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Textile recycling via ionic liquids

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Abstract

Textile waste is a global problem, as it comprises a significant portion of landfill mass. Textile demand is increasing, which places demands on agriculture to produce more cotton. Industry standards of spinning and dyeing cotton fibers is hazardous and consumes large amounts of energy. The viscose method of wet spinning is the most common industry method, and uses large amounts of water, time and energy. Ionic liquids (ILs) have been shown to dissolve organic matter such as cellulose fibers and have shown promise in separating waste polymer-cellulose textile blends. When the cellulose concentration is high enough, the IL-cellulose solution can be wet spun, producing recycled fibers. The remaining polymer fibers can also be respun and possess characteristics competitive to virgin polyester fibers. The process has been shown to preserve dyes, if desired, or remove the original coloring and produce neutral fibers, relieving industry strain in the dyeing process and saving time, water, and energy.

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1. Introduction

According to the EPA, the US produces 25 billion lbs/year of textile waste. Only 15% of this waste is currently recycled. Textile waste occupies 8% of the total landfill mass. Polyester/cotton blends represent a large portion of textiles on the market. The demand for textile fibers is expected to rise at the rate of 3% per year [11]. This demonstrates the importance of further studies on the topic of cellulose regeneration from waste textiles. Additionally, cellulose fibers are increasingly being produced from wood in industry, which is creating a strain on international forest lands, further highlighting the need for cellulose fibers to be recycled rather than sent to a landfill. Regeneration of fibers from textile waste can both meet future textile production needs and reduce overall textile waste. Dyeing textiles is energy and water demanding, and if regenerated fibers can retain their color, it can further reduce energy consumption in future textile production [4, 8]. Currently, recycling of cotton/polyester blends includes either depolymerization or dissolution of one of the components. A common industry method is to subject the polyester to alcoholysis, hydrolysis, or glycolysis reactions, or degrade the cellulose under acidic conditions with a similar reaction. Dimethyl sulfoxide (DMSO) is the most common solvent currently used in the dissolution of polyester, which is toxic, requires high temperatures, and influences the properties of the remaining cellulose component. The least toxic way currently being used in industry is to use hydrochloric acid to hydrolyze cotton and generate a microcrystalline powder, which can then be separated from the polyester fibers, allowing the polyester fibers to be respun while most of the cotton is wasted [10].

This paper investigates newer environmentally benign methods which employ ionic liquids (ILs) to dissolve the cotton component in solutions of up to 1-2% cotton, then filter out the polyester fibers. The polyester fibers can then be respun, and the cotton solution further concentrated to 15-17% cotton from stock fibers, allowing the cotton fibers to be respun as well. Both the reclaimed cotton and polyester fibers generated in this manner are indifferentiable from virgin fibers [1, 2, 3, 5, 8, 9]. Other more recent studies further optimize the IL method by using IL N-Methylmorpholine-N-oxide (NMMO), IL 1-Allyl-3-methylimidazolium chloride (AMIM-CL), or IL 1-butyl-3-methylimidazolium (BMIM-OAc) to dissolve the cotton fibers from textile blends and yield solutions of up to 35% cellulose. The rheological properties of the high concentration cellulose solution render it appropriate for use in wet spinning without further

processing, which eliminates the step of increasing the concentration of the cellulose solution from stock fibers and allows all the cotton fibers to be reclaimed without the need of mixing in virgin fibers [10]. Polyester fibers are readily recyclable, and proof of concepts in recent papers to respin cellulose waste prove promising.

2. Mechanism of dissolution and depolymerization of cellulose fibers via ionic liquids

One reason ILs are attractive for the dissolution of cellulose is their physical properties can be tailored by the selection of ions and substituents on the R cation group. Thus, the water solubility of imidazolium, oxide acetate, and methyl oxide ILs can be tailored for the needs of a specific cellulose fiber depending on the DP [3]. Cellulose fibers are held together by hydrogen bonding. Synchotron X-ray and neutron diffraction data shows the intermolecular bonds between the hydroxyl group on C6 in a cellulose molecule hydrogen bonded to the O atom on C3 of an adjacent cellulose chain (**Figure 1**). When these hydrogen bonds are disrupted, the cellulose fibers will separate and dissolve in an IL [1]. This is accomplished when the anion in the IL form H-bonds with the hydroxyl groups in several adjacent chains, causing the negatively charged anion-cellulose complexes to repel each other and separate. It is noted here that the cellulose fibers are not chemically broken down, rather, the cations in the ionic liquid compete with the intermolecular bonding site the cellulose fibers form H-bonds at, causing the cellulose fibers to dissolve in the IL. They can readily be respun using the IL/cellulose solution as the SD after they are isolated from the poly-cotton blend [9].

