1	EAN	5	8.338 13.989	6	40	• 2-Ethylhexanol • 1,2-Benzenedicarboxylic acid, diethyl ester
2	EAN + [bmim]$_2$[MnCl$_4$] (5%)	5	8.345 12.491 13.250	6	46	• 2-Ethylhexanol • Vanillin • Apocynin
3	EAN + [Pro]$_2$[MnCl$_4$] (5%)	5	6.494 12.450 12.899	6	90	• Styrene • Vanillin • Apocynin
4	EAN + [Pro]$_2$[MnCl$_4$] (5%)	5	12.376 12.891 19.728	2	53	• Vanillin • Apocynin
5	EAN + [Pro]$_2$[MnCl$_4$] (5%)	5	11.829 12.356 13.240	4	90	• Furan derivatives • Vanillin • Ethanone, 1-(3-hydroxy-4-methoxyphenyl)
6	EAN + [Pro]$_2$[MnCl$_4$] (5%)	20	12.352 13.163	4	88	• Vanillin • Apocynin

Fig. 1 GC-MS chromatogram of depolymerized lignin (entry 6 in Table 2).

Scheme 1 Possible H-bonding and metal-oxo complex formation during lignin dissolution, depolymerization and conversion into vanillin.

The chromatogram clearly shows very high abundance of vanillin. It can be clearly seen from GC-MS that lignin has undergone a depolymerization process, and the depolymerized products were extracted in the EtOAc phase. The C–H bond activation reactions by transition metal-oxo compounds are rather common; therefore, metal-oxos are proposed as critical intermediates during the depolymerization process. The population of such complexes depends on the hydrogen bonding ability of the solvent molecules surrounding the active center. EAN used here has a significant ability to form hydrogen bonds. Therefore, the combination of EAN and [Bmim]$_2$[MnCl$_4$]/[Pro]$_2$[MnCl$_4$] facilitates the oxidative depolymerization efficiently *via* a possible metal-oxo bonding between Mn and lignin molecules at ambient temperature.

Scheme 1 shows the H-bonding between EAN and lignin molecules and possible metal-oxo formation for higher dissolution and depolymerization of lignin. The lignin depolymerized for the vanillin yield was confirmed using the standard curve of vanillin (ESI†). The obtained results are given in Table 3.

The further mechanism of lignin depolymerization can resemble the typical aerobic oxidation of alcohols by using transition metals as a catalyst (Scheme 2).[34] The lignin structures before and after depolymerization were confirmed by 2D HSQC NMR (ESI – Fig. S12†). The formation of vanillin and acetovanillone along with other depolymerized fragments shows depolymerization of lignin using the DSIL system. The

Table 3 Yields obtained from various IL/DSIL systems

S. no.	IL/DSIL	Lignin (%)	t (h)	Vanillin yield (%)
1	EAN	5	6	—
2	EAN + [bmim]$_2$[MnCl$_4$] (5%)	5	6	8–10
3	EAN + [Pro]$_2$[MnCl$_4$] (5%)	5	6	9–12
4	EAN + [Pro]$_2$[MnCl$_4$] (5%)	5	4	16–19
5	EAN + [Pro]$_2$[MnCl$_4$] (5%)	5	2	8–10
6	EAN + [Pro]$_2$[MnCl$_4$] (4%)	5	4	15–17
7	EAN + [Pro]$_2$[MnCl$_4$] (3%)	5	4	11–14
8	EAN + [Pro]$_2$[MnCl$_4$] (2%)	5	4	5–9
9	EAN + [Pro]$_2$[MnCl$_4$] (5%)	20	4	18–20

β-O-4 (δ ^{1}H/^{13}C = 3.19–3.77/55.0 ppm) and β-5 (δ ^{1}H/^{13}C = 5.4/135.0 ppm, δ ^{1}H/^{13}C = 3.49/53.2 ppm) linkages which were present in pure lignin are not present in the depolymerized lignin, which clearly indicates the depolymerization of lignin.

