

Mariam Temitope Baker* , Frederick Teghtegh Samoh, Steven Olubunmi Stephen

Department of Chemistry, University of Ilorin, Ilorin, P.M.B. 1515, Nigeria.

*Corresponding author: arowona.mt@unilorin.edu.ng

Received: September 14, 2024 Accepted: November 28, 2024

Abstract: The benefits utilization of dissolved cellulose waste in homogeneous media are among the major goals of minimizing environmental waste. The industrial applications of cellulose and its derivatives are highlighted in this article. The role of ionic liquids in the dissolution of cellulose to obtain cellulose with excellent tunable properties and their advantages were discussed. Thus, this article considered the need for giving better attention to recycling, reprocessing, and reusing organic wastes, especially cellulose-containing wastes, this is in order to compensate for the deficit in economic growth, particularly in developing countries. In developed countries as well, cellulose-based materials could replace non-biodegradable materials made from petroleum feedstock, as well as advanced materials, due to their flexibility. This form of biomaterial satisfies the environmental requirements for renewable resources. Furthermore, by mixing biobased products with environmentally friendly cellulosic wastes or their derivatives, in the IL-based manufacturing processes, there is tendency for an increase in the number of available end-products, with one's imagination as a limit. The authors reviewed studies that have dealt with recycling, reprocessing, and reuse of cellulosic wastes as one of the scientific practices involved in removing useless materials from the environment, changing them to valuable materials and thereafter, returning them to nature for their benefit.

Keywords: Agricultural waste, Cellulose, Ionic liquids, Cellulose dissolution, Cellulose derivatives, Applications

Introduction

Cellulose is undoubtedly one of the most abundantly available types of biomass on earth because every plant material contains cellulose, which is found everywhere in the world. The percentage composition of cellulose in each of these plant materials, however, varies depending on the plant source. It has been reported that the cellulose content of other plant parts is approximately 33%, that of the wooden part of plants is approximately 50%, and that of cotton, which has the purest form of cellulose, is approximately 90%.(Klemm *et al.,* 1998) Cellulose is one of the most important 'sought-after' organic raw materials worldwide owing to its high thermal stability, chemical stability, well-arranged structure, especially in the crystalline region, biocompatibility with most organic and inorganic materials and tunable structure to obtain products for diverse applications (Czaja, Romanovicz and Brown, 2004). Approximately one (1) billion tons of cellulose are estimated to be produced annually by plants through photosynthesis, but only approximately 4 million tons are processed into raw materials for further applications. This means that approximately 100 million tons are used as pulp in paper-making industries alone (Wang *et al.*, 2021). The underutilization of this important plant material was reportedly due to the difficulty usually encountered in an attempt to dissolve it. This underutilization might be due to the prevailing intra- and intermolecular hydrogen bond network within the cellulose molecule making it difficult to break apart. Several solvents, such as Cupriethylenediamine (Cuam), N-methyl-N-morpholine-N-oxide (NMMO), NaOH/Urea/H2O, N2O4-DMF, H3PO4- H2O, PF-DMSO and a host of others which have been employed as derivatizing and non-derivatizing solvent systems in the dissolution of cellulose (Baker *et al.,* 2022). The drawbacks with the use of these systems are that for non-derivatizing solvent systems, because of the solvents' high reactivity, there may be toxic side effects in addition to the solution losing its homogeneity during the reaction (as in the case of partially reacted cellulose aggregates). This can cause the aggregates to precipitate out of the solution or form gels, which prevents the reaction from proceeding to its full potential and consequently lead to issues like making the solution difficult to stir because of its high viscosity. The main disadvantage with derivatizing solvent systems is that they lack reproducibility due to side reactions, which leads to the production of unidentified molecules/structures (Liebert, 2021).

To overcome the problems associated with these solvent systems and to produce high- and standard-quality derivatives, ionic liquids were introduced. Over the years, ionic liquids have proven to be promising green solvents for the dissolution and easy and efficient derivatization of cellulose with or without the use of a catalyst and/or a cosolvent. Ionic liquids combine special characteristics, such as high thermal stability, moderate melting temperature, low toxicity, non-volatility, low viscosity, and recyclability, making them useful in the dissolution of cellulose because any solvent that would be effective in the homogenous dissolution of cellulose must possess the features described above for ionic liquids (Mohd *et al.*, 2017).

Chemistry of Cellulose and its Sources

Cellulose is an organic biopolymer that is composed of hundreds to thousands of ß-D-glucose molecules linked through a 1,4-glucopyrannose ring. The anhydroglucose unit of cellulose has a molecular mass of 165 g/mol. Anselm Payen's 1838 discovery of the elemental makeup of cellulose is credited to this discovery; According to his findings, cellulose is made up of 44–45% carbon, 6–6.5% hydrogen, and the remaining oxygen. These facts led to the empirical formula's deduction, which was $(C_6H_{10}O_5)_n$. The precise macromolecular makeup of cellulose is still unknown, though. Thus, in the late 1920s, Haworth postulated a macromolecular structure resembling a chain, whereas Staudinger offered the conclusive evidence of the

cellulose molecule's highly polymeric nature (Lourdin *et al.*, 2016). Cellulose is mainly obtained from forestry, agricultural wastes and crops, animal (such as the *acetobater* bacteria) and industrial residues.

Identifying the chemical makeup of the cellulose molecule in addition to its solid- state structure and shape will enhance the understanding of the chemical and physical properties of cellulose. A thorough comprehension of the structural characteristics of natural cellulose is necessary to comprehend how various substituents affect the chemical and physical properties of cellulose and its derivatives.The molecular, supramolecular and morphological structures of cellulose have been studied over the years, and several solvents have been shown to efficiently and homogenously dissolve cellulose for proper derivatization with few or no side reactions. These solvents must be thermally stable, melt at moderate temperature, less toxic, non-volatile, less viscous and recyclable (Kunusa *et al.,* 2018).