Chemical Recycling differs from the mechanisms discussed above to dissolve cellulose fibers in either ILs or acid baths. Notably, chemical recycling involved using a catalyst to depolymerize one of the two polymers in a poly-cotton blend. Once the monomers are isolated, they can be repolymerized so that both components of the poly cotton blend are recovered [9].

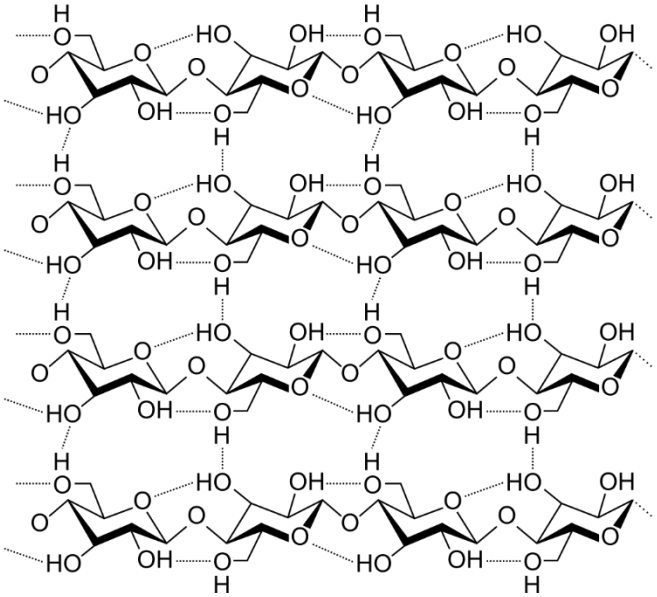

Figure 1. Molecular structure of cellulose. Image by Laghi.l, distributed under a CC BY-SA 3.0 license [12].

3. Overview of chemical recycling methods and applications

3.1. Early research on IL selectivity for fiber separation

Silva et al presents a method to separate cotton and polyester fibers into fibers indistinguishable from virgin fibers. Two ionic liquids were purchased from sigma Aldrich and dried thoroughly until both were less than 0.2% water. AMIM-CL and BMIM-OAc were selected for this project because of their cellulose dissolving properties. It was unknown if these IL's would dissolve polyester, so pure polyester fibers were submerged in each IL for 48 hours. No weight loss of polyester was observed over this period, so it was determined that neither AMIM-CL nor BMIM-OAc would dissolve polyester. To test the efficacy of the IL's in separating cotton and polyester fibers, yarn specimens were oven dried, then 5 samples were prepared of yarn solutions in both BMIM-OAc and AMIM-CL at 80 ºC (2%, 4%, 6%, 8%, and 10% yarn sample by weight). The samples were left for 6 hours, then solids were removed, rinsed, and weighed. To determine the quality of the recovered fibers the recovered cotton was characterized the via DMA, TGA, and FTIR, and these results were compared with data from as received virgin fibers. No difference was noted. Recovered polyester fibers were characterized via DSC, TGA, Carbon NMR, and FTIR, and contrasted with as received virgin fibers, again with no difference noted. AMIM-Cl is shown to selectively dissolve the cotton components of cotton/polyester blends at higher yields than BMIM-OAc, however both ILs produce recovered polyester fibers at very high yields [2].

Seoud et al, proposes several strategies to address the growing need for cellulose fibers in industry through the regeneration of dissolved cellulose in ILs and alkali solutions. Chemical recycling of poly-cotton blends (which differs from chemical and physical dissolution of cellulose fibers in ILs or alkali solutions) is also addressed in this article, because it offers an environmentally benign approach to closing the cellulose gap. The mechanism by which cellulose fibers are chemically recovered is through both depolymerization and preferential dissolution. The article states that IL's completely dissolve cellulose polymers with widely varying degrees of polymerization successfully. Other methods of producing recycled cellulosic fibers chemically include chemical or physical dissolution of cellulose polymers in alkali baths. For instance, the popular viscose rayon fiber is produced by chemical dissolution in which cellulose fibers are regenerated from cellulose xanthate salts dissolved in an acid bath. Lyocell fibers are produced by complete physical dissolution of cellulose fibers in in N-methylmorpholine-N-oxide Hydrate, after which Lyocell fibers are regenerated in an aqueous bath. Many imidazolium IL's are cited as being used in dissolving cellulose fibers [9].