Recycling of the DSIL system

The recyclability of the mixed IL system was tested for up to 5 cycles and any sign of degradation of ILs was monitored by NMR (ESI – Fig. S10†). Deionized water was added to the mixed ILs and lignin mixture after the extraction of the depolymerized products. The filtrate was subjected to rotary evaporation for the removal of deionized water and the dried mixed ILs were used for the subsequent cycles.
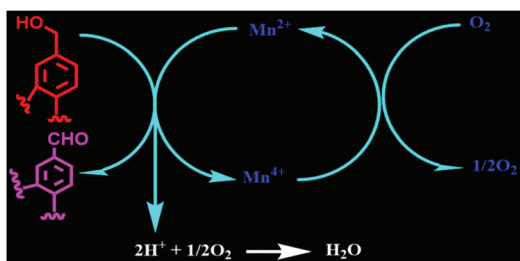
Scheme 2 Conversion of alcohols to aldehydes by using a Mn-based catalyst.

Fig. 3 PXRD diffractogram of pure and regenerated lignin.

Characterization of the depolymerized lignin after extraction

FT-IR analysis. The depolymerization mechanism of lignin in EAN + [Pro]$_2$[MnCl$_4$] was further investigated *via* IR spectroscopy (Fig. 2). The O–H stretching vibration (orange marker) of lignin at 3420 cm^{-1} shows a red shift of 45 cm^{-1} in the mixed IL solution, which can be attributed to the formation of intra- and intermolecular H-bonding between lignin and IL ions.

The C–H stretching vibrations due to the methyl and methylene groups of lignin (blue marker) present in pure lignin at 2928 cm^{-1} show a red shift of 8 cm^{-1} in the treated lignin, whereas when lignin is dissolved and depolymerized, this peak disappears indicating the breaking of lignin C–H bonds which upon regeneration are formed again.[35] On the other hand, the strong peak of the symmetric stretching vibration of the aryl ring remains intact at 1600 cm^{-1} (brown line) indicating that the aryl ring does not undergo any change during the depolymerization process.

PXRD analysis. The crystallinity of the regenerated lignin is decreased and the sharp peak at 35°disappears, which denotes the depolymerization of lignin (Fig. 3).

SEM analysis of processed and unprocessed lignin. Fig. 4 shows the surface morphology of processed and unprocessed lignin particles. Unprocessed lignin particles are much bigger in size compared to regenerated lignin particles. This indicates sig-
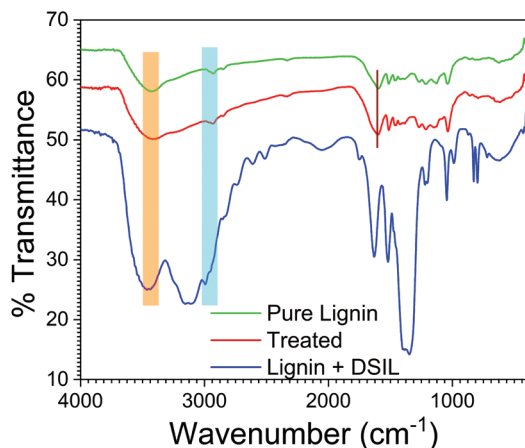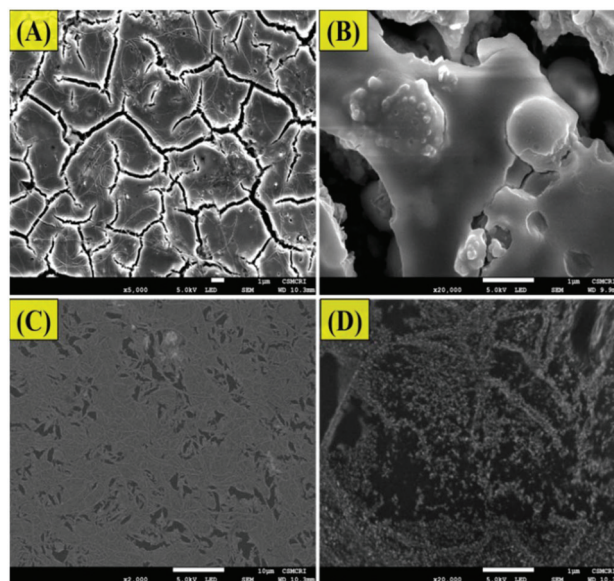

