Separation and development of polymer blends:

An environmentally friendly approach

by

Rasike De Silva, BSc. Eng. (Hons)

Submitted in fulfilment of the requirements for the degree of

Doctor of Philosophy

Deakin University

January, 2016

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Contribution to the knowledge

Journal Papers


Conference Papers


Featured articles

- “Australian breakthrough in recycling textile and other waste”, Recycling international news, August 2015.

- “Australian project claims near total recovery rates”, Closing the loop report, pp.53, 2015.

- “Ionic liquids used to recycle poly/cotton textiles”, Eco textile news, pp.5, July 2015

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<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>AGU</td>
<td>Anhydroglucopyranose units</td>
</tr>
<tr>
<td>AMIMCl</td>
<td>1-allyl-3-methylimidazolium chloride</td>
</tr>
<tr>
<td>ATR</td>
<td>Attenuated total reflectance</td>
</tr>
<tr>
<td>BMIMCl</td>
<td>1-butyl-3-methylimidazolium chloride</td>
</tr>
<tr>
<td>BMIMOAc</td>
<td>1-butyl-3-methylimidazolium acetate</td>
</tr>
<tr>
<td>CA</td>
<td>Cellulose acetate</td>
</tr>
<tr>
<td>CDF</td>
<td>Cellulose/duck feather blends</td>
</tr>
<tr>
<td>(CH$_3$CO)$_2$O</td>
<td>Acetic anhydride</td>
</tr>
<tr>
<td>CF$_3$COOH</td>
<td>Trifluoroacetic acid</td>
</tr>
<tr>
<td>$^{13}$C NMR</td>
<td>$^{13}$Carbon nuclear magnetic resonance</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>Carbon dioxide</td>
</tr>
<tr>
<td>CS</td>
<td>Cellulose/silk blends</td>
</tr>
<tr>
<td>CS$_2$</td>
<td>Carbon disulphide</td>
</tr>
<tr>
<td>CSW</td>
<td>Cellulose/silk/wool blends</td>
</tr>
<tr>
<td>cuam, <a href="OH">Cu(NH$_3$)$_4$</a>$_2$</td>
<td>Cuprammonium hydroxide</td>
</tr>
<tr>
<td>CUEN</td>
<td>Bis (ethylenediamine) copper (II) hydroxide solution (cupri-ethylenediamine hydroxide)</td>
</tr>
<tr>
<td>CW</td>
<td>Cellulose/wool blends</td>
</tr>
<tr>
<td>D$_2$O</td>
<td>Heavy water</td>
</tr>
<tr>
<td>DMA</td>
<td>Dynamic mechanical analysis</td>
</tr>
<tr>
<td>DMAc</td>
<td>N,N-dimethylacetamide</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethyl formamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethyl sulfoxide</td>
</tr>
<tr>
<td>DMSO-$d_6$</td>
<td>Deuterated dimethyl sulfoxide</td>
</tr>
<tr>
<td>DP</td>
<td>Degree of polymerisation</td>
</tr>
<tr>
<td>DS</td>
<td>Degree of substitution</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>EMIMCl</td>
<td>1-ethyl-3-methylimidazolium chloride</td>
</tr>
<tr>
<td>EMIMMe$_2$PO$_4$</td>
<td>1-ethyl-3-methylimidazolium dimethylphosphate</td>
</tr>
</tbody>
</table>
[EMIM][P(OCH₃)(H)O₂] 1-ethyl-3-methylimidazolium methylphosphonate
EMIMOAc 1-ethyl-3-methylimidazolium acetate
EU European Union
FSD Fourier self-deconvolution
FTIR Fourier transform infrared spectroscopy
G' Storage modulus
G'' Loss modulus
¹H NMR Proton nuclear magnetic resonance
H₂O Water
H₂O₂ Hydrogen peroxide
H₂SO₄ Sulphuric acid
IL Ionic liquid
LiBr Lithium bromide
LiCl Lithium chloride
M Morpholine
MCC Micro-crystalline cellulose
N₂O₄ Dinitrogen tetroxide
NaOH Sodium hydroxide
NMM N-methyl-morpholine
NMMO N-methylmorpholine-N-oxide
PAN Polyacrylonitrile
PET Poly ethylene terephthalate (polyester)
PLM Polarising light microscope
PVA Polyvinyl alcohol
Rₛ Gyration radius
RTIL Room Temperature Ionic Liquid
SAXS Small-angle X-ray scattering
SEM Scanning electron microscopy
TBAF Tetra-n-butylammonium fluoride
Tₜ Thermal degradation temperature
TGA Thermogravimetric analysis
USA United States of America
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
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<tbody>
<tr>
<td>WAXD</td>
<td>Wide-angle X-ray diffraction</td>
</tr>
<tr>
<td>wt%</td>
<td>Percentage by weight</td>
</tr>
<tr>
<td>ZnO</td>
<td>Zinc oxide</td>
</tr>
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Abstract

This thesis aimed to regenerate a new cellulose-based fibre with improved properties by using textile waste feedstock. This was achieved via a polymer blending technique in the solution state. Two imidazolium based ionic liquids (ILs); 1-allyl-3-methylimidazolium chloride (AMIMCl) and 1-butyl-3-methylimidazolium acetate (BMIMOAc) were used as the dissolving media. The cellulose used in the fibre regeneration was obtained by recycling polyester/cotton blend yarns into their individual components. The cellulose was blended with three other natural protein polymers at different polymer combinations and blend compositions. The three protein polymers used for blending were silk (wild muga), wool (merino) and duck feathers.

This study originated with the polyester/cotton blend recycling work to obtain cellulose for fibre regeneration. In this context, 50/50 polyester/cotton blend undyed yarns were chemically separated using the above mentioned ILs. This was achieved by selectively dissolving the cotton component, leaving the polyester part intact. The characteristics of the undissolved polyester (recycled) component were shown to be similar to the pure polyester sample, with a purity of no less than 98%.

The dissolved cellulose (recovered from polyester/cotton blend) was then regenerated into film form using distilled water as the coagulant. The regenerated cellulose films were very brittle, with a low tensile strain at break. It was found that the poor tensile properties occurred due to the inevitable reduction of the degree of polymerisation (DP) of the regenerated cellulose during the process. Therefore, the effect of processing parameters on the DP of the regenerated cellulose were further investigated and optimum processing parameters were established.

In order to further improve the properties of the regenerated cellulose (C100), cellulose was blended with silk, wool and duck feather in solution to produce different bi-polymer solutions. The blended polymer solutions were regenerated into film form using distilled water as the coagulant. The tensile properties measured for the regenerated films showed that the addition of duck feathers noticeably improved the elastic properties of the final material. Next, cellulose/duck feather blend films with
different blend ratios were fabricated to determine the optimum blend ratio which showed the greatest improvement in elasticity. The optimum blend ratio for cellulose: duck feather was found to be 90:10 (CDF90). The ability of duck feathers to maintain their $\alpha$-helix confirmation after the regeneration, as revealed by the FTIR deconvolution, accounted for the improvement in the elasticity.

The solution state properties of the cellulose solution (C100) and optimum polymer composition (CDF90) were characterised through fibre formation using a wet spinning method. Diffusion kinetics and rheology of the polymer solutions were assessed in this context. The diffusion equilibrium results for C100 solutions showed that the diffusion was viscosity driven. Further, it revealed that residual IL was trapped in the regenerated fibre. The trapped IL caused the continuous reduction in DP of the regenerated cellulose over the storage time. Polymer solutions in AMIMCl were shown to have a higher diffusion and less trapped IL compared to BMIMOAc. It was proposed from $^1$H-NMR chemical shift of the water peak in glucose-IL-water model that the BMIMOAc interacted strongly with cellulose in solution. Therefore, AMIMCl was selected as the solvent for fibre formation.

The rheology of polymer solutions investigated at different conditions displayed a non-Newtonian behaviour with shear thinning. The viscosity of the solution increased with the polymer concentration. Conversely, viscosity was reduced with the increase of temperature. Therefore, fibre formation of solutions with higher polymer concentration was possible at an elevated temperature. Solutions with 8 wt% polymer concentration of C100 and CDF90 at 40 °C were extruded at a fixed flow rate into a distilled water bath. The produced fibres were manually drawn and the tensile properties were measured. As expected, the elasticity of the CDF90 fibre was further enhanced by applying a stretch ratio of 13.3%. The overall improvement in elasticity in the drawn CDF90 blend fibre was 66.5%. After the regeneration process, the IL was recycled and reused in subsequent processing.

The work presented in this thesis, therefore, has shown a potential path to developing a new regenerated cellulose-based fibre using recycled cellulose and duck feather, which could be used in textile applications. Additionally, the use of recycled cellulose
from polyester/cotton blends could be explored as a way of closing the loop in the
textile supply chain, which could have profound implications both economically and
environmentally.
CHAPTER 1
Introduction to research program

1.1 Background

The global fibre production for the textile industry in 2014 was around 90 million tonnes [1] and its growth is correlated with the growing world population and rapid change in fashion trends [1, 2]. Figure 1.1 shows the global fibre supply in year 2014. Synthetic fibres, such as polyester accounted for the largest portion (62.6%) followed by cotton (29.4%), man-made cellulose fibres (6.7%) and wool (1.3%). Among all the textile fibre types produced, cotton is the most important natural cellulose fibre in the world due to its excellent properties such as good moisture absorbency, comfortable soft handle and drapability [3]. However, cotton crops consume large amounts of land and water, which has limited the cotton supply over the last few decades [3-5]. It is anticipated that the global megatrends (population growth, sustainability, climate change) and a limited cotton supply as a result of the global increase in fibre consumption will lead to a demand overload of cellulose fibres (“cellulose gap”) [1]. As such, man-made cellulose fibres have become increasingly popular as substitute fibres for natural cotton.

Figure 1.1: Global fibre market 2014 [1]
Man-made cellulose fibres, often called regenerated cellulose fibres are produced by dissolving wood pulp in a solvent [1, 4, 5]. To date, there are only two classes of regenerated cellulose fibres commercially available; with viscose currently the most commonly used. In the viscose process, cellulose is converted into sodium cellulose xanthate using carbon disulphide (CS\(_2\)), which makes the cellulose soluble in NaOH, the fibre is then wet spun from the NaOH solution [4, 6, 7]. A major disadvantage of this process is the use of CS\(_2\), a volatile and toxic gas, which is harmful to both the environment and human health [8-10]. In the lyocell process, cellulose is directly dissolved in \(N\)-methylmorpholine-\(N\)-oxide (NMMO) and dry-jet spun from the NMMO solution [4, 5, 11]. This method has long processing times and causes the formation of by-products due to the degradation of both NMMO and cellulose [4, 5].

