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REVIEW ON THE REGENERATION, DERIVATION AND DEGRADATION OF CELLULOSE IN IONIC LIQUID SYSTEM

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ARTICLE DETAILS

ABSTRACT

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Received 26 June 2018 Accepted 2 July 2018 Available online 1 August 2018 With increasing conflict between resources and environment, the High-valuable applications of cellulose in Ionic Liquids (IL) have been attracted increasing attention. In this paper, the derivation and degradation reaction of cellulose in IL was reviewed. First, starting from the dissolution and regeneration of cellulose in ionic liquids, which was the basis of the reactions of cellulose in ionic liquids. Secondly, a set of cellulose derivatives in ionic liquids were introduced, including the cellulose derivative products and regularity of the reaction. Furthermore, the research progress of cellulose degradation reactions in ionic liquids were reviewed. Finally, the defects and the direction of future efforts in the fields of the derivatives and degradation of cellulose in ionic liquids were also discussed.

KEYWORDS

Cellulose, ionic liquid, regeneration, derivation, degradation.

1. INTRODUCTION

People's awareness of environmental protection is increased rapidly with the increasing depletion of fossil resources. Recent years, the natural biomass resources, such as sugarcane bagasse, corn straw, wood and so on, have been widespread concerned by the researchers. Cellulose is the main component of many biomass resources, which is an important renewable energy and primary raw material, it is of great significance and prospect to use cellulose to produce energy and chemicals through effective methods. However, due to the high degree of crystalline and the complex network structure of hydrogen bond, natural cellulose does not melt or dissolve in most solvents, which become the biggest obstacle to the practical application of natural cellulose.

In most studies, regeneration, derivatization and degradation of cellulose are carried out in a heterogeneous system starting with cellulose activation. The unequal accessibility among the OH groups in the amorphous and crystalline regions is the main drawbacks in the application of cellulose. The traditional solvents of cellulose are N,N-dimethylacetamide/lithium chloride,NMMO, and so on [1,2]. However, there are some shortcomings in these solvents, such as limited dissolution capacity, narrow dissolution window, toxic, high cost, difficult solvent recovery, serious side reaction and instability in the process of cellulose homogeneous reaction. Even if the NMMO solvent system has been industrialized, there are still problems with high solvent prices and high recovery costs, heavy pollution and high energy consumption, and it has not yet completely replaced the traditional adhesive technology.

In recent years, Because of the successful application in the field of green chemistry and cleaner production research, room temperature Ionic liquids are considered to be the ideal alternatives for traditional volatile solvents. Ionic liquid is recognized as the green solvent of cellulose, for the advantages of low saturated vapor pressure, good dissolution properties and recycled. 1-butyl-3-methylimidazolium chloride (BmimCl), 1-ethyl-3-methylimidazolium chloride (AmimCl), 1-ethyl-3-methylimidazolium chloride (EmimCl) are reported to be used in the solution and reaction of cellulose, thus the application field of the cellulose are expanded.

In this review, the regeneration, derivatization and degradation from cellulose in ionic liquid were generalized. At last, the drawbacks and direction of future efforts of cellulose/ionic liquid system were discussed.

2. DISSOLUTION AND REGENERATION OF CELLULOSE IN IONIC LIQUID

During the regeneration of cellulose, cellulose is completely dissolved in its effective solvent, and precipitated from the solvent in a specific way to aggregate the expected cellulose products with excellent comprehensive properties. Since Ionic liquids that dissolve cellulose (such as BmimCl and AmimCl, etc.) are hydrophilic, they can be miscible with water in any proportion. Therefore, different forms of cellulose membranes and cellulose fibers can be reclaimed by using water as a solidification bath. After regeneration of the cellulose in the solvent system, the cellulose regeneration film and cellulose fiber can be prepared by further processing, which can be used in many fields.