Hydrogen bonds within molecules give cellulose molecules their relative stiffness and rigidity. Its strong tendency to crystallize, high viscosity in solution, and capacity to form fibrillar strands are indicative of this characteristic. The βglucosidic linkage, which confers the chain's linear structure, further enhances the stiffness attribute of the chain. The pyranose ring's chair shape (Fig. 1) further adds to the rigidity of the chain. This contrasts with the starch's α-glucosidic linkages (Granström *et al.*, 2008).

Fig. 1: Structure of Cellulose showing the reducing and non-reducing end (Rajinipriya *et al.*, 2018)

Three equatorially positioned -OH group; one primary group and two subsidiary groups in the AGU define the chemical makeup and reactivity of cellulose. Furthermore, cellulose's β-glycosidic bonds are vulnerable to hydrolytic disruption. The solubility of cellulose is significantly influenced by the hydroxyl groups, which are also involved in the usual interactions of primary and secondary alcohols on cellulose. Because the hydroxyl groups are in charge of the vast network of hydrogen bonds that generate both intra- and intermolecular hydrogen bonds, cellulose is insoluble in water and typical organic solvents (Fig. 2) (Terzopoulou, Kyzas and Bikiaris, 2015). It is necessary to disrupt the dominant hydrogen bonding network in order to breakdown the cellulose molecule. The solvent that has the best ability to dissolve and tune cellulose, as studied over the years, is ionic liquids (Cho *et al.*, 2011).

Fig. 2: Structure of Cellulose with inter and intramolecular-hydrogen bonds (Terzopoulou, Kyzas and Bikiaris, 2015)

Ionic liquids (ILs)

These compounds belong to a new category of organic molten salts that melt at temperatures lower than 100 °C. Their numerous appealing qualities include low vapour pressure, excellent solvating capabilities, high thermal and chemical stabilities, structural tunability, ease of recycling, and non-flammability, making them the most suitable solvent for effective cellulose dissolution apart from other wide spread industrial applications. These include their use as electrolytes in batteries, as organic and inorganic catalysts and as hosts. Ionic liquids are prepared in two basic steps: (1) QUATERNIZATION, where the heterocyclic tertiary nitrogen of a cyclic compound or the tertiary nitrogen of an open chain compound is quaternized by reacting with alkyl halides (Fig. 3). This step produces the cation and, at times, even the desired ionic liquids depending on one important property of the product, which is that the melting point is usually below 100 °C. Several cations (Fig. 4) have been used in the successful preparation of ionic liquids, including imidazolium (Swatloski *et al.*, 2002), trialkyl ammonium, pyridinium (Liebert, Hussain and Heinze, 2005), phenanthrolinium (Villar-Garcia, Abebe and Chebude, 2012) , prolinium (He *et al.*, 2020), morpholinium (Su, 2012), cholinium (Le $& Bodo, 2021$) and phosphonium (Skoronski *et al.*, 2020).

Fig. 3: Some Common Ionic liquids (Cho *et al.*, 2011)

Common anions

 BF_4 , B(CN)₄, CH₃BF₃, CH₂CHBF₃, C₂F₅BF₃, n-C₄F₉BF₃, PF₆, CF₃CO₂, CF₃SO₃, N(SO₂CF₃)₂, $N(COCF_3)$ (SO_2CF_3) , $N(SO_2F)_2$, $N(CN)_2$, $C(CN)_3$, SCN , $SecN$, $CuCl_2$, $AICl_4$, X , OAc , etc

Fig. 4: Selected Cations and Anions used in the Synthesis of Ionic liquids (Moosavi, 2013)

The second step involved in ionic liquid synthesis is (2) METATHESIS: This process is important if the desired ionic liquid is not formed in the quaternization step. This involves the exchange of anions produced in the first step with a desirable one that will lower the melting point of the product to the standard ≤ 100 °C. In this process, the organic salt formed in the quaternization step reacts with Lewis acid or Na, K, Ag or an acid of NO_2 ⁻, NO_3 ⁻, SO_4 ²⁻, or CH₃COO⁻ (Fig. 4), to obtain the desired ionic liquid.

The imidazolium cation-based ionic liquids are the most widely reported as the best solvent for the dissolution of cellulose. However, recently, researchers have shown that Morpholine-based ionic liquids can also efficiently dissolve cellulose in the presence or absence of a cosolvent (Su, 2012).

Reprocessing Cellulose in Ionic Liquids

Cupriethylenediamine (Cuam), N-methyl-N-morpholine-N-oxide (NMMO), NaOH/Urea/H2O, N2O4-DMF, H3PO4-H2O, PF-DMSO, and a variety of others have been used as derivatizing and non-derivatizing solvent systems in the dissolution of cellulose. The disadvantages of using these systems include their non-suitability due to their high reactivity, side reactions, and toxicity, as well as the formation of undesirable non-identifiable products due to possible loss of homogeneity. A lack of reproducibility is also a major factor affecting this class of solvent systems (Granström, 2009; Liebert, 2021).

In 1934, Graenacher and colleagues reported the first effective dissolution of cellulose in an ionic liquid. According to their findings, N-alkylpyridinium chloride [NAPy]+Cl-can dissolve cellulose, allowing for effective chemical modification of cellulose. Unfortunately, due to the high melting temperature of the pyridinium salts (118– 120 °C), this topic has not received much attention. After preparing dialkyimmidazolium [DAPy]⁺ halide ionic liquids with melting temperatures less than 100 °C, Swalowki and his co-researchers (2002) made a discovery that changed the phase of Ionic liquids applications in cellulose approximately one decade later in 2002 (Kharismi *et al.*, 2018).

