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Dissolution of South African *Eucalyptus* Sawdust Wood in [Emim][OAc]/Co-Solvent Mixtures

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The paper presents a method of obtaining wood cellulose by dissolution of *eucalyptus* sawdust in a mixture of ionic liquid (IL) 1-ethyl-3-methylimidazolium acetate [Emim][OAc] together with co-solvents; dimethylformamide (DMF) and dimethylsulphoxide (DMSO), as a potential alternative to traditional non-ecological processes involving the use of volatile organic solvents or harsh chemicals. The results showed that a fraction of the wood sawdust dissolved in the mixture of [Emim][OAc] and co-solvents, and cellulose precipitated from the mixture after addition of a water /acetone mixture. The yields for the cellulose precipitates were 32.5, 17.8 % and 7.2 % for the [Emim][OAc]/DMF mixture, [Emim][OAc]/DMSO and neat [Emim][OAc], respectively. Analysis of the cellulose precipitates by FTIR spectroscopy confirmed the presence of the dominant amorphous cellulose II anomer in the regenerated cellulose. The changes in the crystalline structure of the regenerated cellulose was confirmed by comparing the XRD analytical data of the untreated sawdust wood with that of the of the regenerated cellulose samples: and it was found that the cellulose structure transformed from crystalline to amorphous after dissolution and regeneration. Scanning electron microscopy indicated that the surface morphology of the regenerated cellulose samples exhibited a structure that was rather loose, disordered and curly: this was probably due to removal of lignin and decrease in cellulose crystallinity.

Keywords: Ionic Liquids, Wood Biomass, Cellulose, Lignin, Co-Solvents

Introduction

Sawmills are major producers of sawdust waste, but other industries that produce sawdust include pulp mills, furniture manufacturers and other carpentry industries. Based on figures obtained from *Forestry South Africa*,[1-2] the total amount of wood processed in the country during 2011/2012 was around 18.8 million tonnes, of which sawmills accounted for 20% or 3.76 million tonnes of this consumption. Olufemi *et al*.[3] estimated that only 56% of a log processed in a sawmill is recovered as sawn timber, while 44% is left as wood residues in the form of wood slab (34%) and sawdust (10%). This means that the remaining 56% may be discarded as waste products e.g., by landfilling. According to environmental regulations (e.g. Act 39 of 2004)[4], these practices are being curtailed as they are environmental hazards. Thus there is a need to find new and innovative uses to beneficiate sawdust. Since sawdust is a lignocellulosic biomass that contains cellulose (45-50%), hemicellulose (15-25%), lignin (23-33%), and extractives (2-12%)[5-7], one way of beneficiation of sawdust is via separate extraction of these components. Various solvents have been used for processing the cellulose but they are problematic[8]. Recently, attention has been drawn towards the application of ILs in lignocellulose processing of biomass in ILs: those based on the imidazolium cation were effective cellulose solvents for cellulose[5,7,8,11-16]. To date, a number of biomass pretreatment approaches including physical, physico-chemical, chemical, and biological methods have been used – all designed to break the recalcitrant lignocellulosic bonds[16]. Many of them require high temperatures and pressures as well as highly concentrated chemicals. In this paper, sawdust wood was pre-treated with ILs to extract cellulose and the structure of the regenerated cellulose was studied by FTIR, XRD, and SEM. The results were compared to those obtained from treatment of a microcrystalline (MCC) standard.

Experimental

Materials

Sawdust was obtained from a mill that used *Eucalyptus grandis*. The sawdust sample was dried in

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a vacuum at 50 °C for 12 hours, and then ground into small particles using a mortar and pestle before use.

An ionic liquid 1-ethyl-3-methylimidazolium acetate [Emim][OAc], with a purity of > 95%, was purchased from IOLITEC USA. Prior to use, the IL was dried at 50 °C using a vacuum pump for 12 hours; and its water content was monitored by Karl Fischer titrimetry. Dimethylsulfoxide (DMSO) and dimethylformamide (DMF) with purity of 99.9% were purchased from Sigma Aldrich and were used as received as co-solvents. Nylon membrane filter papers, (10 and 0.8 μm), were purchased from Sterlitech Corporation, USA. Microcystalline cellulose (MCC) standard, with a depolymerization degree of 270 and purity of 99.9%, was purchased from Sigma Aldrich.