With the increase of global fibre consumption, the amount of waste generated from the textile industry continues to increase, with approximately 12 million tonnes of textile waste generated in the USA [12] and EU [13] per year alone. The waste produced by the global textile industry each year is either disposed of in landfill and/or incinerated. Hence, the textile industry is a considerable contributor to global warming through the release of harmful greenhouse gases such as methane and carbon dioxide [14-16]. A significant hurdle for recycling textile waste, is that most of them are composed of blended fibres, with the most common blend being polyester/cotton [15-17]. Therefore, recycling of polyester/cotton blends greatly influences textile waste management. The three protein polymers used for blending in this study were wild silk, wool and duck feathers. It is worth noting that massive amounts of fibrous waste of silk and wool are discarded to landfills during textile manufacturing [18, 19], and duck feathers on the other hand, has been one of major waste issues in the poultry industry [20, 21].

The use of these textile wastes, however, has not yet been fully exploited due to a number of challenges. Such challenges include the limited number of solvents which can dissolve the textiles waste and the difficulty involved in separating the polyester/cotton blended textile waste into reusable forms for effective recycling [22-24]. In the recycling of polyester/cotton blends, the dissolution of the polyester
component from the blend is not economically or environmentally viable. Polyester has limited solubility in most solvents and those in which it is soluble, are both volatile and very toxic [25].

1.2 Motivation

It should be noted that the production of textiles from raw fibrous materials (both pure natural and synthetic fibres) generates approximately 15 kg of CO₂ per 1 kg of textile produced and consumes a large amount of water, energy and chemicals [23]. This indeed puts both the environment and human health at risk. Therefore, the reuse of textile waste is an opportunity for sustainable global environmental management in view of the conservation of resources, a reduced carbon footprint, as well as reducing landfill.

Current cellulose fibre regeneration methods encounter both processing and environmental drawbacks. Therefore, new cellulose regeneration methods are constantly being sought. One relatively new and growing class of cellulose solvent for regeneration is ionic liquids (ILs). ILs are environmentally friendly designer solvents that have been shown to dissolve a range of natural polymers including cotton, silk, wool, and duck feather [7, 24-27]. Moreover, the design flexibility of ILs opens the possibility for separating polyester/cotton blend wastes into reusable forms, hence allowing for effective utilisation of textile waste.
1.3 Research aims

Therefore, this project is aimed at developing a new regenerated cellulose-based fibre with improved properties, using ILs as processing solvents. The improved fibre properties will be achieved via blending polymers in the solution state. Natural polymers; cellulose (cotton) and proteins (silk, wool and duck feather) will be utilised as the starting polymers for blending. Furthermore, this project seeks to utilise the cellulose, which will be separated from the polyester/cotton blend materials.

With this overall goal, the research strategy for this project can be divided into two research aims.

1. To understand the interactions associated within ionic liquids and polymer blends, for effective separation (for polyester/cotton blends- Chapter 04) and utilisation (natural polymer blends-Chapter 05) of polymers.

2. To develop a structure-property relationship towards designing new regenerated cellulose-based fibre (Chapters 05 & 06).

As a result, development of such regenerated fibre could potentially be a good addition for regenerated fibre market, it is also a good platform for recycling polyester/cotton blend materials by effectively separating the blend into its pure forms.
1.4 Summary of thesis

1.4.1 Research plan

**Hypothesis 1:**
Polyester/cotton blend textiles can be separated by selectively dissolving cotton component by using imidazolium based ILs (Discussed in Chapter 4)

- Varying the processing parameters of separation process:
  - IL, Temperature, Polymer wt%
- Characterisation of undissolved polyester:
  - DMA, SEM, DSC, TGA, FTIR
- Characterisation of Regenerated cellulose from recovered cellulose:
  - SEM, DSC, TGA, NMR, FTIR

**Hypothesis 2:**
Elasticity of regenerated cellulose can be improved by blending it with a dissolved protein polymer in IL (Discussed in Chapter 5)

- Cellulose/Protein polymer compositional variations:
  - Polymer blend combinations, blend ratio, different coagulants
- Characterisation of regenerated cellulose/protein blends:
  - DMA, FTIR, SEM, TGA

Towards developing a new regenerated fibre
(Discussed in chapter 6)

- Solution properties: Rheology, Diffusion
- Spinning parameters: Stretch ratio

New regenerated cellulose-based fibre with improved properties
1.4.2 Thesis outline

This thesis consists of seven chapters. The contents of the remaining chapters are outlined below.

Chapter 2:
Chapter 2 reviews the literature of the related work and will identify gaps which define the research aims and plan. This literature review will briefly summarise the:

1. Natural fibres-structure and properties
2. Regeneration methods for natural polymers
3. Recycling polyester/cotton blends
4. ILs for natural polymer processing
5. Wet Spinning parameters influencing the fibre properties

Chapter 3:
This chapter describes the experimental procedures including materials and preparation, methodology of material characterisation with key techniques used, and finally, methods used for data analysis and error analysis.

Chapter 4:
The content detailed in the chapter 4 describes the use of ILs to separate polyester/cotton blends by selectively dissolving cotton component from the blend. Then, the regeneration of dissolved cellulose in the film form at different processing conditions and material properties are also explained in this chapter.

Chapter 5:
Chapter 5 focuses on improving the tensile properties of the regenerated cellulose via blending cellulose with natural protein polymers. This chapter investigates the material properties of regenerated cellulose blended with various protein polymer compositions in IL.
Chapter 6:
The work in chapter 5, determined the optimum polymer blend composition which improved the tensile properties of the regenerated material. Then, chapter 6 investigates towards wet spinning a new regenerated cellulose-based fibre from the polymer blend composition mentioned above. This chapter also discusses how IL-polymer solution state properties and spinning parameters affect the ‘spin-ability’ of the polymer solution and the material properties of regenerated fibres.

Chapter 7:
This chapter summarises the key outcomes of this research and gives recommendations for future studies.
2.1 Natural fibres-structure and properties

For thousands of years, natural fibres such as cotton, silk, wool and other vegetable fibres have been used in textiles. A ‘textile fibre’ is defined by the Textile Institute [26] as a unit of matter characterised by flexibility, fineness and a high length to thickness ratio. It should also have adequate strength and moderate flexibility, which can be used for general textile purposes. Textile fibres can be classified as natural fibres and synthetic fibres. Natural fibres are derived from natural polymers and man-made fibres are derived from either petroleum based polymers (synthetic) or regenerating natural polymers [27].

2.1.1 Natural fibres

Natural fibres are derived from plants, animals and mineral sources which can be classified according to their origin [28]. Among many natural fibres available, four natural fibre types; cellulose fibre cotton and three protein fibres; silk, wool and duck feather have been used in this work. A brief description of each of these fibres are given in this section.

2.1.1.1 Cotton fibre

Cotton is a natural cellulose fibre which has enormous importance in textiles due to its many desirable textile properties, including strength, absorbance, pilling resistance, flexibility and durability [3, 29].
The major component of cotton is cellulose, which is about 95% of the fibre composition present in plant cell walls [3]. The other minor non-cellulosic components in the cotton are protein, pectic, wax, sugar, organic acids, and other pigments [3].

The molecular structure of cotton cellulose is a polysaccharide of D-anhydroglucopyranose units (AGU) linked by $\beta$ (1→4) glycosidic bonds between C-1 and C-4 of adjacent AGU, as shown in Figure 2.1 [3, 29, 30]. These AGUs are rotated 180° to each other due to $\beta$-linkage. Each AGU has three equatorially located hydroxyl (O-H) groups at C-2, C-3, and C-6. The repeating unit of cellulose is often known as ‘celllobiose’ which is composed of 2 AGU [3, 29]. The terminal groups of the cellulose molecule are different from each other. The C-1 O-H of the molecule is an aldehyde group with a reducing nature. These aldehyde groups create a pyranose ring via intramolecular hemi-acetal form [3, 29, 30]. The C-4 O-H of the molecule is an alcohol-borne O-H component, which is the non-reducing end [3, 29, 30].

![Figure 2.1: Molecular structure of cellulose with the repeating unit of celllobiose](image)

The cellulose chain length often depends on the cellulose source and the subsequent treatments [3]. For example, in untreated raw cotton fibre, the molecular chain length (degree of polymerisation [DP]) could be higher than 10,000 celllobiose units.

The equatorially located O-H groups of the cellulose chain play an important role in the formation of both inter- and intra- molecular hydrogen bonding, as shown in Figure 2.2. The intra-molecular hydrogen bonds (within the same molecule) form between C-2 O-H and C-6 O-H groups (Figure 2.2.a.1) as well as C-3 O-H and
endocyclic oxygen (Figure 2.2.a.2). The inter-molecular hydrogen bonds (with adjacent cellulose molecules) form between C-3 O-H and C-6 O-H groups (Figure 2.2b) [3, 29].

These intra- and inter-molecular hydrogen bonds cause the cellulose chains to group together in highly ordered (crystal-like) structures [3, 29]. In fact, both highly ordered (crystalline) and less ordered (amorphous) regions are present in a single cotton fibre [3]. Generally speaking, cotton fibres have different crystalline and amorphous regions depending on the type of source and consequent treatments corresponding to the location of hydrogen bonds between and within the polymer chains [3]. Natural cellulose has a strong highly ordered cellulose I crystal structure. Cellulose I crystal structure has complex hydrogen bonding systems between the C-3 O-H and O-5 which is very typical for β (1→4) linked molecules [3]. The intra-molecular hydrogen bondings and the β-linked bond angle of 180° make cotton a relatively stiff and rigid linear chain, which makes a good fibre forming polymer [3, 29, 30].

Indeed, the strength of cotton fibres is related to this highly ordered cellulose I crystal structure owing to its hydrogen bond formations. Cotton is one of the few fibres which improves strength when it is wet [3, 29, 30]. It is reported [29] that the improved wet
strength occurs due to a temporary improvement in the molecular chain alignment in the amorphous regions which results in increasing the number of hydrogen bonds.

Due to this extensive hydrogen bond network, cotton does not dissolve in water and many organic solvents [7, 28]. Therefore, this hydrogen bond network has to be disrupted to dissolve cotton.

2.1.1.2 Protein fibres

Silk and wool are the two main protein fibres used in textiles. Duck feather is utilised in the textile industry in small quantity for the manufacture of manchester (i.e. bedding and pillows) [31] and also used in the shuttlecock for badminton [20]. Both wool and duck feather keratin exhibit a similar structural conformation, which is different to the structure of silk. Due to these different protein structures, they offer very distinct properties to each other.

Silk is a natural protein fibre and has been used in textiles since ancient time due to its remarkable tensile properties, unique lustre, tactile properties, durability and dye-ability, as well as in biomedical applications due to its biocompatibility [28, 32, 33]. Silk fibres possess a β-sheet protein structure due to the hydrogen bonds formed between –C=O and –N-H groups among the adjacent chains as illustrated in Figure 2.3 (a) [29, 32, 34]. These fibroin chains are deemed to be fully extended, highly crystalline and aligned with the fibre direction. Such an arrangement contributes to the silk fibre’s excellent tensile properties, such as strength and stiffness. This strong hydrogen bond network makes the silk fibre extremely difficult to dissolve using water and most common organic solvents [23, 35].
Wool is another important natural protein fibre in textiles due to its insulating and high moisture absorbing properties [37, 38]. Wool has a stable cross-linked 3D structure through disulphide bonds, hydrogen bonds, salt links and the peptide bonds among individual amino acids [18, 37]. Duck feather is α-keratin based protein material similar to wool structure, which consists of about 90% keratin that contains about 7% cysteine [21, 31, 39, 40]. It is considered largely to be a waste material [21, 40]. Duck feather is under-utilised as it is a difficult material to solubilise due to the tight arrangement of the α-helix and β-sheet in the polypeptide chain [21, 31, 39].