In the course of the research, Swaloski and co-workers (2002) discovered the best dialkylimmidazolium-based Ionic liquid for dissolving cellulose up to approximately 25 wt% by microwave heating and 10 wt% normal heating, which was 1-butyl-3-methylimidazolium chloride (BmimCl). After this outstanding discovery, several other ionic liquids containing ammonium, pyridinium, cholinium and morpholinium cations with several anions, including halide (Cl, Br), [HCOO], [PhCOO] and [HSCH2COO], which were prepared and used for the successful dissolution (even at room temperature in some cases) and derivatization of cellulose. Some ionic liquids bearing anions, $[BF_4]$, $[PF_6]$, $[N(CN)_2]$, $[MeSO_4]$, $[HSO_4]$ and [Tf₂N]⁻, were also tested for the dissolution of cellulose, but it was discovered that they did not work due to weak hydrogen bond basicity. The good dissolving capabilities of these ILs were directly correlated with their strong hydrogen bond basicity and lower viscosity (Taheri, Abdolmaleki and Fashandi, 2019).

To examine the effectiveness of morpholinium salts in cellulose dissolution, a series of morpholinium salts were prepared. These ionic liquids were prepared under standard bench experimental conditions, making them well suited for industrial-scale applied research. The majority of the ionic liquids made were halide-free, but due to their hygroscopicity, they contained approximately 6×10^4 ppm water. At 120 °C for 20 minutes, [AMMorp][OAc] brine and [AMMorp][HSO4] brine were found to dissolve 26 and 8 wt% cellulose, respectively. In the case of [BMMorp][OAc], [BMMorp][OAc]-brine was unable to dissolve cellulose, and it was necessary to add a small amount of halogen-containing ionic liquid. At 80°C for 24 hours, a mixture of 70% [BMMorp][OAc] with 23.3 w% [BMMorp][Br] and 6.7wt% water allowed the dissolution of 6 wt% cellulose without any pretreatment. Similarly, at 120 °C, 86.7% [BnMMorp][OAc] with 7 wt% [BnMMorp][Cl] and 6.3wt% water dissolved 22 wt% cellulose in 20 minutes. At high temperatures, organic electrolytic solutions of ionic liquids containing various studied amines were unable to dissolve cellulose, while solutions containing ethanol and 2-butanol were able to dissolve 2 and 4 wt% cellulosic materials, respectively, at 70 °C in 24 h. The behaviour of cellulosic fibres in various solvent systems was revealed by optical microscopy images. Importantly, the recovered ionic liquid still had a high capacity for cellulose dissolution. These ionic liquids have the potential to be used in industry for cellulose processing because of their effectiveness in dissolving cellulose in the presence of large amounts of water (Pernak *et al.*, 2011; Su, 2012).

The ammonium-based ILs were able to dissolve cellulose effectively by combining cheap quaternary ammoniumbased ILs with carboxylate anions, such as formate or acetate anions (Kostag *et al.*, 2018). Within 15 minutes, cellulose was dissolved at 85 °C using Triethylmethylammonium Formiate (TEAF) and Tributylmethylammonium Formiate (TBAF). Approximately 15% weight of microcrystalline cellulose may be dissolved by pure molten tetraalkylammonium chlorides containing a single long alkyl chain. Additionally, adding polar and aprotic organic solvents (DMSO, acetone, and DMAc) as co-solvents sped up the cellulose's breakdown (Aziz *et al.*, 2019).

It is also possible to dissolve cellulose with ionic liquids based on pyridinium cations. According to reports, 1-butyl-3-methylpyridinium chloride (BmPyCl) works better than 1-Butyl-3-methylimmidazolium chloride (BmimCl). BmPyCl was able to dissolve cellulose with a Degree of Polymerization (DP) of 593 and attain a 37% weight concentration at 105 °C. Nonetheless, during the dissolution process, there was a considerable reduction in the degree of polymerization of cellulose. In 1 ethylpyridinium chloride (EpyCl), cellulose was totally dissolved and simultaneously depolymerized. Consequently, cellulose conversion and dissolution are frequently carried out in alkylpyridinium-based ILs (Liebert *et al.,* 2005; Kostag *et al.,* 2018).

Combining a variety of super bases (1,1,3,3-tetra methylguanidine (TMG), 1,5-diazabicyclo-[4.3.0]non-5 ene (DBN), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and other organo acids with organo acids) afforded the synthesis of new, distillable acid–base conjugated ILs (Hauru *et al.*, 2014; Ma *et al.*, 2017; He *et al.*, 2020). These ILs dissolved cellulose easily while they were also recycled through distillation with over 99% recovery and purity. Cellulose fibres were successfully fabricated using [DBNH]Ac as the solvent, resulting in properties that are comparable to or better than those of Lyocell fibres. Moreover, after CO² capture in DMSO, DBU, in combination with or without alcohol (such as methanol and ethylene glycol), produced tunable ILs which dissolved cellulose to high concentrations (15 wt%) a low temperature range of $25-40$ °C (Xie and Wang, 2021). The highly efficient acylation of cellulose was also achieved in these switchable ILs. According to the abovementioned literature, a large number of ILs capable of dissolving cellulose have been identified to date, and more ILs are being investigated. Including DMSO or DMAc as co-solvent, may improve the dissolution efficiency of these ILs. (Moshikur *et al.,* 2020). Imidazolium, pyridinium, and ammonium-based cations and halide, carboxylate, and alkylphosphate-based anions make up these ILs. According to reports, imidazolium-based ILs dissolve better than pyridinium-based ILs, pyridiniumbased ILs dissolve better than ammonium-based ILs, and carboxylate-based ILs dissolve better than alkylphosphate-based ILs and halide-based ILs (Zhang *et al.*, 2017).