3.2. Respinning recovered fibers

Ma et al proposes the use of ionic liquids to dissolve cotton fibers in denim then regenerate new fibers via wet spinning. The process can be done in a way that preserves the original

coloring of the fibers or can remove the original coloring and produce neutral fibers, leaving more options available for buyers of recycled fibers. The process uses DMSO and IL BMIM-OAc to dissolve cellulose fibers in denim waste. The addition of DMSO as a cosolvent reduces the viscosity of the spinning dope (SD, the first component of the wet spinning process in textile manufacturing. The dope is a dissolved polymer solution and is formed prior to spinning the solution into filaments using the wet-spinning line) which saves energy in the spinning process of regenerating fibers. The cotton fibers to be recycled were pretreated via grinding into a fine powder of <0.2 mm particles. They were then immersed in an aqueous NaOH solution at 90 ºC then washed with DI water until a neutral pH was regained and dried in an oven. The treated fibers were then dissolved in a 1:4 DMSO and BMIM-OAc solution at 80 ºC for 30 minutes. The degree of polymerization (DP) of the fibers were measure in an Ostwald viscometer. They were then wet spun with the SD kept at 70 ºC. The rheology of the SD of the various samples were analyzed on a Rheometer and recorded. The mechanical properties of the recovered fibers were also analyzed in an Instron load cell and SEM imaging was performed on the sample. The mechanical properties of the recovered fibers were found to be identical with comparable virgin fibers. The rheology of the SD was found to be influenced by temperature, polymer concentration, DP, and the addition of cosolvent DMSO. A 20:80 DMSO and BMIM-OAc solution was found to yield the best spinnability, and polymers with a high DP yielded better tensile properties. Future work should be done to maximize desirable material properties such as yield strength and minimize the cost and energy to produce regenerated fibers [8].

Haslinger et al also aimed to transform the cellulose fibers reclaimed from the above IL methods into man made cellulose fibers (MMCF's). Cotton polyester blend textile samples were obtained from a German industry supplier and were shredded and blended. The content was determined to be 50% cotton and 50% polyester. They were treated to remove silicates and metals, and the viscosity was adjusted via ozone and hydrogen peroxide to reduce the degree of polymerization. The sample was also homogenized then further disintegrated on a Wiley mill before determining the molecular mass distribution of the sample vie Gel Permeation Chromatography. Cellulose solutions of 6.5 %wt. were then prepared in the manner outlined above (selective dissolution of cellulose components via an IL, then filtration of the polyester fibers and extensive rinsing with DI water). The samples allowed to solidify, then placed in a dry-jet wet-piston spinner and the SD was melted and extruded. The resulting filaments were then evaluated for draw ratios and coagulated in a water bath. The resulting MMCF's were analyzed via TGA, GPA, SEM, and tensile tests and were found to have material properties desirable in industry. In every way, the fibers were either identical to virgin fibers, or superior. This method for dry-jet wet-piston spinning successfully demonstrated a method to convert pure cellulose waste to saleable MMCF's. The extensive pretreatment steps are deemed necessary however, as the rheology and MMD of preconsumer cotton waste are far outside of the boundaries for spinning procedures [10].

4. Conclusions

The method by which cellulose dissolves, coupled with the insolubility of polyester in both Acetate and Imidizolium ILs identifies this group of ILs as appropriate solvents for separating cellulose/polyester blends through the dissolution of cellulose fibers in ILs. Research conclusively shows that this method can separate cotton and polyester fibers in high yield that are indistinguishable from virgin fibers. The reclaimed cellulose fibers can then be respun via wet spinning, and the cellulose/IL solution is an appropriate spinning dopant with no further processing necessary, which makes this process incredibly efficient for industry use. The reclaimed cotton fibers can be produced in a manner that preserves their original coloring if desired, making dyeing unnecessary and further improving the efficiency of this method. The reclaimed polyester fibers can also be wet spun when suspended in an appropriate solvent that provides the proper rheological properties necessary for wet spinning.

Conflict of Interest

The author has not conflict of interest to declare.

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