In contrast to silk, wool and duck feather possess a twisted α-helix configuration due to inter-molecular hydrogen bonds between –C=O and –N-H groups within the single chain on the turns of the coil as shown in Figure 2.3 (b). Due to this twisted structure, they are inherently compliant, extensible and can easily recover after large strains are applied [29, 37].

Figure 2.3: Structure of (a) a strand of silk with β-sheets [34], (b): α-helix structure of wool and duck feather [36]
2.1.2 Synthetic fibres

Synthetic fibres are derived from petroleum-based polymers. Despite the environmental issues and the shortage of these non-renewable petroleum-based resources, the demand for the synthetic fibres is increasing due to their low cost [2, 15]. The most common synthetic fibres used in textiles are polyester (PET), polyamide (nylon), polypropylene, polyacrylonitrile (PAN), and aramid fibres [2, 15, 26, 41-43]. As far as textile fibres are concerned, polyester and its blends have been the dominant source of raw materials in the global fibre market due to their lower production costs and easy processing of PET [2, 15].

2.1.3 Polyester and polyester blends

Polyester, known as poly ethylene terephthalate (PET) was discovered by W.H Carothers of Du Pont in the 1930s when he discovered that alcohols and carboxylic acids can be combined through esterification to form a new form of fibre [44]. The formation of polyester is shown in Figure 2.4.

![Figure 2.4: Formation of polyester](image)

In addition to easy processing and lower production costs, desirable properties such as high durable strength, easy washability, quick drying time, and wrinkle and abrasion resistance have made PET useful as both filaments and as a staple fibre in the textile industry.
Blending of polymers is a well-known method to improve the final properties of the textile material [24, 45]. In textiles, the most common blend is that of polyester with cotton due to their distinct textile properties. As a result, the largest textile waste is comprised of polyester/cotton blends [15, 16]. In these blended fabrics, the cotton component adds to the comfort properties such as moisture absorbance and drape of the fabric, whereas polyester gives durable properties such as durability, wrinkle and abrasion resistance.

The combination of polyester with wool is another common textile blend. Polyester is blended with wool to aid shape retention, as well as enhance wrinkle and abrasion resistance of the fabrics in all weather. Wool in the blended fabric gives the material a good drape and elasticity.

The increasing demand for textile materials made from cotton, silk, wool and polyester blends [2] consequently results in the generation of considerable amounts of waste to the environment. The utilisation of these textile wastes has not been fully exploited due to the limited number of environmentally friendly regeneration methods. The current methods to regenerate natural polymers are discussed below, along with recycling methods for polyester blends.

### 2.2 Regeneration methods for natural polymers

Many different dissolution methods have been employed to regenerate cellulose, silk, and wool. The hydrogen bond network of these natural polymers makes processing difficult. Below are some of the common processing methods currently in use.

#### 2.2.1 Regeneration of cellulose

Cellulose is difficult to dissolve, because of its extensive intra- and inter-molecular hydrogen bond network. Solvents that disrupt these hydrogen bonds have been developed over the past years [5, 8, 9, 23, 46]. Solvents used to dissolve cellulose can
be broadly classed as non-derivatised and derivatised solvents, whereby non-derivatised solvents do not chemically modify the structure to achieve dissolution and derivatised solvent chemically modify the cellulose structure to achieve dissolution.

In non-derivatised solvent systems, the molecular structure of cellulose is not chemically modified during dissolution [6]. This approach to dissolving cellulose can be further divided into aqueous and non-aqueous solvent systems. However, it has been reported that the crystal structure of the cellulose is changed from cellulose I crystal to a lower ordered cellulose II crystal structure upon dissolution and regeneration [3, 4].

The commonly used aqueous solvents for cellulose dissolution are cuprammonium hydroxide (cuam, $[\text{Cu(NH}_3]_4(\text{OH})_2$), and NaOH/urea system. The structure of the cuam cation is shown in Figure 2.5. The cuprammonium hydroxide solvent system degrades the cellulose fibre most likely by binding of the metal complex to the deprotonated O-H groups in the C-2 and C-3 positions of the AGU in the cellulose chain [47]. This results in a dark blue colour in solution due to the intense blue colour of the metal complex. Cuprammonium hydroxide method is not effective in dissolving cellulose with a high degree of polymerisation (DP) such as cotton linters. Further, there are environmental concerns such as unwanted metal complex waste and removal of copper from the regenerated material [28, 47, 48]. NaOH/urea is more economical and environmentally friendly, when compared to cuprammonium hydroxide due to its lower toxicity and cost [49]. However, it cannot be used as a common solvent that can dissolve other polymers, such as silk and wool [50-52]. Additionally, molten salt hydrates with formula LiX*H$_2$O (X=Cl$^-$, NO$_3^-$, SCN$^-$, CH$_3$COO$^-$, ClO$_4^-$) can dissolve cellulose up to DP of 1500 [46]. The dissolution is attributed to the polarising anions and a small cation [46].
On the other hand, non-aqueous solvents used for cellulose dissolution include \( N,N\)-dimethylacetamide (DMAc) /lithium chloride (LiCl) solvent system, \( N\)-methylmorpholine-\( N\)-oxide (NMMO)/H\(_2\)O system, dimethyl sulfoxide (DMSO)/tetra-n-butylammonium fluoride (TBAF) system and a relatively new solvent class, ionic liquids. The solvent class of ionic liquids (ILs) will be reviewed in a separate section as it is the focus of this project.

Among these non-aqueous solvent systems used for cellulose, only NMMO/H\(_2\)O is commercially used to date. The main limitation associated with the other methods is the inhomogeneity of the cellulose solution due to partly reacted cellulose aggregates. These aggregates could precipitate out of the solution or form gels, which hinder the complete dissolution [4, 8, 11, 46]. It can also cause practical problems such as difficult stirring and handling due to high viscosity.

The NMMO/H\(_2\)O solvent method has led to the formation of a new type of regenerated fibre called ‘Lyocell fibres’ [5]. Johnson [4] of Eastman Kodak is credited with the use of NMMO monohydrate solvent system for cellulose dissolution in 1980s. The strong intermolecular interaction between cellulose and strong N→O dipole, can dissolve cellulose [4, 5] as shown in Figure 2.6.
However, this system has detrimental effects, such as the uncontrolled thermal stability of the NMMO/cellulose/H₂O system. NMMO decomposes at high temperatures causing the risk of explosions, loss of the degree of cellulose polymerisation, formation of coloured oxidation products, high tendency of fibrillation of the regenerated fibre and high energy costs, thus preventing the mass scale of production [4-6, 8]. The main by-products formed in the process are N-methyl-morpholine (NMM), morpholine (M), and chromophores which cause severe discoloration of the solution [4, 5, 53]. To make the Lyocell commercially competitive, more optimisation is required with respect to solvent recovery and reduction of by-product formation. This requires minimising the formation of by-products, as well as solvent recovery.

In derivatised solvent systems, cellulose forms derivatives during dissolution. The derivatised solvents used for cellulose are carbon disulfide (CS₂), acetic anhydride ((CH₃CO)₂O), trifluoroacetic acid (CF₃COOH) and N, N-dimethylformamide/N₂O₄. These solvent systems have been used to regenerate commercially available cellulose derivatives such as viscose and cellulose acetate fibres.

The viscose fibre production system was invented by Cross and co-workers in 1892 to produce regenerate cellulose fibres (commercially called ‘viscose’) [7]. The viscose fibres offer better absorbency, breathability and comfort than some other natural fibres [4]. Due to its silk-like appearance, viscose fibre is often referred to as ‘artificial silk’. In the viscose process, the cellulose is alkalised in NaOH and by the addition of CS₂ derivatised to cellulose xanthogenate [6] by replacing cellulose O-H groups (C-2, C-3, and C-6) by xanthate groups. The substitution of the C-6 O-H group with xanthate group is shown in Figure 2.7.
However, as reported by Heinze and Liebert [8], and Zhu et al.[9], in the viscose process, the use of CS$_2$, a volatile and toxic gas, can harm humans through the respiratory system, skin, and digestive tract. Moreover, waste containing CS$_2$ will decompose the roots of plants and destroy the equilibrium of the soil causing major environmental problems [54].

The process of producing cellulose acetate (CA), a considerably more soluble form of cellulose is achieved via a solvent approach. The bulkier structure of CA due to the acetyl groups, gives softer, more comfortable properties, and easy dye-ability to CA fibres [55]. In the CA process, cotton is acetylated (cellulose esterification) with acetic anhydride using sulphuric acid as the catalyst. During the cellulose esterification, O-H groups of cellulose are replaced by acetyl groups. On average, approximately 5 out of 6 O-H groups of cellobiose are replaced in this way [55]. The substitution of acetyl group with the C-6 O-H group is shown in Figure 2.8. The degree of substitution (DS) of O-H groups by acetyl groups can be determined by an NMR method adopted by Goodlett et al.[56].

\[ \text{Figure 2.7: Structure of cellulose xanthogenate} \]
However, the use of acid catalysts in the CA process suffers from problems such as uncontrolled side reactions, corrosion of equipment, and huge quantities of salt waste during acid neutralising [55, 57].

Moreover, the common problem of the derivatised solvent systems is that the solvents are difficult to recover and reuse due to the uncontrolled side reactions and unidentified structures formed during dissolution [4, 55]. The solubility and derivatisation of cellulose can be analysed by investigating the changes in the chemical structure and physical properties by means of light scattering, rheology and NMR techniques [8, 11, 46].

### 2.2.2 Regeneration of protein fibres

As highlighted in the previous section, silk, wool and duck feather possess two different protein structures, however both have an extensive hydrogen bonded network making them extremely difficult to dissolve.

Traditional dissolution methods for silk involve the use of harsh solvents and multiple, time consuming processing steps [58, 59]. The traditional procedure for silk dissolution is to boil it in an alkaline solution (soap solution or sodium bicarbonate) to remove sericin (degumming), dissolve the silk fibre in 9M LiBr solution, dialyse the solution to remove the salt and re-dissolve the resultant silk powder in either formic
acid [60] or hexafluoroisopropanol [61]. This re-dissolved silk can be regenerated into new materials such as fibres, films, gels, scaffolds or powders, which can be used not only for textiles but also in biotechnological and biomedical applications [62-64].

In addition to the toxicity of the solvents used in silk regeneration, regenerated silk has been shown to have poor tensile properties compared to native silk. This is due to an incomplete refolding of the proteins native structure during coagulation. To improve the tensile properties of regenerated silk, it has been blended with other polymers such as polyvinyl alcohol (PVA), cellulose [65-67] and chitosan [68]. Silk blending with PVA and cellulose has been achieved using either the NMMO/H₂O solvent system or the cuprammonium hydroxide solutions [65-67], while formic acid was used to blend silk with chitosan [68].