Roger's research team first studied the ionic liquid used as a solvent of cellulose, they found that imidazole-based ionic liquids containing Cl- are suitable for dissolving cellulose, 1-butyl-3-methyl methylimidazolium chloride (BmimCl) ionic liquid can dissolve cellulose effectively, the solution of cellulose/ionic liquid was stable in dry environment, and the cellulose could precipitate when it meets water, which has opened up a new direction of cellulose solvent system [3]. A researcher found that the synthesized 1-allyl-3-methylimidazolium chloride (AmimCl) ionic liquid, through the introduction of allyl to the imidazole ring, had the excellent dissolving ability to cellulose [4]. After cellulose dissolved completely in the effective solvent, regenerated cellulose products with excellent comprehensive performance, such as regenerated cellulose film and regenerated cellulose fiber, can be obtained from the ionic liquid solvent in a specific precipitated way. Some researchers prepared regenerated cellulose film in AmimCl, the structure and performances of the regenerated cellulose film were also studied [5]. From the research, AmimCl is a direct solvent of the cellulose, and the cellulose crystalline form changed during the regeneration process. Then different kinds of cellulose, such as cornhusk cellulose, Hybrid Giant Napier cellulose and sugarcane bagasse cellulose, were used to study the regeneration of cellulose in ionic liquid [6-9].

New bio-based composite films from cellulose, starch and lignin were prepared in AmimCl ionic liquids by WU, and interactions among the components were also studied [6]. A researcher also successfully prepared regenerated cellulose membrane materials in AmimCl and 1- ethyl-3-methylimidazoles (EmimAc) with corn straw cellulose as raw material [7]. The results showed that AmimCl and EmimAc were nonderivative excellent solvents for corn straw cellulose. In the process of dissolving, crystal transformation changes from cellulose I to cellulose II; The structure of regeneration cellulose film is uniform and dense, and the mechanical properties are high, can reach 119 MPa and 47 MPa; The thermodynamic stability of cellulose membrane of recycled corn straw is high, and the initial thermal decomposition temperature is higher than 250 °C. AmimCl is more suitable as a solvent for straw cellulose regeneration than EmimAc.

A studied the solubility of cellulose in ionic liquid 1- butyl -3- methyl imidazole chloride (BmimCl) [8]. The structural changes of cellulose in ionic liquids were characterized. Unactivated cellulose can be directly dissolved in Ionic liquids, the lower the polymerization of procellulose without other derivative reactions occurring in Cl the easier it is to dissolve. The molecular weight of regenerated cellulose is lower than that of original cellulose.

Regenerated sugarcane bagasse cellulose film was successfully prepared from sugarcane bagasse cellulose in ionic liquid 1-allyl-3-methylimidazolium chloride ([Amim]Cl). The dissolution process of sugarcane bagasse cellulose, the properties and structures of the obtained regenerated cellulose films and the tensile strength of regenerated sugarcane baggage cellulose film were studied [9].

The dissolution and regeneration mentioned above used the cellulose extracting from straw as raw material. In recent research, the cellulose was extracted and regenerated successively from sugarcane bagasse, fir powder, pine sawdus and rice straw in ionic liquid, NaOH was added during the dissolution process [10-14]. A studied the dissolution and regeneration directly of Chinese parasol sawdust in AmimCl, the highest value of dissolution ratio could reach 23% [15]. The ionic liquid could partially dissolve Chinese parasol sawdust by destructing the inter- and intra-molecular hydrogen bond among lignocelluloses, and the regenerated Chinese parasol with homogenous and dense structure could be obtained.

Due to the good solubility of the cellulose in ionic liquid, researchers began to study, preparation of regenerated cellulose fibers through spinning in the ionic liquid. Some researchers discussed the rheological properties of cellulose/BmimCl solution, the preparation of cellulose fiber, the structure and the characterization of cellulose fiber [16]. The degree of fiber orientation and crystallinity increased with the increasing of tensile ratio, so that the mechanical properties of regenerated cellulose fiber also improved. Kosan investigated the cellulose in ionic liquid spinning performance [17]. Hermanutz prepared the regenerated cellulose fiber in ionic liquid using a dry-jet wet spinning method [18]. Zhang prepared functional and renewable cellulose composite fibers successfully, having a multi-walled carbon nanotube enhanced [19]. This kind of cellulose fiber has excellent mechanical properties, thermal properties and electrical conductivity.

3. THE DERIVATION OF CELLULOSE IN IONIC LIQUID

In the recent years, the homogeneous functional of cellulose has received increasing interest around the world. Homogeneous reaction is easier to get the products with the uniform performance, controllable degree of substitution and the simple reaction. As we know, cellulose acetate cellulose (CA) is an important derivative of cellulose, so the acetylating of cellulose in ionic liquids is reported frequently.