Chemistry of sawdust

The sawdust was analysed for cellulose and lignin contents using standard TAPPI methods[17-18].

Dissolution and regeneration of cellulose in sawdust

Two IL co-solvent mixtures, each containing 25 wt.% co-solvent, were prepared. Approximately 5 wt.% slurries of sawdust were prepared in the [Emim][OAc]/DMSO and [Emim][OAc]/DMF mixtures, that were then stirred with a magnetic stirrer at 120 °C for 10 hours in an oil bath. Once dissolution was completed, the samples were cooled to room temperature and a 50ml mixture of water/acetone (1:1, v/v) was added as an anti-solvent to separate the solid materials and dissolved lignin and IL. The mixture was stirred for 1 h and then transferred to a centrifuge tube. The solution was then centrifuged in a Clays Adams centrifuge at 700 rpm for 10 minutes. A whitish material settled at the bottom of the centrifuge tube. The supernatant was removed and the white material was further washed with 50 mL of the water/acetone mixture twice more. The white material was recovered by filtration on a Nylon membrane filter paper (10 μm) and then dried in an oven at 80 °C for one hour. The dried weight of the precipitate was recorded and the percentage recovery of the precipitate was calculated by using the equation below:

$$\text{Cellulosic material recovery (\%)} = \frac{\text{Mass of regenerated cellulosic material (g)}}{\text{mass of pulp for dissolution (g)}} \times 100\% \ldots (1)$$

Recycling of ionic liquids

The IL liquor (filtrate) obtained after washing was transferred into a round bottom flask, attached to a rotary evaporator, and distilled to remove any water and acetone remaining in the mixture. The [Emim][OAc] recovered was then dried under vacuum at 50 °C for 12 hours and characterized by FTIR and the spectrum was compared with that of the IL spectrum before the dissolution process to ascertain its purity.

Characterization of regenerated cellulose samples

The cellulose samples were cut into small pieces and ground into very small particles for analysis by FTIR. FTIR spectra of MCC standard and the regenerated cellulose samples were obtained using a Bruker Alpha FTIR spectrometer, and the spectra were collected over the range of ν_{max} = 400–4000 cm^{-1}. SEM images of the regenerated cellulose samples were taken at 300 x magnifications using a Jeol 6310 Electron Probe analyser SEM instrument which was operated at 5-10 kV accelerating voltage. Prior to imaging, the samples were sputter-coated with gold to make the fibres electrically conductive, thus avoiding degradation and build -up of charge on them. Powder X-ray diffraction (pXRD) patterns were recorded in the high angle 2θ range of 5-40º using a Bruker D2 Phase Powder XRD instrument. The patterns were recorded using a nickel filtered Cu Kα radiation (λ=1.5418Å) at 30 kV, 10 mA, over 2θ from 5 to 40º and at room temperature. The scan speed and step sizes were 0.2 min^{-1} and 0.01314, respectively. For each sample, a thin layer of neat powder was loaded onto a single crystal silicon low background sample holder.

Results and Discussions

Dissolution of eucalyptus wood and regeneration of cellulose

The cellulose content in the sawdust was 43.22 % whereas the lignin content was 29.07 %: these results are in agreement with reported literature values for cellulose content in eucalyptus wood[5,9,15]. Results for cellulose yield (based on weight of the regenerated cellulose) are shown in Table 1. The cellulose yield regenerated from sawdust previously dissolved in neat [Emim][OAc], [Emim][OAc]/DMSO and [Emim][OAc]/DMF were 7.21, 17.83 and 32.50 %, respectively. Dissolution of biomass in IL depends on the initial sample load, particle size, and high hydrogen bond basicity of IL.[14] It has also been reported that ILs that can incorporate anions with strong hydrogen bonding acceptors such as acetate, are the most effective solvents for cellulose due to their ability to disrupt the extensive hydrogen bonding network of cellulose and lead to its dissolution.[11,16,19] The viscosity

Table 1—Percentage yield of regenerated cellulose after dissolution of sawdust samples in [Emim][OAc]/DMSO and DMF mixtures.