Fig. 4 FE-SEM micrographs of (A (×5000) and B (×20 000)) pure and (C (×2000) and D (×20 000)) regenerated lignin.

nificant changes in the morphology and size of lignin upon dissolution, depolymerization and regeneration of lignin. The morphology and size of the lignin particles are very different in processed lignin compared to those of unprocessed lignin.

Mechanical analysis. Chitosan is well known for its film-forming ability and as an effective matrix to load other materials. Hence, it was used a matrix to load the regenerated lignin. After the extraction of the depolymerized products, the dissolved and depolymerized lignin was regenerated by using water as an antisolvent. The regenerated lignin was dried and mixed with chitosan solution to prepare chitosan–lignin films. The mixed IL system was recycled 4 times and NMR showed almost no degradation (ESI – Fig. S10†). The mechanical properties of the prepared films are shown in Fig. 5.

From Fig. 5, it is evident that when compared with pure chitosan, the mechanical strength of the films is slightly increased by the insertion of lignin into the films. This is likely due to the hydrogen bonding between lignin molecules
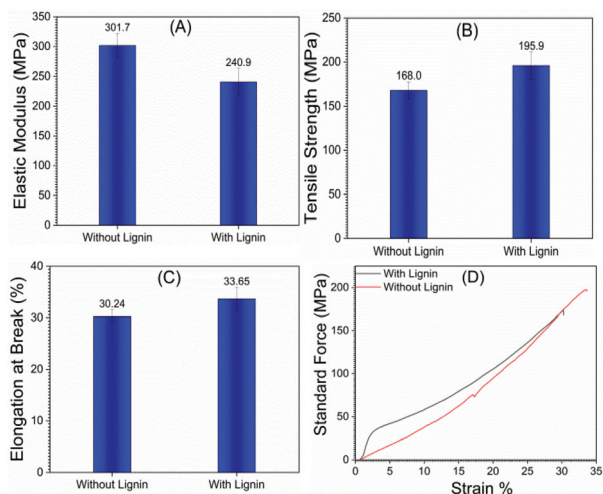

Fig. 2 FT-IR spectra of pure and regenerated lignin.

Fig. 5 Mechanical properties of films: (A) Young's modulus, (B) tensile strength, (C) elongation at break, and (D) stress−strain curves.

and chitosan molecules.[36] The surface morphology of the prepared film was observed using FE-SEM (ESI – Fig. S11†) and found to be very smooth for practical applications.

UV-shielding properties and photocatalytic degradation of rhodamine B

The UV-shielding ability of the prepared films was analyzed by UV visible spectroscopy and the SPF values were calculated using our previously derived method.[5] Since lignin is rich in aromatic compounds due to its basic phenylpropane unit and contains UV-absorbing functional groups such as phenolic, ketone and other chromophores, the films were tested for UV-shielding property. As can be seen in Fig. 6A, pure chitosan films are transparent to the UV region (200–400 nm) while the films with the regenerated lignin block a very high amount of UV irradiation (Fig. 6B).