In a studied the homogeneous acetylation of cellulose in ionic liquid AmimCl by one step method [20]. Acetic anhydride is the esterifying agent, the reaction is carried out under relatively mild conditions (60 to 80 ° C), without any catalyst, the degree of substitution is between 0.94 and 2.74. The method has the advantages of simple process and no catalyst. And the product has the characteristics of controllable substitution degree and excellent solubility. Cao also reported the homogeneous acetylation reaction of cellulose in the ionic liquid AmimCl without any catalyst, different degree of substitution of cellulose acetate, the acetone-soluble and water-soluble cellulose acetate can be obtained [21-24]. The homogeneous acetylating reaction at the high concentrations (12 wt%) of cellulose / [Amim] Cl system was also studied, the obtained CA Showed a good solubility and thermal stability. Then the one step acetylated reaction of Pine wood chips in AmimCl was also discussed by Cao. Without any catalyst, the pine was successfully acetylated with the weight percentage gain(WPG) in the range of 89% to 156%. Some kinds of cellulose esters, such as Cellulose furoates, cellulose carbamate cellulose succinates, cellulose phthalates, cellulose sulfates, hydroxyalkyl cellulose cellulose acetate butyrate (CAB) and cellulose acetate propionate (CAP) have been prepared in ILs using SBC as raw material.

A studied the chemical modification of succinic anhydride on bagasse cellulose using BmimCl/DMSO as reaction medium, they found that reaction occurred at C6, C2 and C3 positions of cellulose, and the thermal stability of succinic cellulose decreased during modification [25,26]. Then, A series of phthalated cellulosic derivatives were prepared from sugarcane bagasse cellulose derivatives in BmimCl ionic liquid with phthalic anhydride. The degree of substitution (DS) of the product was 0.12-2.54. The Studies have shown that the increasing of the reaction time, the reaction temperature or the anhydride/cellulose AGU molar ratio can cause the increasing substitution of the product.

The homogeneous sulfonation of bagasse cellulose and chlorinated sulfuric acid - two methyl formamide was studied in ionic liquid BmimCl system [27]. The results showed that the degree of substitution of the bagasse cellulose sulfated product was 0.52-2.95. The sulfated bagasse cellulose has typical anticoagulant activity, and the anti coagulating activity of bagasse cellulose sulfonate is obviously related to the degree of substitution.

Water-soluble hydroxyalkyl cellulose with a molar degree of substitution of up to 2.79 was prepared under completely homogeneous reaction conditions in various ionic liquids without addition of inorganic bases. In acetate containing solvents the IL acts as a catalyst. The substitution patterns of the cellulose ethers were analyzed by 13C NMR spectroscopy, 1H NMR spectroscopy after peracetylation and GLC/MS after permethylation and depolymerization [28].

Cellulose acetate butyrate (CAB) and cellulose acetate propionate (CAP) were prepared homogeneously in a 1-allyl-3-methylimidazolium chloride (AmimCl) ionic liquid system from sugarcane bagasse (SB). sugarcane bagasse cellulose was successfully utilized in the homogeneous preparation of CAB and CAP using AmimCl ionic liquid as solvent, in the absence of any catalyst. CAB (acetyl content of 3.6-10% and butyl content of 27-46%) and CAP (acetyl content of 2.9-10% and propionyl content of 23-45%) can be obtained by controlling the reaction conditions. The structures of CAB and CAP were confirmed by $^1\mathrm{H}$ NMR and $^{13}\mathrm{C}$ NMR, which reveal the distribution of acetyl and butyl moieties in CAB and the acetyl and propionyl moieties in CAP [29].

Water-soluble hydroxyalkyl cellulose with a molar degree of substitution of up to 2.79 was prepared under completely homogeneous reaction conditions in various ionic liquids without addition of inorganic bases [30].

4. THE DEGRADATION OF CELLULOSE IN IONIC LIQUID

Efficient hydrolysis of cellulose-to-glucose or DMF is critically important in producing fuels and chemicals from renewable feed stocks. The methods of cellulose degradation include acid hydrolysis and traditional enzyme hydrolysis. Acid water solution requires high temperature, high

acid conditions, acid resistance, pressure resistant containers, although the yield of glucose can reach 50 %, but it seriously pollutes the environment, so it has now been abandoned. The appearance of Ionic liquids and their excellent solubility to cellulose have led researchers to start experimenting with cellulose / Ionic liquid systems. In this section, the monosaccharide (glucose and fructose) and 5-hydroxymethyl furfural (5-HMF) degraded from cellulose in ionic liquid were reviewed, respectively.