Furthermore, our group achieved effective dissolution of cellulose obtained from various cellulosic wastes (Rice husk, corncob, and various species of wood shavings) using 1-butyl-3-methyl-immidazolium chloride ionic liquid. Direct esterification and etherification of cellulose were accomplished by dissolving up to 20% of the cellulose samples in DMSO as a co-solvent. The derivatives were regenerated by immersing the IL/cellulose derivative in dichloromethane or acetone, while the ILs were recovered and reused. A Degree of Substitution (DS) of up to 2.77 for cellulose acetate, 1.5 for cellulose phthalate, and 1.3 for ethyl cellulose. In conclusion, the FTIR spectrum of an ethyl cellulose derivative demonstrated that an IL can be used to directly etherify cellulose. Spectroscopic investigation also revealed the non-destructive nature of ILs in the processing of cellulose (Baker, 2022).

Fig. 5: A description of how to treat cellulosic wastes using an ionic liquid to dissolve cellulose to create fresh material for improved application while also reusing the ionic liquid for another cycle (Baker, 2022)**.**

Mechanism of Dissolution

The necessity of dis-oreintating the hydrogen-bonding network in cellulose backbone for cellulose dissolution is well known. The anions in ILs play a dominant role by forming strong hydrogen bonds with the hydrogen atoms of the hydroxyl groups in cellulose. The function of cations in ILs, on the other hand, is still debated. In 2005, Zhang *et al*., (Zhang *et al.*, 2016) proposed a method for cellulose dissolution in ILs. The driving force behind cellulose dissolution was discovered to be the synergistic effect of anions and cations in ILs. For these reasons, unlike in the reports of Swalowski *et al.* in 2002 (Swatloski *et al.*, 2002), which described that the role of cations in the dissolution of cellulose was not absolutely negligible.

Nuclear Magnetic Resonance (NMR) experiments were used to demonstrate how cellulose hydroxyls form hydrogen bonds with both anions and cations in ILs. Because of the relatively small anions, the aromatic protons in the imidazolium cation, especially H-2, preferred to associate with the oxygen atoms of the hydroxyls with less steric hindrance, allowing the formation of hydrogen bonds with the hydroxyl hydrogen atoms (Hina, Zhang and Wang, 2015). After the free-energy simulation and coarse-grain study, it was further discovered that hydrogen bonding interactions between anions and cations with glucose units contributed significantly to their dissolution. Through a series of dissolution experiments and NMR experiments, it was further discovered that the cation of ILs was related to the breakage of hydrogen bonds in cellulose, and infrared spectroscopy and solid-state NMR experiments were used to show that the cation of ILs was related to the collapse of hydrogen bonds in cellulose (Uto, Yamamoto and Kadokawa, 2018). .

Fig. 6: Immidazolium-based ILs for cellulose pretreatment (Cao *et al.*, 2017)**;**

Applications of Dissolved Cellulose and Cellulose Derivatives in Ionic Liquids

There is no doubt that dissolving cellulose in ionic liquids is one of the best methods and easiest ways to prepare cellulose derivatives of various types. Examples of cellulose derivatives include cellulose nitrate, cellulose xanthogenate, cellulose acetate, cellulose phthalate, ethyl cellulose, methyl cellulose, hydroxypropyl cellulose, carboxymethyl cellulose and a host of others. Cellulose acetate is used in membranes and coatings; cellulose nitrate is used during the production of membranes and coatings; cellulose xanthate is applied in the production of textiles; carboxymethyl cellulose is used in coatings, paints, adhesives, food and pharmaceuticals; methyl cellulose has also been applied in the food and tobacco industries as an additive; and ethyl cellulose is used in the pharmaceutical industry as an enteric coating for drugs. Cellulose derivatives with unsubstituted C_6 -OH groups tend to form gels upon dissolving (Chang, Zhang and Hsu, 2015).

Furthermore, cellulose dissolved in ionic liquid (without functionalization) can be used to produce materials such as cellulose fibres used in the production of textiles (Olsson, 2014; Parviainen *et al.*, 2015; Hou *et al.*, 2017) . Cellulose films, are utilized in green packaging, printable labels, biomedical materials, electronic devices and optical products; (Li *et al.*, 2014; Wawro *et al.*, 2015; Kontturi and Spirk, 2019) and cellulose gels and aerogels, are made into beads, films and fibres for electrolytic applications to enhance the electrochemical properties of materials (Cheng *et al.*, 2013; Demilecamps *et al.*, 2015; Hoenders *et al.*, 2018; Manafi *et al.*, 2021). Cellulose blends have also been made by dissolving cellulose in ionic liquids together with other polysaccharides and proteins, such as agarose, xylan, chitin, chitosan, collagen, glucomannans, starch, lignin, silk, collagen and keratin, to improve the functionality of these materials (Kadokawa *et al.*, 2009; Singh and Savoy, 2020). Moreover, cellulose composites are also prepared by compounding cellulose with organic or inorganic fillers to improve the physical properties and enable widespread application of these materials (Liu *et al.,* 2012; Lv *et al.,* 2014; Mahmoudian *et al.,* 2015; Soheilmoghaddam *et al.,* 2013).

Microcrystalline cellulose produced from cellulose obtained from cotton and rice husk has also been applied with silica gel (50:50) by our group as an adsorbent in the stationary phase of preparative thin layer plates (Arowona *et al.*, 2018). Several applications of cellulose and its derivatives have been reported in recent years, including pharmaceutical excipients (Nwachukwu and Ofoefule, 2020; Rahman *et al.*, 2020), drug delivery,(Hussin *et al.*, 2016; Putro *et al.*, 2019), adsorbents for dyes and heavy metals (Ateia *et al.*, 2018; Garba *et al.*, 2020), wound healing (Kumar, Pathak and Bhardwaj, 2020), and aldehyde volatile organic compound capture in polluted water bodies (Bravo *et al.*, 2020). Cationic cellulose derivatives have also been used as flocculants in the manufacture of paper (Aguado *et al.*, 2017) and grafted cellulose acetaoacetate has also been prepared for use in the purification of biofuel (Hassan and Abdellatif, 2018). The Biginellini reaction of cellulose acetoacetate has also been reported, and this significantly opens new doors for various cellulose derivatizations for application in diverse fields for interesting industrial and laboratory applications (Rong *et al.*, 2019). Advanced porous hierarchical activated carbon was prepared from cellulose containing agricultural wastes and applied for high-performance capacitors (Wei *et al.*, 2020). The applications of cellulose are too numerous, and more studies are on the utilization of this beautiful biomaterial with innumerable applications due to its unique characteristics and ability to dissolve cellulose homogenously for easy functionalization.