IL + co-solvent mixtures	% Sawdust wood
[Emim][OAc]	7.21
[Emim][OAc]/DMSO	17.83
[Emim][OAc]/DMF	32.50

of the ILs also plays a crucial role in the dissolution of biomass because detailed knowledge on the rheological flow properties is crucial for scale up of laboratory procedures to commercial applications to estimate the energy input required for the processing and design of reaction vessels, stirrers, pipe systems and other technical devices[15]. Additionally, viscosity of the ILs plays an important role in the dissolution speed. Addition of co-solvents reduces the viscosity of the mixture, which leads to accelerated dissolution due to facilitated diffusion of the ILs into the biomass, thereby enhancing further processing by the polymer solution[20]. Dissolution of cellulose in ILs is attributed to the ability of the solvents to break the extensive network of hydrogen bonding that exists in cellulose. Thus the IL [Emim][OAc] disrupts the hydrogen bonding interactions present in the cellulose allowing it to diffuse into the interior of the cellulose, which then results in the complete dissolution of cellulose[5,20]. The acetate-based IL has been reported to show better dissolution of wood[12] and cellulose[21] than ILs that are devoid of acetate. One possible reason for this is that the acetate anion favours dissolution because the acetate moiety has higher hydrogen bond basicity (a property of the anion that is influenced primarily by the size and charge localization on the anion) than other anions[20,21-22]. Thus it has the ability to disrupt hydrogen bonds in cellulose and therefore a high potential for cellulose dissolution. The positive correlation between the hydrogen bond basicity of the IL anion and the IL's ability to dissolve cellulose or lignocellulose is discussed more in the literature[1,9,11]. However, Swatolski *et al.*[11] claimed that [Bmim][Cl] is the most effective IL for dissolving pure cellulose, such as in cellulose-dissolving pulps, fibrous cellulose, and Whatman cellulose filter papers. However, the relatively high melting points and viscosities of this IL limit their practical application in cellulose processing[6]. This indicates that IL dissolution is selective on the type of substrate, and the selectivity of ILs could be attributed to their ionic functional groups. Dissolution of sawdust in [Emim][OAc]/DMF mixture resulted in higher regenerated cellulose yields than those obtained from dissolution in [Emim][OAc]/DMSO mixture and pure [Emim][OAc]. This is because DMSO has a higher dielectric constant of 46.7 than DMF that has a dielectric constant of 36.7, which makes DMSO more polar than DMF. This has some effect on the dissolution process because the stronger ion-dipole interactions in DMSO result in stronger attraction forces between ions in solution and the dipole-dipole interaction (hydrogen bonding) between solvent molecules. This effect results in reduced cellulose solubility because DMSO forms competing hydrogen bonding to the macromolecular chains of cellulose[13,15]. Dadi *et al*.,[23] have reported that in dissolution of maple wood powder in [Emim][OAc], the crystalline structure of cellulose in the wood powder was disrupted when the experiment was performed at higher temperatures exceeding130 ˚C. At the same time, lignin extraction also took place.

FTIR Spectroscopy of the regenerated cellulose fibres

On comparing the FTIR spectra of the regenerated cellulose samples to that of the MCC standard it was seen that the spectra of the MCC standard and regenerated cellulose materials showed the same basic profiles which were similar to the results reported in the literature[24]. The spectra of the regenerated cellulose samples reveal that there might a possibility that lignin dissolved in the IL/co-solvent mixture since lignin was not detected on the regenerated cellulose materials. Hermanutz *et.al*.[25] reported that ILs used as solvents for manufacturing cellulose fibres were almost entirely recoverable at 99.5%. In the present study, the colorless [Emim][OAc] IL turned reddish brown after recycling: this may be as a result of exposure to elevated temperatures and contaminants present in [Emim][OAc], which could be degradation products from [Emim][OAc], the wood biomass as well as carbohydrate[26]. In addition, the reddish brown color of the recovered [Emim][OAc] may also be due to dissolved lignin. Additionally, the FTIR spectrum of the recovered IL was similar to that of the dried IL spectrum before dissolution with the only difference being an increase in the O-H absorption, which reflects both the use of water in the washings of the regenerated cellulose and the hygroscopic nature of the IL. It was clear that the recovered IL contains water, hence the drying method needs to be done over longer periods of time, maybe 24 hours instead of 12 hours. The drying should also be done under a glove box, to avoid the absorption of water from the environment.