In wool dissolution, a mix of solvents have been used to dissolve wool in which different components have different functions to disrupt these strong interactions between the polypeptide chains [18, 69]. For example, a solvent mixed with either a strong oxidant or reductant has been used, where the solvent disrupts the non-covalent bonds (hydrogen bonds, salt links) and the oxidant or reductant disrupt the covalent bonds (disulphide bonds) [18, 70]. Generally, couple of solvent mixtures; carbamide/H₂O₂/H₂O (solvent/oxidant) and carbamide/2-mercaptoethanol (solvent/reductant) [18, 70] have been used to dissolve wool. In addition to textile use, regenerated wool has been utilised in other fields such as additives for animal feed, neatening reagents for leather [18]. To improve the tensile properties of regenerated wool, it has been blended with cellulose. Cuprammonium hydroxide solution with a reductant has been successfully used to prepare wool/cellulose blends [18].

The use of duck feather to produce regenerated materials with improved properties has not been studied in detail. Recently, it was shown that ionic liquids can dissolve duck feather [21, 40]. This will be reviewed separately in section 2.4.
Among current literature, only the cuprammonium hydroxide solution is reported as the common solvent used to dissolve all three polymers; cellulose, silk and wool. However, the environmental issues involved with cuprammonium hydroxide; such as unwanted metal complex waste and removal of copper from the regenerated material limit its widespread application [28, 47, 48]. Therefore, to utilise these natural polymers by converting them into suitable materials, there is a need for alternative common solvent which is efficient in dissolving cellulose, silk, wool and duck feather.

2.3 Recycling polyester/cotton blends

Among polyester blends, separating methods have been studied only with polyester/cotton blends. Moreover, there is only limited work to date on separating polyester/cotton blends.

Since the PET is intricately mixed with the cotton, mechanical treatments cannot be used to separate this blend for reuse [25]. Therefore, chemical dissolution treatments have to be employed to separate the blend into its pure components. In general, the cotton component is about 40-50 wt% of PET/cotton blends [2]. The cotton is extracted by using highly concentrated acids such as 70-75 % aqueous sulphuric acid [71] and 85 % aqueous phosphoric acid [72], and aqueous sodium hydroxide solutions [73]. These high acidic concentrations cause hydrolysis of the glycosidic linkage of the cellulose chain which results in the degradation of the cotton fibre and losing the cellulose I crystal structure [3]. Thus the DP of recovered cellulose is reduced, which reduces the tensile properties [3]. Therefore, the properties of the materials prepared from the recovered cellulose are inferior. Moreover, these methods are not environmentally friendly, and can be corrosive to the equipment due to the use of highly concentrated acids.

To separate the polyester/cotton blend, dissolving only polyester fibre is not economical or environmentally friendly, as the number of polyester dissolving agents is very limited and toxic [25]. Polyester fibre is often dissolved in harsh volatile
solvents such as hexafluoroisopropanol [74] and phenol/tetrachloroethane [75]. Generally, polyester blend textile wastes are disposed of in landfill. The slow degradation of the polyester component not only creates environmental pollution, but also results in significant waste of the valuable resources which could have been utilised in new material preparation.

In 2010, Ouchi et al.[76] reported a two-step process to separate a range of polyester/cellulose fabric blends which included cotton, viscose, tencel and cupra blends with polyester. During the first step, the blend fabric undergoes a high temperature acid treatment followed by mechanical stirring. The cellulose is separated from the blend as a powder. The optimum conditions were found to be the use of aqueous highly concentrated 10 N H₂SO₄ (sulphuric acid) treatment at 95° C. After the reaction time, the solution was cooled to room temperature with the addition of water, followed by mechanical stirring for separation. The authors claimed this method achieved complete separation as well as high recovery of cellulose (over 90%).

2.4 Ionic liquids for natural polymer processing

Research on ionic liquids (ILs) has greatly expanded in recent years. Indeed, ILs, once considered niche solvents, are now finding applications in a variety of fields [77-79]. An IL or a Room Temperature Ionic Liquid (RTIL) is a material containing only ionic species without any neutral molecules and has a melting point lower than 100° C [80, 81]. The ability to tailor the properties of the ionic liquid supports its wide applications [82, 83]. Different cations and anions can be combined to design ILs having different physical and chemical properties. The reputation for ILs as “environmentally friendly” solvents results from certain ILs being non-flammable, having chemical and thermal stability, as well as very low or even negligible vapor pressure.

In the context of green chemistry, ionic liquids are taking centre stage, with the processing of natural polymer being one application [84-86], which has greatly benefited from the use of ILs.
2.4.1 Ionic liquids for natural polymer dissolution

A range of IL types for natural polymer dissolution have been reported in current literature, while most of them have been developed to dissolve cellulose. Among those many IL types, in this context, only imidazolium based IL types will be reviewed as they have shown to be a common solvent type for both natural cellulose and protein polymers. Generally, ILs consisting of 1-R1-3-R2- imidazolium cation and either the chloride or acetate anion have been used for dissolving natural polymers acting as non-derivatised solvents [18, 21, 35, 40, 69, 85, 87-89]. Figure 2.9 shows the imidazolium cation and the common natural polymer dissolving anions.

Below, Table 2.1 lists the imidazolium based ILs used to dissolve natural polymers namely; cellulose, silk, and wool and duck feather keratin.
Table 2.1: Imidazolium based ionic liquids used in natural polymer dissolution

### ILs used to dissolve cellulose

<table>
<thead>
<tr>
<th>Ionic Liquid</th>
<th>Solubility (%w)</th>
<th>DP (Degree of Polymerisation)</th>
<th>Dissolving conditions</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMIMCl</td>
<td>14.5</td>
<td>pulp</td>
<td>80</td>
<td>-</td>
</tr>
<tr>
<td>BMIMCl</td>
<td>25</td>
<td>1000</td>
<td>microwave heating</td>
<td>-</td>
</tr>
<tr>
<td>EMIMCl</td>
<td>15.8</td>
<td>569</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HMIMCl</td>
<td>5</td>
<td>1000</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>OMIMCl</td>
<td>poor</td>
<td>1000</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>BMIMBr</td>
<td>5 to 7</td>
<td>1000</td>
<td>microwave heating</td>
<td></td>
</tr>
<tr>
<td>BMIMOAc</td>
<td>13.2</td>
<td>569</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>EMIMOAc</td>
<td>19.6</td>
<td>569</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>BMIMSCN</td>
<td>5 to 7</td>
<td>1000</td>
<td>microwave heating</td>
<td></td>
</tr>
<tr>
<td>EMIMMe2PO4</td>
<td>10</td>
<td>250</td>
<td>40-65</td>
<td>-</td>
</tr>
</tbody>
</table>

### ILs used to dissolve silk

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>Solubility (%w)</th>
<th>Silk type</th>
<th>Dissolving conditions</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMIMCl</td>
<td>10</td>
<td>Wild silk fibroin</td>
<td>100</td>
<td>6</td>
</tr>
<tr>
<td>BMIMCl</td>
<td>12.2</td>
<td>Wild silk cocoon</td>
<td>120</td>
<td>-</td>
</tr>
<tr>
<td>DMBIMCl</td>
<td>8.3</td>
<td>Mulberry silk cocoon</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>EMIMCl</td>
<td>23.3</td>
<td>Mulberry silk cocoon</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>BMIMOAc</td>
<td>10.14</td>
<td>Wild silk cocoon</td>
<td>120</td>
<td>-</td>
</tr>
</tbody>
</table>

### ILs used to dissolve wool and duck feather keratin

<table>
<thead>
<tr>
<th>Ionic Liquid</th>
<th>Keratin type</th>
<th>Solubility (%w)</th>
<th>Dissolving conditions</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMIMCl</td>
<td>Wool</td>
<td>10</td>
<td>100</td>
<td>8</td>
</tr>
<tr>
<td>BMIMCl</td>
<td>Wool</td>
<td>11</td>
<td>130</td>
<td>10</td>
</tr>
<tr>
<td>AMIMCl</td>
<td>Duck feather</td>
<td>45</td>
<td>130</td>
<td>10</td>
</tr>
<tr>
<td>BMIMCl</td>
<td>Duck feather</td>
<td>45</td>
<td>130</td>
<td>10</td>
</tr>
</tbody>
</table>

**Cations:**
- [AMIM] = 1-allyl-3-methylimidazolium
- [BMIM] = 1-butyl-3-methylimidazolium
- [DMBIM] = 1-butyl-2,3dimethylimidazolium
- [EMIM] = 1-ethyl-3-methylimidazolium
- [HMIM] = 1-hexyl-3-methylimidazolium
- [OMIM] = 1-octyl-3-methylimidazolium

**Anions:**
- Br = bromide, Cl = chloride, OAc = acetate, SCN = thiocyanate, Me2PO4 = dimethyl phosphate
2.4.1.1 Dissolving cellulose in imidazolium ionic liquids

Many studies on the dissolution of cellulose in ILs can be found in the literature [18, 35, 69, 85, 88, 89, 92]. Most dissolution studies have used micro-crystalline cellulose (MCC), which is a refined wood pulp of DP 300-600. Some important works in cellulose dissolution are reviewed in this section.

In 2002, Swatloski et al. [85] first reported the use of ILs towards the dissolution and regeneration of cellulose. They tried dissolving MCC in seven different imidazolium based ILs. 1-butyl-3-methyimidazolium chloride (BMIMCl) was found to be the most effective IL to dissolve cellulose since; it could dissolve MCC up to 10 wt% at 100°C with conventional heating and up to 25 wt% at 80°C with microwave heating. Additionally, it was observed that the non-coordinating anions like BF₄⁻ and PF₆⁻ were not successful at dissolving cellulose. Further, the presence of water in imidazolium based ILs considerably reduced the solubility of cellulose. Even a 1 wt% water impurity in the IL resulted in no cellulose dissolution [85].

In 2005, Zhang et al. [84, 88] reported the use of 1-allyl-3-methylimidazolium chloride (AMIMCl) as a non-derivatised solvent for cellulose. The authors claimed that AMIMCl could dissolve cellulose up to 14.5 wt% at 80°C without microwave heating. Figure 2.10 shows the structures of BMIMCl and AMIMCl.

![Figure 2.10: Structure of (a) BMIMCl and (b) AMIMCl](image-url)

In 2005, Zhang et al. [84, 88] reported the use of 1-allyl-3-methylimidazolium chloride (AMIMCl) as a non-derivatised solvent for cellulose. The authors claimed that AMIMCl could dissolve cellulose up to 14.5 wt% at 80°C without microwave heating. Figure 2.10 shows the structures of BMIMCl and AMIMCl.

![Figure 2.10: Structure of (a) BMIMCl and (b) AMIMCl](image-url)
Viscosity of the IL is thought to play an important role in cellulose dissolution. Low viscosity of the IL allows a high mobility of the anion, which can interact with the polymer effectively. Kosan et al. [93] reported that the acetate (Ac) containing ILs could dissolve more cellulose due to the lower viscosity of the solution when compared to the Cl⁻ anion. Fukaya et al. [91, 94] developed new ILs aimed to further reduce the viscosity by using a functionalised phosphate anion see Figure 2.11 [91]. In particular, the lowest viscosity IL; 1-ethyl-3-methylimidazolium dimethylphospate (EMIMMe₂PO₄) showed the best dissolving capacity which was 10 wt% at 45°C.