Notably, the two most popular ionic liquids used for tuning and functionalizing cellulose for a wide range of applications are 1-Allyl-3-methylimmidazolium Chloride (AmimCl) and 1-Butyl-3-methyimmidazolium Chloride (BmimCl), with DMSO or DMAc being used as cosolvents to reduce the viscosity of the cellulose solution for easier processing.

Recycled, Reused and Reprocessed Cellulosic Wastes using Ionic Liquids.

Recycling, reprocessing and reusing cellulose in ionic liquids involves the use of ionic liquids for the dissolution and functionalization of cellulose obtained from cellulosic wastes for further applications. Consequently, several publications on this topic have been published, and some of these include works reported in this review. For example, Heinze's group produced cellulose furoate and phenyl carbonate with Degree of Substitution (DS) in the range of 0.4–3.0 by homogeneously acylating cellulose with 2 furoyl chloride and phenyl chloroformate, respectively, in the presence of pyridine. When employing pyridine, cellulose degradation was disregarded. Cellulose naphthoate and 9-anthracenecarboxylate with a DS range of 0.85–2.61 in AmimCl which were produced in AmimCl. Both strong fluorescence properties and increased solubility in several organic solvents were displayed by the new cellulose esters. The ability to construct membranes was particularly strong for cellulose naphthoates. A very transparent and flexible membrane was created using a solution-casting technique (Xu *et al.*, 2011).

Using sugarcane bagasse as a raw material, Huang *et al*. 2021, produced two cellulose mixed esters, Cellulose Acetate Butyrate (CAB) and Cellulose Acetate Propionate (CAP), in AmimCl. By using high-intensity ultrasonic irradiation without a catalyst, the glutarylation of sugarcane bagasse cellulose in BmimCl was examined by Ma *et al.,* 2019 (Huang *et al.*, 2021).

Wang *et al*. 2021, investigated the anticoagulant activity of cellulose sulfates synthesized in BmimCl. It was stated that the molar mass played a significant role in the anticoagulant properties. *In vitro* applications benefited from a high molar mass, while in vivo applications benefited from a low molar mass. They successfully sulfated bagasse cellulose with chlorosulfonic acid using a combination of AmimCl and dimethylformamide. The resulting bagasse cellulose sulfates had significant anticoagulant activity, with DS values ranging from 0.52 to 2.95 (Kunusa *et al.,* 2018).

To study the esterification of sugarcane bagasse cellulose with succinic anhydride and phthalic anhydride in BmimCl, AmimCl, and BmimCl/DMSO without a catalyst or with DMAP, N-bromosuccinimide, or iodine as a catalyst, Liu and colleagues carried out a series of studies.

DS values between 0 and 2.54 were used to create cellulose esters (Cao *et al.,* 2017, Liu *et al.,* 2016).

Crude Norway spruce cellulosic pulp was chemically modified by homogeneous acylation and carbanilation in ILs, according to Zoia *et al*., 2011. They discovered that by treating wood dissolved in ILs with acetyl chloride, benzoyl chloride, and acetic anhydride in the presence of pyridine, highly substituted wood-based lignocellulosic esters could be produced under benign conditions (Zoia, King and Argyropoulos, 2011).

Corn husk cellulose was effectively acetylated in AmimCl. corn husk Cellulose Acetates (CAs) with a controlled DS in the range of 2.16–2.6 were produced in one step without the use of a catalyst. In several organic solvents, such as acetone and DMSO, the resulting corn husk CAs were easily dissolved. The cast cornhusk CA films made from acetone solutions exhibited strong mechanical characteristics. This study offers a technically workable and environmentally acceptable approach for producing acetone-soluble cellulose diacetates in one step by utilizing corn husk as the source of cellulose because AmimCl is recyclable after each acetylation (Rahman *et al.*, 2020).

Conclusion

The tunability of cellulose has provided cellulose-based materials to have the potential to replace materials obtained from other sources such as crude oil based substrates and as candidates for advanced materials. Biomaterials such as cellulose meet the environmental prerequisites for renewable resources. In addition, modifying cellulose to produce cellulose derivatives by utilizing ILs results in a large number of end products. ILs have demonstrated great potential for the dissolution and processing of cellulose over the past two decades. With the significant progress in fundamental research on the dissolution of cellulosic derivatives, there is a need to focus research on their potential industrial applications. Taking advantage of these recyclable and ''green'' ILs, many efforts have to be made to accomplish the eco-friendly utilization of bio renewable cellulose resources and to serve as an alternative source of income generation in underdeveloped as well as developing countries that are blessed with abundant cellulosecontaining natural resources but face the challenges of recycling, reprocessing and reusing. Achieving this therefore, means wastes are obtained from the environment, they are processed following green chemistry principles and then returned to the environment in their beneficial form.