X-Ray diffraction

XRD analysis was conducted to further examine the crystallinity of the regenerated cellulose samples. The crystallinity index (CrI) gives a quantitative measure of the crystallinity in powders, and can be related to the strength and stiffness of fibres[27].

The CrI of MCC and regenerated cellulose samples were calculated according to equation 2 as proposed by Segal *et.al*[28].

$$CrI = I_{TOT}\text{-}I_{AM}/\ I_{TOT} \times 100\ \% \quad \ldots (2)$$

Where I_{TOT} is the maximum intensity of the principal peak (002) lattice diffraction at (2θ = 22.7° for cellulose I and 2θ = 21.7° for cellulose II) and I_{AM} is the intensity diffraction attributed to the amorphous cellulose at 2θ = 18° for cellulose I and 2θ = 16° for cellulose II[28]. The diffraction patterns of the untreated sawdust sample, shown in Fig. 1, displayed typical cellulose I structure, with a sharp peak at 22.5° and cellulose II a wide peak between 12° and 18° [20,29] and a weak band peak at 35°. The regenerated cellulose from neat [Emim][OAc], shown in Fig. 2, displayed typical cellulose II structure with a very small broad band around 12° and a small peak 20.5°. The regenerated cellulose from sawdust previously dissolved in [Emim][OAc]/DMSO or DMF mixtures showed peaks at 12° and 22º as can be seen in Figure 3. Figures 2 and 3 also show that the crystallinity of the regenerated cellulose (indicated by the decrease in the sharp peak at 22.5° when compared to the untreated sample shown in Fig.1) decreased significantly, which indicated that the [Emim][OAc]/DMF or DMSO mixtures broke the intermolecular hydrogen bonds of the original cellulose during the dissolution process[20]. There are no obvious differences between diffraction patterns correlated with changing the co-solvent. Wei *et. al*.[30] investigated structural differences between cellulose regenerated from [Bmim][Cl] and untreated cellulose, using FTIR, XRD and TGA. Their results showed that the crystalline form of wood pulp cellulose was transformed completely from cellulose I to cellulose II after regeneration – the results are in agreement with the results obtained in this study. The XRD analysis from the present study indicated that MCC has a more crystalline structure than the regenerated cellulosic samples. The changes in diffractograms were analysed in order to determine the crystallinity indices of the samples and the calculated values are reported in