![Figure 2.11: EMIM ionic liquids with different phosphonates investigated by Fukaya et al. [91]](image)

2.4.1.2 Dissolving protein fibres in imidazolium ionic liquids

Very limited research is available in the literature regarding silk, wool and duck feather protein fibre dissolution in ILs.

In 2002, Phillips et al. [89] firstly reported the use of ILs to dissolve domestic Bombyx mori silk fibroin. They chose imidazolium based ILs to determine the solubility of silk. The authors stated that the pre-existing ability to dissolve cellulose in these ILs lead to selection of these ILs. In this work, 1-ethyl-3-methylimidazolium chloride (EMIMCl) dissolved the highest amount of silk 23.3 wt% whilst BMIMCl was found to dissolve 13.2 wt%. The authors also reported that applying microwave heating was not successful, due to thermal decomposition of the silk.
In 2012, Byrne et al. [35] reported the on the dissolution of up to 10 wt% of wild muga silk cocoons in 1-butyl-3-methylimidazolium acetate (BMIMOAc) at 120°C. Further, they investigated the effect of coagulant type on the structure of regenerated silk using water, methanol, ethanol, and iso-propanol. The results showed that the coagulant type did impact the properties of the regenerated silk.

In 2005, Xie et al. [18] firstly reported on dissolving wool in a series of ILs using combinations of BMIM+ and AMIM+ cations and Cl-, Br-, BF4- and PF6- anions. The results show ILs containing BF4- and PF6- anions are incapable of dissolving wool, whereas only Cl- and Br- based ILs were shown to dissolve wool similar to cellulose dissolution behaviour reported by Swatloski et al. [85]. BMIMCl and AMIMCl were the most efficient at dissolving wool, with 11 wt% and 8 wt% dissolved at 130°C respectively. Investigations of the structure of regenerated wool using the coagulants, water, methanol and ethanol revealed that the regenerated wool structure is different to that of the native wool structure. The regenerated wool exhibited a β-sheet structure with the disappearance of the α-helix structure. A similar study was carried out by Li and Wang [69] to prepare regenerated wool films from ILs. The ability of wool dissolving in ILs eliminates the use of harsh and volatile solvent mixtures.

The dissolution of duck feather keratin in ILs was first reported by Zhao et al. [40] in 2010. The results show that the duck feather was soluble in both BMIMCl and AMIMCl, with the AMIMCl being the most effective solvent. The authors claimed that the secondary structure of the regenerated duck feather was similar to that of the original feather, which indicates that ILs are non-derivatised solvents for duck feather.

In 2013, Idris et al. [21] used the same ILs to dissolve turkey feathers. In particular, it was found that at 130°C, turkey feather keratin was soluble up to 45 %wt. It was also reported that the dissolution occurred without major chemical change of the polypeptide chain confirmation, which agreed with the previous findings of Zhao et al. [40]. However, material properties of regenerated duck feather or the use of duck feather as a blending material have not been reported to date.
It could be anticipated that the ability of dissolving cellulose and protein fibres in a common IL could potentially lead to new bio-based blend materials, which are a prime focus of this project.

The value of IL solvents lies in their design flexibility. ILs can be designed simply by varying the cation and anion to meet such requirements [80, 81]. The above studies on natural polymer dissolution in ILs suggest that the effect of cation and anion of the IL clearly determine its dissolving capability, which is discussed below.

2.4.2 Effect of imidazolium ionic liquid cation and anion on natural polymer dissolution

In the first publication of cellulose dissolution in IL, Swatloski et al. [85] investigated the nature of the anion and the alkyl substituent of the cation on cellulose dissolution. They suggested that the strong hydrogen bond acceptance properties of the Cl⁻ anion could effectively disrupt the prevailing hydrogen bond network in cellulose. Indeed, this has readily been accepted for dissolution studies of silk, wool and duck feather conducted by Phillips et al. [89], Byrne et al. [35], Xie et al. [18], Li and Wang [69], Zhao et al. [40], and Idris et al. [21]. Therefore, the dissolution of natural polymers such as cellulose, silk, wool and duck feather in ILs has been attributed to the ability of the IL to disrupt the hydrogen bond network.

All natural polymer dissolution studies in ILs conducted to date, agreed that the strong hydrogen bond acceptance property of the IL anion enhances its dissolving capability. In particular, imidazolium based ILs with strong hydrogen bond acceptance anions such as Cl⁻, OAc⁻, and Me₂PO₄⁻ were highlighted as effective ILs [18, 35, 52, 69, 85, 88, 89, 91, 93-95]. On the other hand, imidazolium based ILs with non-coordinating anions such as BF₄⁻ and PF₆⁻ do not dissolve natural polymers due to their weak hydrogen bond acceptance properties [18, 85, 89].

The effect of IL cation on cellulose dissolution was first explored by Swatloski et al. [85]. They varied the chain length from short 1-butyl-3-methylimidazolium to a long
chained alkyl cation; 1-octyl-3-methylimidazolium for cellulose dissolution experiments. When the length of the alkyl chain was increased from C4 to C8 the solubility of cellulose decreased. It was then found that the chain length of the IL cation influenced the dissolution due to changing hydrophilicity/hydrophobicity of the IL. The shorter alkyl chain ILs which are hydrophilic, have been shown to dissolve cellulose more. (i.e. BMIM$^+$ cation, which was the shortest IL cation used in this study seemed to be more effective)

It can be seen that the maximum dissolution is achieved with short chain IL cations of methylimidazolium core with allyl (AMIM), ethyl (EMIM), and butyl (BMIM) chains [18, 35, 52, 69, 85, 88, 89, 91, 93-95].

In addition to the strong hydrogen bond acceptance IL anion and short chain length IL cation, the low viscosity of the IL is also important to effective dissolution as reported by Kosan et al. [93], and Fukaya et al. [94]. Furthermore, Kosan et al. [93] reported on achieving higher cellulose concentration solutions (up to 19.6 wt%) in OAc anion based ILs compared to Cl$^-$ based ILs due to less viscosity. As the size of the anion is increased (OAc size $>$ Cl$^-$ size), the melting point decreases, which is common in all imidazolium-based ILs [96]. This is because of the increased distance between the IL cation and anion. This makes the ionic interactions weaker, which increases the mobility of the ions in the liquid.

In addition, the viscosity of the imidazolium IL is also dependent on the chain length of the IL cation - when the chain length increases, the viscosity increases [85]. Generally, when the chain length is increased, the decrease in overall electrostatic interactions is expected to decrease its viscosity [42].

Moreover, the presence of double bond in the alkyl chain of the imidazolium ring or a substitution of one of the alkyl chain carbon atom with an oxygen atom has been found to reduce the viscosity of the IL [97]. However, the ILs of alkyl chain carbon replaced with oxygen have not been able to dissolve cellulose [97]. On the other hand, ILs
containing double bonds (AMIM cation based ILs) have been shown to dissolve cellulose [84, 88].

The above literature shows that the low viscosity ILs promote the mobility of the ions, with short chain cations and strong hydrogen bond acceptance anions favouring more efficient natural polymer dissolution. Next section will explain the current methods that have been used to understand the IL dissolution mechanism by investigating IL-natural polymer interactions in solution.

2.4.3 Dissolution mechanism of natural polymers in imidazolium ionic liquids

While ILs have been used to dissolve wool, silk, duck feather and cellulose to date, only the dissolution mechanism of cellulose has been reported.

Zhang et al. [88] reported that both IL cation and anion are involved in the dissolution process. Figure 2.12 shows a proposed mechanism of cellulose in ILs (AMIMCl). They proposed that the AMIM$^+$ cation and Cl$^-$ anion are dissociated into individual ions above a critical temperature. The oxygen and hydrogen atoms of the cellulose O-H groups form electron donor-electron acceptor complexes with the charged dissociated species of the IL. The free Cl$^-$ ions associated with cellulose O-H proton and free cations complex with cellulose O-H oxygen, thus disrupting the hydrogen bond network in the cellulose chain.

![Figure 2.12: Proposed dissolution mechanism of cellulose in AMIMCl by Zhang et al. [88]](image-url)
The work of Kosan et al. [93] suggested that this mostly occurs between the C-3 O-H and C-6 O-H groups of adjacent cellulose chains. Such interactions cause the separation of O-H groups of the different cellulose chains to dissolve cellulose in IL.

To better understand the mechanism of dissolution of cellulose in BMIMCl at the microscopic level, Remsing et al. [43] reported $^{13}\text{C}$ and $^{35/37}\text{Cl}$ NMR relaxation measurements at varying temperatures and concentrations of the dissolved cellulose solution. Their findings demonstrated that the dissolution of cellulose in BMIMCl involves a 1:1 stoichiometric hydrogen bonding between the cellulose O-H proton and the Cl$^-$ anion of the BMIMCl (Figure 2.13). Surprisingly, they found that there were no specific interactions between the IL cation and cellulose O-H oxygen, as opposed to the previous suggestion made by Zhang et al. [88].

Figure 2.13: Possible dissolution mechanism of cellulose reported by Remsing et al. [43]

Heinz et al. [90] also studied the interactions of IL cation (of EMIMOAc, EMIMCl and BMIMCl) and cellulose using (cellooligomers with a degree of polymerisation of DP 6 to 10). Based on their $^{13}\text{C}$ NMR measured for BMIMCl displayed a poor resolution of the D-anhydroglucopyranose (AGU) in the cellulose region, which led to the assumption that there is a cellulose aggregation and thus a high viscosity. However, they have determined all signals for carbon atoms of the AGU. In particular, the C-1 signal was clearly observed. Surprisingly, these signals were not present when the cellulose was dissolved in EMIMOAc that indicates a good solubility of cellulose chains in the IL. They suggested that the EMIMOAc forms a covalent bond between
the C-1 carbon of the AGU and the C-2 of the imidazolium ring as shown in Figure 2.14. This suggestion was made based on the disappearance of the C-1 signal of the AGU after dissolving in EMIMOAc. This suggests the dissolution mechanism is different for BMIMCI and EMIMOAc.

Figure 2.14: Structure proposed for a covalent bond of EMIMOAc to cellulose by Heinz et al. [90]

The dissolution mechanism of EMIMOAc suggested by Heinz et al. [90] has been verified by Ebner et al. [41] from their $^{13}$C-isotopic labelling and fluorescence labelling experiments. Their work indicated that a covalent bond formation occurred between the C-2 carbon of 1-alkyl-3-methyl-imidazolium ILs (EMIMOAc and BMIMOAc) and the reducing end (C-1 carbon) of the cellulose.

Surprisingly, this was not the case when the cellulose was dissolved in Cl$^{-}$ based ILs [90]. In the case of cellulose dissolved in EMIMCl, the C-1 signal of the cellulose reducing end was still found. The authors suggested that the Cl$^{-}$ containing ILs do not bind efficiently to the reducing end of cellulose, but the bond formation is strongly promoted by bases (Cl$^{-}$ ion acting as a base), as suggested by Remsing et al. [43]. One likely reason for this difference could be the H-bond network within Cl$^{-}$ based ILs, as shown in Figure 2.15.