Conflict of Interest

The authors declare no conflict of Interest

References

- Aguado, R. *et al.* (2017) 'Cationic cellulosic derivatives as flocculants in papermaking', *Cellulose*, 24(7), pp. 3015–3027. doi: 10.1007/s10570-017-1313-y.
- Arowona, M. T. *et al.* (2018) 'Thermally stable rice husk microcrystalline cellulose as adsorbent in PTLC plates', *Journal of the Turkish Chemical Society, Section A: Chemistry*, 5(3), pp. 1177–1184. doi: 10.18596/jotcsa.327665.
- Ateia, M. *et al.* (2018) 'Rapid Removal of Poly- and Perfluorinated

Alkyl Substances by Poly(ethylenimine)-Functionalized Cellulose Microcrystals at Environmentally Relevant Conditions', *Environmental Science and Technology Letters*, 5(12), pp. 764–769. doi: 10.1021/acs.estlett.8b00556.

- Aziz, T. *et al.* (2019) 'Facile modification and application of cellulose nanocrystals', *Iranian Polymer Journal (English Edition)*, 28(8), pp. 707–724. doi: 10.1007/s13726-019- 00734-2.
- Baker, M. T. (2022) 'Characterization of Synthesized Cellulose Derivatives in 1-Butyl-3-Methylimidazolium Chloride Ionic Liquid'.
- Bravo, I. *et al.* (2020) 'Cellulose particles capture aldehyde VOC pollutants', *RSC Advances*, 10(13), pp. 7967– 7975. doi: 10.1039/d0ra00414f.
- Cao, Y. *et al.* (2017) 'Imidazolium-based ionic liquids for cellulose pretreatment: recent progresses and future perspectives', *Applied Microbiology and Biotechnology*, 101(2), pp. 521– 532. doi: 10.1007/s00253-016-
- Chang, H. C., Zhang, R. L. and Hsu, D. T. (2015) 'The effect of pressure on cation-cellulose interactions in cellulose/ionic liquid mixtures', *Physical Chemistry Chemical Physics*, 17(41), pp. 27573–27578. doi: 10.1039/c5cp04607f.
- Cheng, W. *et al.* (2013) 'Preparation and characterization of oxidized regenerated cellulose film for hemostasis and the effect of blood on its surface', *Cellulose*, 20(5), pp. 2547– 2558. doi: 10.1007/s10570-013- 0005-5.
- Cho, T. Y. *et al.* (2011) 'Effect of ionic liquids with different cations in I-/I 3-redox electrolyte on the performance of dye-sensitized solar cells', *Bulletin of the Korean Chemical Society*, 32(6), pp. 2058– 2062. doi:10.5012/bkcs.2011.32.6.2058.
- Czaja, W., Romanovicz, D. and Brown, R. malcolm (2004) 'Structural investigations of microbial cellulose produced in stationary and agitated culture', *Cellulose*, 11(3/4), pp. 403–411. doi: 10.1023/b:cell.0000046412.11983.61.
- D. Klemm, B. Philipp, T. Heinze, U. Heinze, W. W. (1998) *WILEY-VCH Comprehensive Cellulose Chemistry Volume l Fundamentals and Analytical Methods*.
- Demilecamps, A. *et al.* (2015) 'Cellulose-silica aerogels', *Carbohydrate Polymers*, 122, pp. 293–300. doi: 10.1016/j.carbpol.2015.01.022.
- Garba, Z. N. *et al.* (2020) 'Microcrystalline cellulose (MCC) based materials as emerging adsorbents for the removal of dyes and heavy metals – A review', *Science of the Total Environment*, 717(Mcc), p. 135070. doi: 10.1016/j.scitotenv.2019.135070.
- Granström, M. *et al.* (2008) 'Tosylation and acylation of cellulose in 1-allyl-3-methylimidazolium chloride', *Cellulose*, 15(3), pp. 481–488. doi: 10.1007/s10570-008-9197-5.
- Granström, M. (2009) *Cellulose Derivatives: Synthesis, Properties and Applications*.
- Hassan, F. and Abdellatif, H. (2018) 'Grafted cellulose acetate

derivatives for the purification of biofuels by a sustainable membrane separation process Faten Hassan Hassan Abdellatif To cite this version : HAL Id : tel-01673821

soutenance et mis à disposition de l 'ensemble de la

Contact^{:'}

- Hauru, L. K. J. *et al.* (2014) 'Dry jet-wet spinning of strong cellulose Liu, Q.-P. *et al.* (2012) 'Green Chemistry Ionic liquids from filaments from ionic liquid solution', *Cellulose*, 21(6), pp. 4471–4481. doi: 10.1007/s10570-014-0414-0.
- He, T. *et al.* (2020) 'molecules The Proton Dissociation of Bio-Protic Ionic Liquids: [AAE]X Amino Acid Ionic Liquids'. doi: 10.3390/molecules2.
- Hina, S., *et al.,* (2015) 'Role of ionic liquids in dissolution and regeneration of cellulose', *Reviews on Advanced Materials Science*, 40(3), pp. 215–226.
- Hoenders, D. *et al.* (2018) 'Photochemical ligation meets nanocellulose: A versatile platform for self-reporting functional materials', *Materials Horizons*, 5(3), pp. 560– 568. doi: 10.1039/c8mh00241j.
- Hou, Q. *et al.* (2017) 'molecules Pretreatment of Lignocellulosic Biomass with Ionic Liquids and Ionic Liquid- Based Solvent Systems'. doi: 10.3390/molecules22030490.
- Huang, Y.-B. *et al.* (2021) 'Room-Temperature Dissolution and Mechanistic Investigation of Cellulose in a Tetra-Butylammonium Acetate/Dimethyl Sulfoxide System', 18, p. 56. doi: 10.1021/acssuschemeng.5b01749.
- Hussin, M. H. *et al.* (2016) 'Physicochemical of microcrystalline cellulose from oil palm fronds as potential methylene blue adsorbents', *International Journal of Biological Macromolecules*, 92, pp. 11–19. doi: 10.1016/j.ijbiomac.2016.06.094.
- Kadokawa, J. *et al.* (2009) 'Preparation of cellulose-starch composite gel and fibrous material from a mixture of the polysaccharides in ionic liquid', *Carbohydrate Polymers*, 75(1), pp. 180–183. doi: 10.1016/j.carbpol.2008.07.021.
- Kharismi, A. & Suryadi Y. (2018) 'Microwave-assisted solvent-free acetylation of cellulose with acetic anhydride in the presence of iodine as a catalyst', *Molecules*, 10(3), pp. 758–778. doi: 10.3390/molecules25245975.
- Kontturi, E. and Spirk, S. (2019) 'Ultrathin films of cellulose: A materials perspective', *Frontiers in Chemistry*, 7(July), pp. 1–18. doi: 10.3389/fchem.2019.00488.
- Kostag, M. *et al.* (2018) 'Recent advances in solvents for the dissolution, shaping and derivatization of cellulose: Quaternary ammonium electrolytes and their solutions in water and molecular solvents', *Molecules*, 23(3). doi: 10.3390/molecules23030511.
- Kumar, V. *et al.,* (2020) 'Waste paper: An underutilized but promising source for nanocellulose mining',
Waste Management, 102, pp. 281–303. doi: *Waste Management*, 102, pp. 281–303. doi: 10.1016/j.wasman.2019.10.041.
- Li, X. *et al.* (2014) 'Cellulose fibers from cellulose/1-ethyl-3 methylimidazolium acetate solution by wet spinning with increasing spinning speeds', *Journal of Applied Polymer Science*, 131(9), pp. 1–9. doi: 10.1002/app.40225.
- Liebert, T. (2021) *Cellulose Solvents-Remarkable History, Bright* Future. UTC. Available at: https://pubs.acs.org/sharingguidelines (Accessed: 16 April 2021).
- Liebert, T., Hussain, M. A. and Heinze, T. (2005) 'Structure determination of cellulose esters via subsequent functionalization and NMR spectroscopy', in *Macromolecular Symposia*. Wiley-VCH Verlag, pp. 79–