The calculated SPF values of lignin films were found to be very high. Under the same conditions, pure chitosan films showed an SPF value of 8 while the lignin-containing films showed a three-fold increase in UV shielding. The prepared films were utilized as a cover material to demonstrate their effect on the photocatalytic degradation of rhodamine B (Fig. 7).
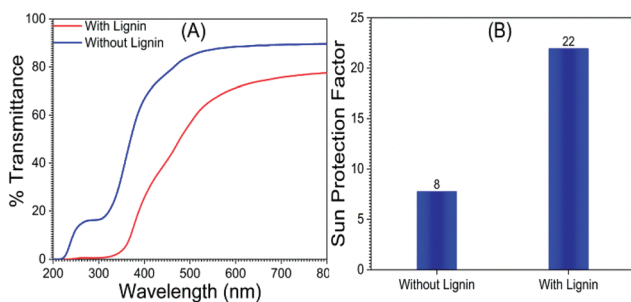

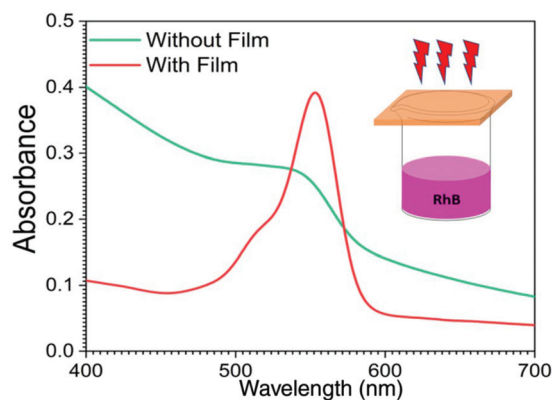**Fig. 6** (A) Optical transmittance and (B) the calculated SPF values of the prepared films.

Fig. 7 UV visible spectra of RhB solution after 5 h under UV irradiation with and without the film.

Conclusion

In conclusion, a suitable strategy has been devised to perform lignin depolymerization under ambient conditions. The catalytic depolymerization of lignin is achieved using a combination of a low viscosity, high hydrogen bonding ability protic IL, EAN, as the base solvent and a metal-based ionic liquid $[Pro]_2[MnCl_4]$ as the catalytic solvent. Very high abundance of vanillin in the depolymerized products indicates the selective conversion of lignin to vanillin. H-Bonding between EAN and lignin plays a vital role in dissolution, and subsequent depolymerization follows with the assistance of $[Pro]_2[MnCl_4]$ *via* the formation of metal-oxo complexes. The dissolution and depolymerization of lignin were successfully integrated with the regeneration and construction of a UV-shielding material, thus developing an integrated approach towards an economical and sustainable bio-refinery process.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

References

1 C. Xu, R. A. D. Arancon, J. Labidi and R. Luque, Lignin depolymerisation strategies: towards valuable chemicals and fuels, *Chem. Soc. Rev.*, 2014, **43**(22), 7485–7500.

2 S. Son and F. D. Toste, Non–Oxidative Vanadium–Catalyzed C–O Bond Cleavage: Application to Degradation of Lignin Model Compounds, *Angew. Chem., Int. Ed.*, 2010, **49**(22), 3791–3794.

3 S. S. Tan, D. R. MacFarlane, J. Upfal, L. A. Edye, W. O. Doherty, A. F. Patti, J. M. Pringle and J. L. Scott, Extraction of lignin from lignocellulose at atmospheric pressure using alkylbenzenesulfonate ionic liquid, *Green Chem.*, 2009, **11**(3), 339–345.

4 M. J. Mehta, P. Bharmoria, K. Bhayani and A. Kumar, Gelatin Solubility and Processing in Ionic Liquids: An Approach Towards Waste to Utilization, *ChemistrySelect*, 2017, **2**(31), 9895–9900.

5 M. J. Mehta and A. Kumar, Ionic Liquid Stabilized Gelatin-Lignin Films: A Potential UV-Shielding Material with Excellent Mechanical and Antimicrobial Properties, *Chemistry*, 2019, **25**(5), 1269–1274.