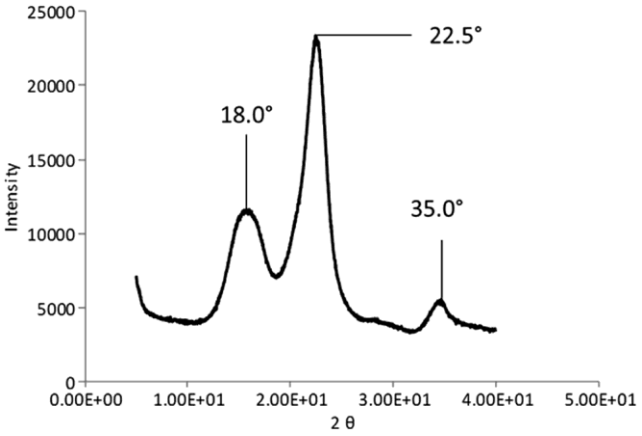

Fig. 1—XRD diffractogram of sawdust wood untreated sample

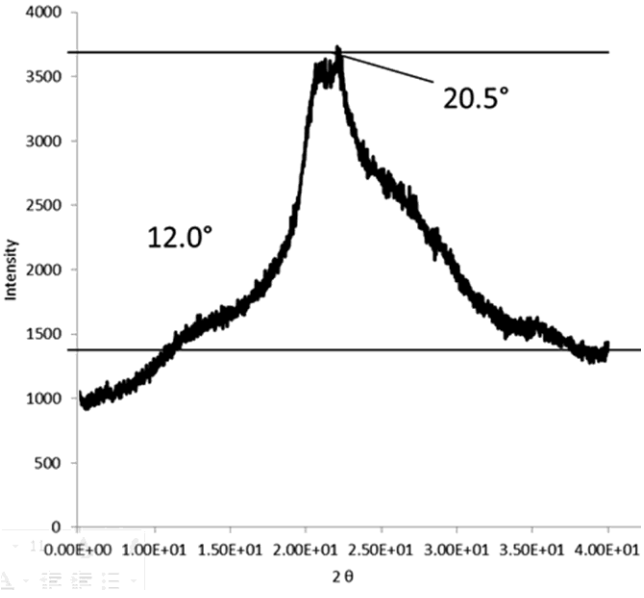

Fig. 2—XRD diffractogram of cellulose sample extracted from sawdust wood and [Emim][OAc]

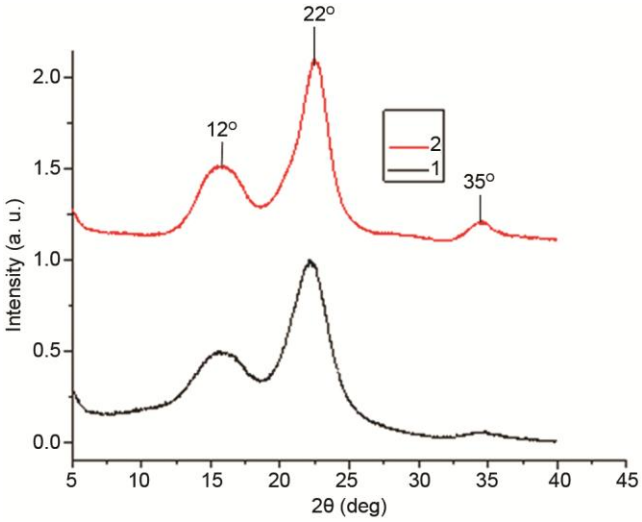

Fig. 3—XRD diffractograms of cellulose regenerated from sawdust wood previously dissolved in [Emim][OAc]/ DMSO (1.Black diffractogram) and DMF mixtures (2.Red diffractogram).

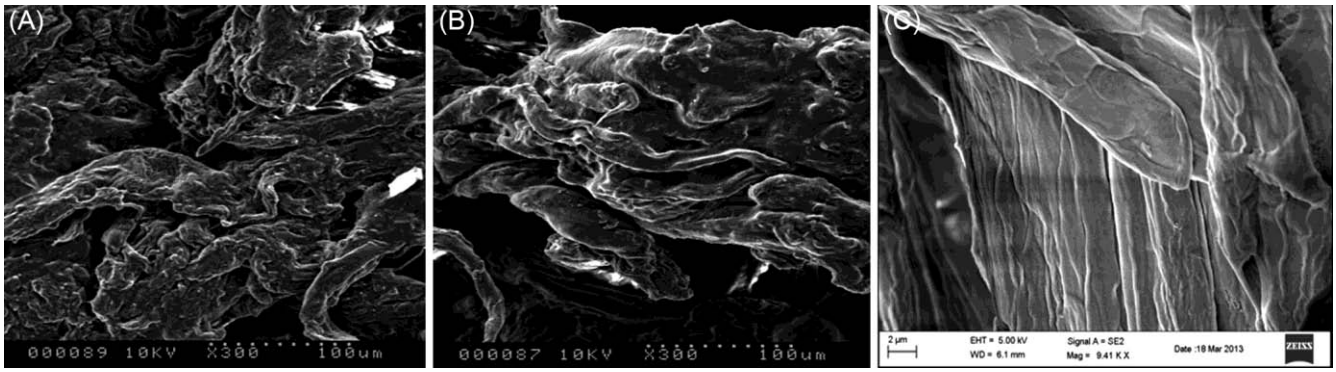

Fig. 4—SEM photographs of the cellulose regenerated from sawdust wood in (A) [Emim][OAc]/DMSO mixture, (B) [Emim][OAc]/DMF mixture compared to pure cellulose sample (C) MCC standard.