92. doi: 10.1002/masy.200550506.

- renewable biomaterials: synthesis, characterization and application in the pretreatment of biomass †'. doi: 10.1039/c2gc16128a.
- Liu, Y.-R. *et al.* (2016) 'Predictive screening of ionic liquids for dissolving cellulose and experimental verification', *Green Chemistry*, 18(23), pp. 6246–6254. doi: *Chemistry*, 18(23), pp. 6246–6254. doi: 10.1039/c6gc01827k.
- Lourdin, D. et al. (2016) 'Concentration driven cocrystallisation and percolation in all-cellulose nanocomposites', *Cellulose*, 23(1), pp. 529–543. doi: 10.1007/s10570-015-0805-x.
- Lv, F. *et al.* (2014) 'Characterization of chitosan microparticles reinforced cellulose biocomposite sponges regenerated from ionic liquid', *Cellulose*, 21(6), pp. 4405–4418. doi: 10.1007/s10570-014-0440-y.
- Ma, Y. *et al.* (2017) 'High performance man-made cellulosic fibres from recycled newsprint', *Green Chemistry*, 20. doi: 10.1039/c7gc02896b.
- Mahmoudian, S. *et al.* (2015) 'Bionanocomposite fibers based on cellulose and montmorillonite using ionic liquid 1-ethyl-3-methylimidazolium acetate', *Journal of Materials Science*, 50(3), pp. 1228–1236. doi: 10.1007/s10853-014-8679-0.
- Manafi, P. *et al.* (2021) 'A study on the microstructural development of gel polymer electrolytes and different imidazoliumbased ionic liquids for dye-sensitized solar cells', *Journal of Power Sources*, 481(July 2020), p. 228622. doi: 10.1016/j.jpowsour.2020.228622.
- Md Moshikur, R. *et al.* (2020) 'Design and Characterization of Fatty Acid-Based Amino Acid Ester as a New "Green" Hydrophobic Ionic Liquid for Drug Delivery', *Cite This: ACS Sustainable Chem. Eng*, 8, pp. 13660–13671. doi: 10.1021/acssuschemeng.0c03419.
- Mohd, N. *et al.* (2017) 'Dissolution of cellulose in ionic liquid: A review', *AIP Conference Proceedings*, 1809(February). doi: 10.1063/1.4975450.
- Moosavi, F. (2013) 'The Structure of Supported Ionic Liquids at the Interface', in *Ionic Liquids - New Aspects for the Future*. InTech. doi: 10.5772/53646.
- Nwachukwu, N. and Ofoefule, S. I. (2020) 'Effect of drying methods on the powder and compaction properties of microcrystalline cellulose derived from gossypium herbaceum', *Brazilian Journal of Pharmaceutical Sciences*, 56, pp. 1–17. doi: 10.1590/s2175- 97902020000118060.
- Olsson, C. (2014) *Cellulose processing in ionic liquid based solvents*. Available at: file:///Users/Tiago/Google Drive/Mendeley Desktop/Olsson/Unknown/196970.pdf.
- Parviainen, A. *et al.* (2015) 'Sustainability of cellulose dissolution

and regeneration in 1,5- diazabicyclo[4.3.0]non-5 enium acetate: a batch simulation of the IONCELL-F process †'. doi: 10.1039/c5ra12386k.

- Pernak, J. *et al.* (2011) 'Green Chemistry Synthesis, toxicity, biodegradability and physicochemical properties of 4 benzyl-4-methylmorpholinium-based ionic liquids †'. doi: 10.1039/c1gc15468k.
- Putro, J. N. *et al.* (2019) 'Nanocrystalline cellulose from waste paper:

Adsorbent for azo dyes removal', *Environmental Nanotechnology, Monitoring and Management*, 12, p. 100260. doi: 10.1016/j.enmm.2019.100260.