6 M. J. Mehta and A. Kumar, Ionic Liquid Assisted Gelatin Films: Green, UV Shielding, Antioxidant, and Antibacterial Food Packaging Materials, *ACS Sustainable Chem. Eng.*, 2019, **7**(9), 8631–8636.

7 D. Glas, C. Van Doorslaer, D. Depuydt, F. Liebner, T. Rosenau, K. Binnemans and D. E. De Vos, Lignin solubility in non-imidazolium ionic liquids, *J. Chem. Technol. Biotechnol.*, 2015, **90**(10), 1821–1826.

8 C. Chio, M. Sain and W. Qin, Lignin utilization: a review of lignin depolymerization from various aspects, *Renewable Sustainable Energy Rev.*, 2019, **107**, 232–249.

9 A. Vigneault, D. K. Johnson and E. Chornet, Base–catalyzed depolymerization of lignin: separation of monomers, *Can. J. Chem. Eng.*, 2007, **85**(6), 906–916.

10 G. Wu, M. Heitz and E. Chornet, The depolymerization of lignin via aqueous alkaline oxidation, in *Advances in Thermochemical Biomass Conversion*, Springer, 1993, pp. 1558–1571.

11 J. Long, R. Shu, Z. Yuan, T. Wang, Y. Xu, X. Zhang, Q. Zhang and L. Ma, Efficient valorization of lignin depolymerization products in the present of NixMg1− xO, *Appl. Energy*, 2015, **157**, 540–545.

12 M. Verziu, A. Tirsoaga, B. Cojocaru, C. Bucur, B. Tudora, A. Richel, M. Aguedo, A. Samikannu and J. P. Mikkola, Hydrogenolysis of lignin over Ru-based catalysts: The role of the ruthenium in a lignin fragmentation process, *Mol. Catal.*, 2018, **450**, 65–76.

13 D. Fu, S. Farag, J. Chaouki and P. G. Jessop, Extraction of phenols from lignin microwave-pyrolysis oil using a switchable hydrophilicity solvent, *Bioresour. Technol.*, 2014, **154**, 101–108.

14 B. Güvenatam, E. H. Heeres, E. A. Pidko and E. J. Hensen, Lewis acid-catalyzed depolymerization of soda lignin in supercritical ethanol/water mixtures, *Catal. Today*, 2016, **269**, 9–20.

15 M. Saisu, T. Sato, M. Watanabe, T. Adschiri and K. Arai, Conversion of lignin with supercritical water− phenol mixtures, *Energy Fuels*, 2003, **17**(4), 922–928.

16 A. M. Socha, R. Parthasarathi, J. Shi, S. Pattathil, D. Whyte, M. Bergeron, A. George, K. Tran, V. Stavila and S. Venkatachalam, Efficient biomass pretreatment using ionic liquids derived from lignin and hemicellulose, *Proc. Natl. Acad. Sci. U. S. A.*, 2014, **111**(35), E3587–E3595.

17 L. Das, S. Xu and J. Shi, Catalytic oxidation and depolymerization of lignin in aqueous ionic liquid, *Front. Energy Res.*, 2017, **5**, 21.

18 G. Chatel and R. D. Rogers, Review: Oxidation of Lignin Using Ionic Liquids—An Innovative Strategy To Produce Renewable Chemicals, *ACS Sustainable Chem. Eng.*, 2014, **2**(3), 322–339.

19 R. Prado, A. Brandt, X. Erdocia, J. Hallet, T. Welton and J. Labidi, Lignin oxidation and depolymerisation in ionic liquids, *Green Chem.*, 2016, **18**(3), 834–841.

20 L. D. Tolesa, B. S. Gupta and M.-J. Lee, Degradation of lignin with aqueous ammonium-based ionic liquid solutions under milder conditions, *New J. Chem.*, 2019, **43**(8), 3357–3365.

21 Z. Sun, B. Fridrich, A. de Santi, S. Elangovan and K. Barta, Bright side of lignin depolymerization: toward new platform chemicals, *Chem. Rev.*, 2018, **118**(2), 614–678.