Therefore, it can be seen that two different dissolution mechanisms occurred for Cl$^{-}$ based ILs and OAc based ILs.
Since the ILs reported to dissolve natural polymers are hydrophilic, there are a large number of solvents with which they are miscible. Therefore, dissolved natural polymers in ILs can be regenerated by mixing with coagulants like water, ethanol, methanol or acetone [85, 88]. Regenerated polymers then can be converted into various forms, such as films, fibres, and powders depending on the type of coagulation process (casting into films or spinning into fibres). Once the polymer is regenerated, the ILs can be recycled by evaporating the coagulant [84, 98].

However, the high viscosity of the ILs has become a problem to the commercial application of ILs for regeneration of natural polymers. Addition of co-solvents such as dimethylsulfoxide (DMSO), and dimethyl formamide (DMF) to the IL can decrease the overall viscosity of the mixture. However, the addition of co-solvents can reduce or have no effect on the solubility rate [99-102]. Xu et al. [103] reported that the addition of DMSO to cellulose/AMIMCl solution decreased the viscosity and the surface tension of the solution, and they were able to make 5 wt% cellulose solution.
for electrospinning. Moreover, ILs of strong dissolving power with low viscosity, such as EMIMOAc and EMIMMe$_2$PO$_4$, have been reported. As a result, up to 19.6 wt% cellulose solutions were obtained in pure ILs, which were used for wet spinning to regenerate cellulose fibres [93]. However, only few works have been reported on regenerating cellulose fibres from wet spinning using single IL systems. Since this project looks to use the natural polymers in IL solution to create new bio-based fibres, current works of wet spinning of cellulose in IL are discussed below.

2.5 Wet spinning Ionic liquid/natural polymer solutions

Wet spinning is a fibre forming technique, which utilises the polymers in their dissolved state in a solvent. The majority of wet spun fibres are produced from the viscose process [104]. Direct solvents such as NaOH/urea and NaOH/ZnO solvent mixtures have also been employed in wet spinning to regenerate cellulose fibres [49, 104].

To date very few works on wet spinning cellulose with ILs exist. Previous reports have used the low viscosity EMIMOAc as the dissolving IL. Hermanutz [105] reported that the cellulose fibres spun with EMIMOAc had tensile and elasticity properties similar to the fibres made from the viscose and NMMO processes. Olsson and Westman [106] also reported the use of EMIMOAc to wet spin cellulose fibres (10 wt%) without drawing. They reported that the tensile properties of the regenerated fibres were not satisfactory due to the low DP of the cellulose they used. The high DP of the cellulose often makes the polymer stronger and stiffer [3].

Kosan et al. [93] reported on forming regenerated fibres from dry-wet spinning using cellulose dissolved in BMIMCl, EMIMCl, BMIMOAc and EMIMOAc. Moreover, they found that EMIMOAc led to lower viscous cellulose in solution that could make the spinning dope consist of 19.6 wt% cellulose. Their results indicate that the cellulose exists in different solution states, which is likely driven by the different cellulose IL interactions [41, 43].
In addition to wet spinning cellulose fibres in ILs, wet spinning of silk fibres in ILs has also been reported. In 2005, Phillips et al. [59] reported the use of EMIMCl to regenerate silk fibres directly from wet spinning. This process did not require multiple steps, which is usually involved with traditional silk regeneration methods [58, 59]. Additionally, these traditional methods for regenerating silk fibres in wet spinning need harsh solvents such as hexafluoroisopropanol, formic acid, and trifluoroacetic acid [107-109].

Regeneration of wool fibres, duck feather fibres or blended fibres of cellulose and natural protein polymers in ILs has not been reported to date. In this project, developing such blended bio-based fibres from ILs will be explored. The fibres in this project will largely be produced using wet spinning. The wet spinning parameters are known to impact the final properties of the regenerated fibre. In this context, wet spinning parameters that influence the regenerated fibre properties are discussed next.

2.5.1 Wet Spinning parameters influencing the fibre properties

Wet spinning involves a combination of rheological and diffusional phenomena [110, 111]. In this process, the dissolved polymer solution is extruded through a spinneret and immersed in a coagulant for precipitation.

2.5.1.1 Rheological behaviour of the polymer solutions in IL

It is known that the rheological properties of the solution influence the structural formation and the final properties of the wet spun fibre [104, 112]. The particle size (aggregates) in the solution impacts the rheological properties of the solution, influencing the spinning ability [113]. Large-sized particle aggregations often lead to an increase in the viscosity of the solution [11, 113]. To date, the particle size characterisation of the silk, wool and duck feather solutions has not yet been carried out. Only the cellulose particle size characterisation in solution has been investigated.
It is known that in the dissolved state cellulose exists in the aggregate form, whereby the aggregate size is determined by the type of solvent and the dissolution mechanism [11, 113]. The size of these aggregates is defined by the gyration radius \( R_g \) measured from light scattering techniques [114, 115].

Roder and Morgenstern [114] investigated the cellulose particle size in the NMMO solvent system. This work revealed that both small and large cellulose aggregates existed in solution. The \( R_g \) of these aggregates was found to exceed 160 nm. The scattering function was to be a bimodal distribution, consisting of large and small aggregates. The authors assumed that these aggregates consist of cellulose crystallites, which were not fully disintegrated during dissolution.

Kuzmina et al. [113] investigated the cellulose particle size in ILs. In their study, they dissolved cellulose in EMIMOAc and BMIMCl. It was concluded that the cellulose particle size in EMIMOAc was found to be slightly higher than those in BMIMCl.

The viscosity of the solution can be characterised by determining the loss modulus \( (G'') \) and the storage modulus \( (G') \) as a function of frequency [11]. Determination of these shear moduli is essential to know if the solution has formed a true solution or a gel [113]. Based on the cross-over point (where \( G'' = G' \)), the relaxation time can be determined for the solution. This implies the change in the degree of physical or chemical cross-linking of the polymers in solution [106].

Fink et al. [11] investigated the viscosity of the dissolved cellulose in NMMO. Their experimental results concluded that increasing cellulose concentrations also resulted in increased particle aggregation of cellulose. This resulted in an increased viscosity of the solution.

In the study of Olsson and Westman [106] using EMIMOAc to wet spin cellulose, their rheological results displayed typical polymer solutions characterised by a Newtonian area at low shear rates and reduced viscosity with increasing shear rate. Further, these results showed that the solution viscosity is increased with increasing
DP of the cellulose in solution. Additionally, the work of Hermanutz et al. [105] on processing cellulose in EMIMOAc showed that the solution viscosity increased with the increase of cellulose concentration in IL. This has been attributed to the rise in polymer chain entanglements at higher polymer concentrations. Conversely, it has been found that the solution viscosity could be reduced by increasing the temperature due to enhanced mobility of polymer chain molecules in solution.

2.5.1.2 Diffusion kinetics during coagulation

The shaped and oriented wet fibre, immersed in the coagulant, precipitates due to the two diffusional interchanges occurring between the freshly formed fluid fibre and the coagulant, as shown in Figure 2.16. The two diffusional phenomena are: diffusing solvent out of the wet fibre to the bath and coagulant from the bath to the wet fibre. When the polymer, solvent and coagulant concentrations overcome the phase equilibrium, the polymer precipitates in the fibre form [110, 111]. This process is termed ‘coagulation’.

![Figure 2.16: Schematic representation diffusion kinetics during fibre regeneration](image)
Many experimental models, such as the moving boundary model [110], constant flow ratio model [116] and Crank’s equation [111], have been developed to understand the diffusion kinetics occurring during the coagulation in the wet spinning of synthetic polyacrylonitrile (PAN) fibres. Depending on the coagulant and other various parameters, such as solvent type, and polymer concentration, different diffusional interchanges occur during coagulation, thus changing the properties of the coagulated fibre.

Among the cellulose regeneration methods, the diffusional phenomena occurring in the viscose process is rather complex to understand. Therefore, only the diffusion dynamics of the direct cellulose solvent systems like cellulose/NMMO (Lyocell process), cellulose/IL, and cellulose/NaOH solutions have been reported [117-120]. It was reported that there were two diffusion phases of NMMO during coagulation. The rapid diffusion phase was attributed to the formation of hydrogen bonds between NMMO and water, while the slow diffusion process was similar to that of normal wet-spinning process [119]. It was also found that the diffusion of NMMO to water was independent to the cellulose type, but very sensitive to the cellulose concentration [121]. The diffusion of two ILs reported; 1-ethyl-3-methylimidazolium acetate (EMIMOAc) and 1-butyl-3-methylimidazolium chloride (BMIMCl) were practically the same as the both solvents were similar [118]. However, at a given cellulose concentration, the diffusion of these two ILs were 4 to 5 times lower than the diffusion of NaOH [118, 122] and around 2 times lower than the diffusion of NMMO [122] due to the larger molecular size of the IL (the diffusing entity). Recently, Hauru et al. [117] reported that the diffusion of a protic IL; 1,5-diazabicyclo(4.3.0)non-5-ene acetate ([DBNH]OAc) was relatively better than NMMO, which suggested a mechanically orientable strong cellulose network was formed during the regeneration.

However, this phenomenon has not been explored in the natural composite fibre formation in wet spinning using ILs. Therefore, it would be interesting to explore and understand the effect of diffusion kinetics would have on natural composite fibre formation in ILs.
2.5.1.3 The draw ratio

The draw ratio is another important spinning parameter which influences the properties of the fibre, such as fibre diameter, crystallinity and tensile strength [11, 49, 59, 123]. The draw ratio can be calculated as a ratio between the take up speed and the spinning solution speed through the spinneret [104]. Li et al. [124] investigated the draw ratio of wet spun cellulose fibres in ILs, using EMIMOAc. It was found that the tensile properties and uniformity was improved and then reduced with the increase of drawing. This has been attributed to an increase in crystallinity and the molecular orientation along the fibre axis. However, when the draw ratio was close to ‘break’ draw ratio, the tensile properties were reduced. This is due to internal fractures and defects that occurred at very high draw ratios. Overall, due to the draw ratio applied, the tensile properties of the regenerated cellulose fibres have been improved compared to the fibres produced by Olsson and Westman [106] previously.

2.6 Summary

Cotton, silk and wool are the three main natural polymers used in textile processing, which generates a significant amount of waste. Among all textile waste, polyester/cotton is the most common waste produced globally. Additionally, duck feathers are another underutilised waste type that are a potential source of natural protein polymers, if suitable processing techniques can be developed.

Conversion of textile waste back to high quality fibres remains a challenge. The major barrier for such conversion is that most of textile materials composed of blended fibres, -the most common being polyester/cotton blends. From the literature review, it has been identified that the use of textile waste has not yet been exploited due to the limited number of environmentally friendly solvents that can dissolve these textiles waste. Likewise, little has been reported on the separation of polyester/cotton blended textile waste into reusable forms for effective recycling.
Ionic liquids (ILs), which are considered to be environmentally friendly solvents, have shown great potential in natural polymer dissolution and processing. Among the wide range of ILs, imidazolium based ILs are common solvents which effectively dissolve textile fibres, including cotton, silk, wool, as well as duck feathers. This ability could be exploited towards blending polymers in solution state to design new bio-composites with improved properties as well as separating polyester/cotton blends into its pure forms.