Table 2. From the results it can be seen that cellulose in the untreated sawdust wood had the highest crystallinity index of 80% when compared to the crystallinity indices of the regenerated cellulose samples from pure [Emim][OAc], [Emim][OAc]/DMSO, and DMF mixtures, which gave CrI values of 71 %, 68 % and 47 %, respectively: this confirms the presence of a strong crystalline peak at 2θ = 23° as shown in Figure 1 [31]. Wood contains both amorphous and crystalline cellulose as well as para-crystalline regions of cellulose fibrils. If the amorphous polysaccharides are degraded more than the crystalline cellulose, the overall crystallinity content is then expected to increase[32,33]. These results imply that the inter- and intramolecular hydrogen bonds between cellulose molecules were rapidly broken during the dissolution process, thus destroying the original crystalline as postulated by Pang *et.al*[34]

Table 2—Calculated crystallinity index values of MCC and regenerated cellulose samples.

Sample	Crystallinity index (%)
Sawdust untreated	80
Cellulose from sawdust and pure [Emim][OAc]	71
Cellulose regenerated from sawdust wood in [Emim][OAc]/DMSO	68
Cellulose regenerated from sawdust wood in [Emim][OAc]/DMF	47

Morphology of regenerated cellulose

SEM has been useful in monitoring the altered structure of pretreated lignocellulosic biomass via various ILs[11]. SEM images of the morphologies of regenerated cellulose (Fig A and B) samples from this study are compared with that of the MCC standard (Fig C) as shown in Figure 4. The MCC standard (image C) has a compact framework whereas the regenerated cellulose (images A-B) was highly disrupted after dissolution of the sawdust wood in [Emim][OAc]/DMSO and DMF mixtures. The regenerated cellulose-rich material (Fig. 4 images A-B) shows a different morphology when compared to the MCC (Fig. 4 image C) which shows a more crystalline structure where the wood fibres are fused into a relatively more homogeneous macrostructure. Similar results have been reported in the literature[6, 11,14]. The results indicate that the decrease in cellulose crystallinity resulted in the formation of a rough surface because of lower polymer chain entanglement and larger free chain mobility[20]. Regenerated cellulose samples show a structure that is rather loose, disordered and curly, and this was probably due to the removal of lignin and decrease of cellulose crystallinity which have already been confirmed by FTIR[34].

Conclusions

The present work has reported the successful use of ionic liquids/ co-solvent mixtures as solvents for dissolution of *Eucalyptus grandis* biomass. It was observed that ILs possess the ability to dissolve biomass and reconstitute the cellulose upon addition of precipitating solvents, in agreement with what has been previously reported. Cellulose was regenerated successfully from South African *Eucalyptus* sawdust wood sample in [Emim][OAc]/DMSO or DMF mixtures with the cellulose yield recovery being greatest in cellulose regenerated after dissolution in [Emim][OAc]/DMF mixture. The addition of a co-solvent to the [Emim][OAc] solution increased the yields of the cellulosic material regenerated from Southern African *Eucalyptus* sawdust samples, in comparison with those obtained using only [C_2mim][OAc], possible due to the lower viscosities of the solutions and the solvent-IL interactions, that favored

the breaking of the hydrogen bonds of the biopolymers. After regeneration, FTIR spectra indicated the presence of cellulose and the absence of lignin in the cellulosic materials. The XRD results indicated that the crystallinity of the regenerated cellulose samples decreased after the dissolution and regeneration process of sawdust wood in the mixture of IL/co-solvent mixtures. The SEM images show that the surfaces of the regenerated cellulose samples were homogeneous after dissolution in IL/co-solvent mixtures. Preliminary investigations indicate that recovery of ILs is feasible at 99.9%. For large-scale applications of ILs, development of energy-efficient recycling methods for their recovery is required and should be investigated in detail in further studies. This work probes new routes to dissolve cellulose, thereby improving the potential to commercially dissolve cellulose in an inexpensive and environmentally friendly manner.

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List of abbreviations

IL	Ionic Liquid
[Emim][OAc]	1-Ethyl-3-imidazoliumacetate
DMF	Dimethylformamide
DMSO	Dimethylsulphoxide
FTIR	Fourier Transform Infrared Spectroscopy
XRD	X-Ray Diffraction
SEM	Scanning Electron Microscopy
TGA	Thermogravimetric Analysis
MCC	Microcrystalline cellulose
[Bmim][Cl]	1-Butyl-3-methylimidazolium chloride
CrI	Crystallinity Index

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