- Rahman, M. S. *et al.* (2020) 'Conversion of Lignocellulosic Corn Agro-Waste into Cellulose Derivative and Its Potential Kunusa,W *et al.,* (2018) 'FTIR, XRD and SEM Analysis of Application as Pharmaceutical Excipient', *Processes*, 8(6), p. 711. doi: 10.3390/pr8060711.
- Rajinipriya, M. *et al.* (2018) 'Importance of Agricultural and Industrial Waste in the Field of Nanocellulose and Recent Industrial Developments of Wood Based Nanocellulose: A Review'. doi: 10.1021/acssuschemeng.7b03437.
- Ronald Aseer, J. *et al.* (2013) 'Morphological, Physical, and Thermal Properties of Chemically Treated Banana Fiber', *Journal of Natural Fibers*, 10(4), pp. 365–380. doi: 10.1080/15440478.2013.824848.
- Rong, L. *et al.* (2019) 'Biginelli reaction on cellulose acetoacetate: a new approach for versatile cellulose derivatives', *Carbohydrate Polymers*, 209(2999), pp. 223–229. doi: 10.1016/j.carbpol.2019.01.036.
- Singh, S. K. and Savoy, A. W. (2020) 'Ionic liquids synthesis and applications: An overview', *Journal of Molecular Liquids*, 297, p. 112038. doi: 10.1016/j.molliq.2019.112038.
- Skoronski, E. *et al.* (2020) 'Use of phosphonium ionic liquids for highly efficient extraction of phenolic compounds from water', *Separation and Purification Technology*, 248(March), p. 117069. doi: 10.1016/j.seppur.2020.117069.
- Soheilmoghaddam, M. *et al.* (2013) 'Regenerated cellulose/halloysite nanotube nanocomposite films prepared with an ionic liquid', *Materials Chemistry and Physics*, 141(2\ 3), pp. 936–943. doi: 10.1016/j.matchemphys.2013.06.029.
- Su, W. (2012) *A study of cellulose dissolution in ionic liquid- water brines*.
- Swatloski, R. P. *et al.* (2002) 'Dissolution of Cellose with Ionic Liquids', *J. AM. CHEM. SOC*, 124, pp. 4974– 4975. doi: 10.1021/ja025790m.
- Taheri, N., Abdolmaleki, A. and Fashandi, H. (2019) 'Impact of nonsolvent on regeneration of cellulose dissolved in (carboxymethyl)pyridinium chloride ionic liquid', *Polymer International*, 68(12), pp. 1945–1951. doi:10.1002/pi.5903.
- Terzopoulou, Z., Kyzas, G. Z. and Bikiaris, D. N. (2015) 'Recent Advances in Nanocomposite Materials of Graphene Derivatives with Polysaccharides', *Materials*, 8, pp. 652– 683. doi: 10.3390/ma8020652.
- Uto, T., *et al.,* (2018) 'Cellulose Crystal Dissolution in Imidazolium-Based Ionic Liquids: A Theoretical Study', *Journal of Physical Chemistry B*, 122(1), pp. 258–266. doi: 10.1021/acs.jpcb.7b09525.
- Villar-Garcia, *et al.,* (2012) '1,10-Phenanthrolinium ionic liquids exhibiting excellent solubility for metal complexes:

Potential solvents for biphasic and supported ionic liquid phase (SILP) catalysis', *Inorganic Chemistry Communications*, 19, pp. 1–3. doi: 10.1016/j.inoche.2012.01.014.

Microcrystalline Cellulose (MCC) Fibers from Corncorbs in Alkaline Treatment', *Journal of Physics: Conf. Series 1028*, 1(1), pp. 258–266. doi: 10.1088/1742- 6596/1028/1/012199.

- Wang, Z. *et al.* (2021) '3D Printable, Highly Stretchable, Superior Stable Ionogels Based on Poly(ionic liquid) with Hyperbranched Polymers as Macro-cross-linkers for High-Performance Strain Sensors', *Appl. Mater. Interfaces*, 13. doi: 10.1021/acsami.0c21121.
- Wawro, D. *et al.* (2015) 'Impact of water in the casting of cellulosic film from ionic liquid solutions', *Fibres and Textiles in Eastern Europe*, 23(4), pp. 25–32. doi: 10.5604/12303666.1152718.
- Wei, H. *et al.* (2020) 'Advanced porous hierarchical activated carbon derived from agricultural wastes toward high performance supercapacitors', *Journal of Alloys and Compounds*, 820. doi: 10.1016/j.jallcom.2019.153111.
- Xie, W. and Wang, H. (2021) 'Grafting copolymerization of dual acidic ionic liquid on core-shell structured magnetic silica: A magnetically recyclable Brönsted acid catalyst for biodiesel production by one-pot transformation of low-quality oils', *Fuel*, 283. doi: 10.1016/j.fuel.2020.118893.
- Xu, D. *et al.* (2011) 'Studies on regioselective acylation of cellulose with bulky acid chlorides', *Cellulose*, 18(2), pp. 405– 419. doi: 10.1007/s10570-010-9476-9.
- Zhang, J. *et al.* (2016) 'Understanding cellulose dissolution: effect of the cation and anion structure of ionic liquids on the solubility of cellulose', *Science China Chemistry*, 59(11), pp. 1421–1429. doi: 10.1007/s11426-016-0269-5.
- Zhang, J. *et al.* (2017) 'Application of ionic liquids for dissolving cellulose and fabricating cellulose-based materials: State of the art and future trends', *Materials Chemistry Frontiers*, 1(7), pp. 1273–1290. doi: 10.1039/c6qm00348f.
- Zoia, L., King, A. W. T. and Argyropoulos, D. S. (2011) 'Molecular weight distributions and linkages in lignocellulosic materials derivatized from ionic liquid media', *Journal of Agricultural and Food Chemistry*, 59(3), pp. 829–838. doi: 10.1021/jf103615e.

.

Fig. 7: Uses for Reprocessed Cellulose and Cellulose Derivatives in Ionic Liquids