Wet spinning is a technique widely used to regenerate fibres from the polymers dissolved in a solvent. The solution state properties, coagulant type and the draw ratios, all affect the fibre formation and final fibre properties. Wet spinning of bio-based fibres using ILs is a relatively new area of research and consequently, the effect of spinning parameters in IL wet spinning has not been fully explored.

The next chapter will discuss the experimental methods used in this work.
CHAPTER 3
Experimental design

3.1 Starting materials

**Ionic liquids used in biopolymer dissolution:** 1-allyl-3-methylimidazolium chloride (AmimCl > 98%; lot no. 100319.2.1) was purchased from Io-Li-Tec, Germany. 1-Butyl-3-methylimidazolium acetate (BMIMOAc > 95%; lot no. BCBM49O5V) was purchased from Sigma Aldrich, Australia. The structures of the ILs used are shown in **Figure 3.1.** All ILs were dried under reduced pressure at 85°C to remove water prior to biopolymer dissolution. The water content of AMIMCl and BMIMOAc were measured using a Karl-Fischer coulometer and was determined to be less than 0.8% and 1.1% respectively for all dissolutions.

![Figure 3.1 a-b: Structure of 3.1.a) AMIMCl & 3.1.b) BMIMOAc](image)
CUEN solution to determine the degree of polymerisation of regenerated cellulose: Bis (ethylenediamine) copper (II) hydroxide solution (1.0 M in H₂O; lot no. MKBR2127V) was purchased from Sigma Aldrich, Australia. See Figure 3.2 for the structure of CUEN.

![Figure 3.2: Structure of CUEN](image)

Polymers used in blend separation, dissolution and regeneration studies: The cellulose based materials (100% cotton yarns), 100% polyester yarns and 50/50 polyester/cotton blended yarns were provided by Leading Textiles, Melbourne, Australia. These yarns have not undergone pre-treatment, such as scouring or bleaching. The degree of polymerisation (DP) of the starting cellulose material was measured to be 1260. Duck feathers were obtained from a duck feather pillow purchased from Spotlight retailers, Geelong, Australia. All the feather parts except the calamus (see Figure 3.3) were used in the dissolution process. Wild muga silk was provided by Fabric Plus Ltd, Assam, India. Original merino wool fibres were provided by CSIRO, Geelong Laboratory, Australia. All the polymers (received in the forms of yarns and fibres) were used as received without any treatment, but the samples were oven dried for 24 hours at 105°C before dissolution.

![Figure 3.3: Parts of a duck feather](image)
3.2 Sample preparation

The dissolution of polymers in ILs was carried out in 20 ml vials under inert N₂ atmosphere. The dissolution process was carried out under magnetic stirring, using a pre-heated heating block with an auto regulated thermocouple to maintain a constant temperature at desired values. The time was measured using a stop watch to determine the total dissolution time of the dissolution process.

3.2.1 Dissolution of polyester/cotton blend yarns to separate the blend

Initially, to determine if the IL would dissolve polyester, 100% polyester yarn was submerged in the IL at 80°C, 100°C, 120°C and monitored using polarising light microscope (PLM). Over a 48 hour period, no dissolution was observed. A schematic of the dissolution set-up is shown in Figure 3.4.

Then, polyester/cotton blended yarn as received (polyester: cotton blend ratio 50:50) was added to the IL at 100°C at 2 wt% increments up to 10 wt% (equating to 5 wt% of cotton). After 6 hours, the undissolved component (polyester part) was removed, rinsed with water and weighed. The undissolved component was characterised and compared with 100% polyester as received. The dissolved cotton was regenerated into films and characterised. The characteristics of the material properties of the recovered polymers are discussed in chapter 04.

3.2.2 Dissolution of natural polymers

Both single and blended polymer solutions at different polymer amounts in IL were obtained at different temperatures in this study. The desired polymer amounts were added at increments of 1 wt% under magnetic stirring. After required total polymer dissolution, a clear and viscous solution was obtained. The complete dissolution was observed and verified using a Nikon 80i eclipse polarising light microscope (PLM). A dissolved solution was obtained when no crystallinities in the polymer solution were
observed. The solution properties for wet spinning of these solutions are discussed in chapter 06.

3.2.3 Preparation of regenerated films from the dissolved polymer solutions

The dissolved polymer solution (approximately 1 mL) was cast evenly between two glass slides and immersed in a coagulant bath for 10 minutes. The coagulants used for polymer regeneration were water, methanol and iso-propanol. This immersion was repeated 3 times to ensure removal of the IL from the bio film. During the immersion in the 2nd and 3rd bath, the film was removed from between the glass slides (see Figure 3.5). After which, the film was again immersed in water for 24 hours and then dried for 48 hours at room temperature. The average film thickness was measured to be 65 μm. After film preparation, the residual solvent (IL + coagulant) was collected separately to recycle the IL. The IL was recycled by solvent evaporation as described [84, 98]. Additionally, this recycled IL was used for further dissolution studies. The characteristics of the regenerated composite bio films are discussed in chapter 05.
3.2.4 Preparation of regenerated fibres from the dissolved polymer solutions

The desired bio polymer solution (spinning dope) was transferred into a glass syringe (internal diameter of 10.5 mm) and mounted onto a syringe pump. The temperature of the spinning dope was maintained at 40°C by a heating jacket attached to the glass syringe. Then the spinning dope was extruded into a water bath through a 25G needle (internal diameter of 0.260 mm) at a fixed flow rate. The extruded proto fibre, without a stretch was slowly dragged into a known length (30 cm) between two points X & Y marked in the water bath as illustrated in Figure 3.6. The coagulation time was measured from the fibre passed point X. When the fibre reached point Y, the fibre was held in position until the desired coagulation time was achieved.
After the desired coagulation time (10 minutes) was reached, the fully coagulated fibre (undrawn fibre) was immediately removed from the water bath and fixed between two clamps as shown in Figure 3.7 as such the draw was applied to the wet fibre fixed between the clamps. The fixed spacing between the two clamps was set to 15 cm. Then, the bottom clamp was slowly drawn downwards to elongate the fibre. For each fibre sample, the maximum stretch % was calculated at the fibre breaking point due to the stretching. The stretch % for each specimen was calculated as \((e/15) \times 100\%\). Four samples for each fibre specimen were made including a non-stretched fibre and three fibre samples with three different stretch %. The applied stretch ratios are given in Table 3.1. For each fibre sample a one batch of fibre was produced. The material characteristics of these fibre batches made at different flow rates and stretch % are discussed in chapter 06.

![Figure 3.7: Schematic of the setup used in stretching the fibres](image)

Table 3.1: Stretch ratios applied to the fibres produced

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Initial length (cm)</th>
<th>Final length (cm)</th>
<th>e (cm)</th>
<th>Stretch ratio (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15</td>
<td>15</td>
<td>0</td>
<td>0 (no stretch)</td>
</tr>
<tr>
<td>2</td>
<td>15</td>
<td>16</td>
<td>1</td>
<td>6.66</td>
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<td>4</td>
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<td>18</td>
<td>3</td>
<td>20.00</td>
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<tr>
<td>5</td>
<td>15</td>
<td>19</td>
<td>4</td>
<td>26.66</td>
</tr>
</tbody>
</table>
3.2.5 Recycling of the IL

After the regeneration, the residual solvent (IL+ coagulant) was collected separately to recycle the IL. The IL was recycled by evaporating the coagulant using BÜCHI B480 ROTAVAPOR, followed with a vacuum drying until the coagulant content was removed less than 1.0%, measured using a Karl-Fischer coulometer.

3.3 Techniques

3.3.1 Calculating the trapped ionic liquid in the regenerated cellulose

A known quantity of dissolved cellulose (n wt% cotton yarn dissolved) solution was taken in to a syringe and the initial weight \( M_1 \) was measured. The tip of the syringe was immersed into the water bath followed by injection of the solution. After a certain coagulation time, the wet fibre was taken out and filter paper was used to absorb the water and IL from the fibre surface. Then, the wet fibre consisted of cellulose, water diffused in to the fibre and residual IL. Since both the IL and cellulose were shown to be stable at 120°C, the amount of water diffused was removed by heating the sample to 120°C at a heating rate of 5°C/min using thermogravimetric analysis (TGA). The residual combined weight of regenerated cellulose and trapped IL was measured \( M_2 \). Following equations have been used to calculate the trapped IL in the regenerated cellulose.

\[
\text{Cellulose concentration (\%) = } n \\
Initial \text{ cellulose + IL weight (in solution)} = M_1 \\
Cellulose weight in solution = n\% \times M_1 \\
Initial IL weight in the system = (1 - n\%) \times M_1 \\
regenerated cellulose + residual IL (from TGA by removing water) = M_2
\]
3.3.2 Measuring the average DP of regenerated cellulose

The intrinsic viscosity–average (DP) of native cellulose and regenerated cellulose were measured using an Ostwald viscometer in Bis (ethylenediamine) copper (II) hydroxide (CUEN) solution [125].

3.3.2.1 Preparation of solution

The concentration of CUEN solution was 0.5 M. A known amount of cellulose sample and 10 ml of 0.5 M CUEN solution were added to the 20 mL vial. The suspension was then strongly agitated until the cellulose was completely dissolved. Complete dissolution was found to occur within 15 minutes. The viscosities of each of the samples were maintained nearly constant to each other to reduce the effect of rate of shear upon the measurements. For this, the cotton concentrations in solution were chosen according to the rule:

\[ [\eta]'c = 3.09 \pm 0.5 \]

\([\eta]'\), intrinsic viscosity (dL/g); c, cellulose concentration (g/dL)

3.3.2.2 Measurement of viscosity

The dissolved cellulose solution (7 mL) was transferred by means of a pipette to the Ostwald viscometer. By applying nitrogen pressure, the top of the meniscus of the solution was raised above the bulb to the top mark (A) as illustrated in Figure 3.8. The outflow time required for the meniscus to pass from the top mark (A) to the lower mark (B) below the bulb was measured. The average time taken was determined from five measurements where the measurement did not differ more than 0.3 % from each.
### 3.3.2.3 Calculations

The DP was calculated according to the following equations.

\[ \eta_r = \frac{t}{t_0} \quad (1) \]

\([\eta]_o\), relative viscosity; \(t\), outflow time of CUEN cotton solution; \(t_0\), outflow time of 0.5 M CUEN solution.

\[ [\eta]' = \frac{[\eta].c}{c'} \quad (2) \]

\([\eta]'\), intrinsic viscosity; \(c'\), actual concentration of cotton solution, \([\eta].c\), determined corresponding to the \([\eta]_r\) from the table provided in the test method [125].

\[ DP = 190.[\eta]' \quad (3) \]
3.3.3 Rheological analysis

The rheological tests of polymer solutions (dissolved cotton and duck feathers) were conducted on a Discovery HR-3 hybrid rheometer with a 40 mm parallel plate to plate geometry. The set gap was approximately 0.5 mm for all the samples. Steady shear measurements (flow sweep) were carried out in the shear rate range of 0.1 to 5000 s\(^{-1}\) which is the upper limit of the instrument. Oscillatory shear measurements (frequency sweep) were carried out in the frequency range of 0.1 to 100 Hz at applied strain \(\gamma = 10\%\) to measure the shear moduli of solutions. 10\% strain was chosen for the frequency sweeps since the solution was in the linear viscoelastic region at that strain value. A strain sweep from 0.1 to 100\% at a fixed angular frequency of 10 rad/s was performed to determine the linear viscoelastic region before each frequency sweep. To investigate the influence of the temperature, all tests were carried out over the temperature range of 25°C to 60°C.