22 M. Fache, B. Boutevin and S. Caillol, Vanillin production from lignin and its use as a renewable chemical, *ACS Sustainable Chem. Eng.*, 2016, **4**(1), 35–46.

23 M. Fache, R. Auvergne, B. Boutevin and S. Caillol, New vanillin-derived diepoxy monomers for the synthesis of bio-based thermosets, *Eur. Polym. J.*, 2015, **67**, 527–538.

24 B. G. Harvey, A. J. Guenthner, H. A. Meylemans, S. R. Haines, K. R. Lamison, T. J. Groshens, L. R. Cambrea, M. C. Davis and W. W. Lai, Renewable thermosetting resins and thermoplastics from vanillin, *Green Chem.*, 2015, **17**(2), 1249–1258.

25 L. Mialon, A. G. Pemba and S. A. Miller, Biorenewable polyethylene terephthalate mimics derived from lignin and acetic acid, *Green Chem.*, 2010, **12**(10), 1704–1706.

26 J. F. Stanzione III, J. M. Sadler, J. J. La Scala, K. H. Reno and R. P. Wool, Vanillin-based resin for use in composite applications, *Green Chem.*, 2012, **14**(8), 2346–2352.

27 L. D. Tolesa, B. S. Gupta and M.-J. Lee, The chemistry of ammonium-based ionic liquids in depolymerization process of lignin, *J. Mol. Liq.*, 2017, **248**, 227–234.

28 B. Yan, K. Li, L. Wei, Y. Ma, G. Shao, D. Zhao, W. Wan and L. Song, Understanding lignin treatment in dialkylimidazolium-based ionic liquid–water mixtures, *Bioresour. Technol.*, 2015, **196**, 509–517.

29 B. J. Cox and J. G. Ekerdt, Depolymerization of oak wood lignin under mild conditions using the acidic ionic liquid 1-H-3-methylimidazolium chloride as both solvent and catalyst, *Bioresour. Technol.*, 2012, **118**, 584–588.

30 S. Nanayakkara, A. F. Patti and K. Saito, Lignin depolymerization with phenol via redistribution mechanism in ionic liquids, *ACS Sustainable Chem. Eng.*, 2014, **2**(9), 2159–2164.

31 P. C. R. Pinto, E. A. B. da Silva and A. E. Rodrigues, Lignin as source of fine chemicals: vanillin and syringaldehyde, in *Biomass Conversion*, Springer, 2012, pp. 381–420.

32 Y. Wang, J. Su, T. Li, P. Ma, H. Bai, Y. Xie, M. Chen and W. Dong, A novel UV-shielding and transparent polymer film: when bioinspired dopamine–melanin hollow nanoparticles join polymers, *ACS Appl. Mater. Interfaces*, 2017, **9**(41), 36281–36289.

33 O. Y. Abdelaziz, S. Meier, J. Prothmann, C. Turner, A. Riisager and C. P. Hulteberg, Oxidative Depolymerisation of Lignosulphonate Lignin into Low-Molecular-Weight Products with Cu–Mn/δ-Al 2 O 3, *Top. Catal.*, 2019, **62**(7–11), 639–648.

34 C. Parmeggiani and F. Cardona, Transition metal based catalysts in the aerobic oxidation of alcohols, *Green Chem.*, 2012, **14**(3), 547–564.

35 N. M. Stark, D. J. Yelle and U. P. Agarwal, Techniques for characterizing lignin, *Lignin Polym. Compos.*, 2016, 49–66.

36 M. J. Mehta and A. Kumar, Green and Efficient Processing of Cinnamomum cassia Bark by Using Ionic Liquids: Extraction of Essential Oil and Construction of UV-Resistant Composite Films from Residual Biomass, *Chem. – Asian J.*, 2017, **12**(24), 3150–3155.