Li found that cellulose can degrade absolutely in the ionic liquid with the inorganic acid catalyst, at condition of atmospheric reaction and 100 °C [31,32]. Then, Hydrolysis properties of different dilute acids in different Ionic liquids on plant cellulose were investigated. The results show that the catalytic activity order of various acids on cellulose in Ionic liquids is $HCl>HNO_3>H_2SO_4>Maleic$ acid>Phosphoric acid. The reasearch fond that acidic Ionic liquid, such as [bmim] [HSO_4] And [Sbmim] [HSO_4] can not only be used as a solvent for cellulose, but also as a catalyst for cellulose hydrolysis. Hydrolysis of corn stalks, straw, pine, sugarcane bagasse as raw material in BmimCl containing 7% HCl was studied. However, the use of acid catalyst can cause environmental pollution to some certain extent, researchers study the hydrolysis of cellulose in ionic liquids with the enzyme-catalyzed. In the studied of Dadi, the cellulose was dissolved in IL and precipitated rapidly from IL, then lycosidase was used in the hydrolysis of the obtained regenerated cellulose [33,34].

Eight kinds of ionic liquids were used to investigate the reactivity and stability of cellulases by optical and calorimetric techniques, and tris-(2-hydroxyethyl) methyl ammonium methylsulfate (HEMA) was recognized as the most promising solvent, for the enzymes are stable to temperatures as high as 115°C [35]. A series of acidic ionic liquids (methylimidazolium-based acidic ionic liquids and pyrrolidonium-based acidic ionic liquids), used as catalyst, were synthesized and characterized [36-38]. BmimCl was used as the solvent of cellulose, the hydrolysis of cellulose into glucose in the presence of acidic ionic liquid was investigated systematically, pyrrolidonium-based acidic ionic liquids are indentified better than methylimidazolium-based acidic ionic liquids.

5-hydroxymethyl-2-furfural, abbreviated as 5-hydroxymethylfural(5-HMF), is an important chemical raw material that spans between carbohydrate chemistry and petrochemistry. Its molecules contain an aldehyde group and a hydroxymethyl group that can be hydrogenated, oxidized dehydrogenated, esterified, halogenated, polymerized and hydrolyzed, and other chemical reactions. Lima studied the degradation of cellulose to HMF, in the system of ionic liquid [Bmim] $CI/CrCl_3$ with the reaction time was 4 h and temperature was $100\,^{\circ}$ C, when adding B acidic ionic liquid [Emim] HSO_4 or H_2SO_4 , the conversion of cellulose to HMF yields can achieve 8% and 9%, respectively [39]. 5-hydroxymethyl furfural was prepared from the degradation of cellulose in ionic liquids.

A studied the efficient catalytic conversion of microcrystalline cellulose (MCC) to HMF in acidic ionic liquids (ILs) as the catalysts and metal salts as co-catalysts, and 69.7% yield of HMF is obtained [40]. In a studied cellulose one-step catalytic conversion to HMF in EmimAc Ionic liquid at the presence of a series of complex catalysts [41]. The results show that when only a single catalyst (CuCl $_2$ or CrCl $_2$) exists, the catalyst activity is very low and the product yield <10; Complex catalysts CuCl $_2$ /CrCl $_2$ has the highest activity. When the CuCl $_2$ ratio is 0.83-0.95, the yield of HMF can reach 65%. Li fond that under microwave condition, cellulose can convert to HMF in [Bmim]Cl using CrCl $_3$ as catalyst, and the yield can reach 61% in 2min [42]. It shows that microwave can promote the conversion of cellulose to HMF greatly.

5. CONCLUSION

In the development of novel, high performance cellulose material field, lonic liquids as a new green solvent have become a new, very practical platform of cellulose chemistry, it also brings great opportunities to the development of regeneration, derivatization and degradation of cellulose. However, the current research of cellulose/ionic liquid system is still preliminary, each link and association of cellulose / ionic liquid process will be a studied and further optimized systematically. Efficient synthesis

and recycling research can greatly reduce the cost of ionic liquids.

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