3.3.4 Fourier transform infrared spectroscopy (FTIR) analysis

FTIR spectra of the regenerated films were measured on a Bruker LUMOS FTIR microscope in ATR mode. Firstly, samples were scanned in the frequency range of 600 to 4000 cm\(^{-1}\) at the scan resolution of 4 cm\(^{-1}\). All spectra were background subtracted and baseline corrected and sample scan time of 64 scans. Then the samples were again scanned in the regions of interest in the O-H stretch region in 2900cm\(^{-1}\) to 3600cm\(^{-1}\) and amide I region in 1590 cm\(^{-1}\) to 1710 cm\(^{-1}\) for the deconvolution. FTIR measurement was repeated 3 times, taken over 3 places on the same film.

The hydroxyl region (2900-3600 cm\(^{-1}\)) was de-convoluted, and the curve was fitted adopting Gaussian model using OPUS 7 software. Deconvolution was carried out adapting a Lorentzian model using a deconvolution factor of 2 and noise reduction factor 0.3. A straight baseline correction of FSD spectrum was performed followed by curve fitting using a Gaussian model. De-convoluted spectra were automatically adjusted by the auto fit program using a local least square algorithm. Band positions were determined based on fixed number bands determined according to the second
derivatives of the original spectra. Three peaks were found in the hydroxyl region which represent inter- and intra- molecular hydrogen bonding of the regenerated films. The intra-molecular hydrogen bonds for O(2)H … O(6), and O(3)H … O(5) (endocyclic oxygen) and the inter-molecular hydrogen bonds for O(6)H … O(3) in the cellulose of the bio films appeared between 3455-3410, 3375-3340 and 3310-3230 cm\(^{-1}\) respectively [126-128]. Finally, the spectrum was area normalised to obtain the percentage conformations of three bands which represent inter- molecular and intra- molecular hydrogen bonding of the regenerated films.

The amide I region (1595-1705 cm\(^{-1}\)) was deconvoluted, and the curve was fitted as described above. Three peaks were found in the amide I region in 1654-1658 cm\(^{-1}\) (α-helix), 1621-1630 cm\(^{-1}\) (β-sheet) and 1646-1652 cm\(^{-1}\) (random coils) [129-132].

3.3.5 Dynamic mechanical analysis (DMA)

The stress-strain (tensile) properties of the regenerated films were measured using dynamic mechanical analysis. Tensile properties of films were measured on a TA Q800 DMA testing machine in tensile mode, with a maximum load capacity of 18N. Stress-strain curves for the thin rectangular bio film strips having the dimension of 25 x 5 x 0.065 mm were obtained at room temperature at a controlled force rate of 0.25N/min. DMA measurements were repeated with 5 specimens of each sample type. The Young’s modulus was obtained by calculating the gradient of the linear part of the stress-strain curve. All samples were conditioned at 20°C ± 2°C and 60 ± 2% RH for 24 h prior to testing.

3.3.6 Single fibre strength analysis

Tensile tests of the regenerated fibres were performed using the Instron Tensile Tester fitted with a 5.00 N load cell. All tests were conducted at a fixed gauge length of 14.00 mm and at a controlled extension rate of 1.5 mm/min. The instrument was programmed to apply a pre-tension of 0.15 cN before recording load-extension data. Tensile test measurements were repeated with 5 fibres of each sample type. The Young’s modulus
was obtained from calculating the gradient of the linear part of the stress-strain curve. All samples were conditioned at 20°C ± 2°C and 65 ± 2% RH for 24 h prior to testing.

3.3.7 Proton nuclear magnetic resonance (\(^1\)H NMR)

\(^1\)H NMR was used in **TWO** experiments. First, to verify the purity of the recycled ionic liquid after the regeneration of natural polymers.

All proton NMR spectra of the ILs were recorded using a Jeol 270 MHz spectrometer in either DMSO-\(d_6\) or D\(_2\)O. The residual solvent peaks were used as the internal reference.

To determine the interactions occurring within the glucose-ionic liquid-water solution, the chemical shifts of the various components were monitored using \(^1\)H NMR. The amount of glucose (10 wt%) was kept constant however the IL and water concentrations were varied accordingly (see **Table 3.2** below).

*Table 3.2: Concentrations varied within glucose-IL-water solutions*

<table>
<thead>
<tr>
<th>Glucose concentration (wt%)</th>
<th>IL concentration (wt%)</th>
<th>Water concentration (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>70</td>
</tr>
</tbody>
</table>

3.3.8 \(^{13}\)Carbon nuclear magnetic resonance (\(^{13}\)C NMR)

The solid state of \(^{13}\)C NMR spectra of the pure and recovered polyester samples were recorded on Bruker AVANCE III 125 MHz Wide Bore using 4.00 mm MAS HX probe. The experiments were carried out at the spinning rate of 12.5 kHz at 25°C for 5677 scans.
3.3.9 Differential scanning calorimetry (DSC)

The DSC experiments on pure and recovered polyester samples were performed on TA DSC Q 200 differential scanning calorimetry using 4-6 mg of the sample. Firstly the samples were heated to 100°C at a heating rate of 10°C/min under N₂ atmosphere. Then the samples were held at 100°C for 5 minutes to remove the thermal history. The samples were cooled down 0°C at a cooling rate of 10°C/min and held for 5 minutes. Subsequently, the samples were heated from 0°C to 300°C at a heating rate of 10°C/min (second scan). The second scans of the samples are shown in the results.

3.3.10 Thermogravimetric analysis (TGA)

Thermal stability of the samples were measured using thermogravimetric analyses (TGA) on a Netzsch STA 409 thermogravimetric analyser. Measurements were performed using 5-8 mg of the samples. The specimens were heated from 30°C to 500°C at a heating rate of 10°C/min under N₂ atmosphere. The thermal degradation temperature at which the weight loss begins (T<d>) was calculated as the onset.

3.3.11 Scanning electron microscopy (SEM)

The morphology of samples was observed using Zeiss Supra 55VP scanning electron microscope (SEM) at an accelerating voltage of 5.00 kV. The sample surface was gold coated before observation.

3.3.12 Contact angle measurements

The contact angle of the regenerated films was measured using a Malvern contact angle measurement instrument.
3.4 Error analysis

All the sample preparations and experiments were duplicated (and in some cases repeated up to 5 times) in order to verify the reproducibility of the experimental data. Error bars determined from the multiple runs have been displayed wherever possible. Analysis of data through least-square fitting routines have provided an estimate of the uncertainty of the fit in the form of standard errors.

The next chapters of the thesis comprehensively discuss the results obtained from the work carried out according to the research plan showed in section 1.4.1. Above mentioned starting materials, sample preparation methods and suitable techniques have been used to fabricate and characterise the materials which are discussed in the following chapters.
CHAPTER 4
Processing and characterisation of regenerated cellulose

4.1 Introduction

The significant limitation associated with the recycling of clothing back into the original fibres is that the majority of clothing is comprised of blended fibres [15-17]. Globally, the most common blend used in clothing is the polyester/cotton blend [15, 16, 25]. This chapter investigates the use of ionic liquids (IL) for separating the polyester component from polyester/cotton blends and regenerating cellulose from the cotton component. This is aimed towards formulating a complete recycling solution for textile clothing waste as illustrated in Figure 4.1. While polyester and cotton can easily be recycled individually, it is rather difficult when they are intimately mixed with each other as is the case when they are blended for textile use. As such, mechanical separation methods cannot be used to separate polyester and cotton. It was highlighted in the literature that only limited attempts have been made to separate these blends chemically, which involved either dissolving the polyester component or the cotton component [71, 73, 76, 133]. However, these chemical methods were not environmentally sustainable solutions.

Figure 4.1: Complete recycling solution for polyester/cotton blends
In this study, we have used ILs, as environmentally friendly processing solvents for the chemical separation of polyester/cotton blends. The ILs selected for this study were the cellulose dissolving 1-allyl-3-methylimidazolium chloride (AMIMCl) and 1-butyl-3-methylimidazolium acetate (BMIMOAc). These ILs have the ability to selectively dissolve the cotton component, with the added advantage that the IL can be recycled and reused.

This chapter is aimed at using imidazolium based ILs to separate polyester/cotton blended materials by selectively dissolving the cotton component. After the separation process, both the undissolved polyester and the cellulose regenerated from the dissolved cotton were characterised. A combination of SEM, $^{13}$C NMR, FTIR, DSC, and TGA, DMA and DP measurements were used to understand the structure, purity and the material properties of the recovered materials.

4.2 Results and Discussion

4.2.1 Dissolution of polyester and cotton in ionic liquids

For this process both AMIMCl and BMIMOAc have been studied. These ILs have been selected on the basis of their both cellulose protein polymer dissolving capabilities. Indeed, both these ILs have previously been reported to have a high cellulose dissolution capability [134]. Now, to determine if the IL would dissolve polyester, 100% polyester yarn (used as received) was submerged in the IL at the different temperatures of 80°C, 100°C and 120°C. After heating the polyester yarn at the various temperatures in both the ILs, no evidence of structural changes nor dissolution, was observed. Figure 4.2 shows the PLM images of polyester yarn submerged in AMIMCl at 100°C where clearly no dissolution was observed.
Additionally, 1% wt of polyester yarn was subjected to dissolve in the IL at the above two temperatures for a period of 48 hours. The weight of the polyester yarn specimen before and after dissolution time was measured to be the same. Therefore, both PLM and dissolution observations showed that the polyester was insoluble in AMIMCl and BMIMOAc. Next, the dissolution of cotton in these ILs was carried out at the same temperatures.

Table 4.1 shows the impact of dissolution temperature on the time taken to completely dissolve 5 wt% cotton in AMIMCl and BMIMOAc. This data was used to set the reaction temperature and time in the polyester/cotton separation process. At room temperature, both ILs swelled the cotton yarn, but didn’t dissolve the cotton. However, the cotton yarn was found to readily dissolve at 80°C with magnetic stirring. For both ILs, with increasing temperature, dissolution occurred more rapidly. Temperature is known to play an important role in increasing the dissolution rate of cellulose in these ILs [85, 88]. For both AMIMCl and BMIMOAc, there was only a slight difference in dissolution time as a function of temperature.
The dissolution process of cotton in AMIMCl at 100 °C was monitored by PLM as shown below in Figure 4.3. Noticeably, the individual cotton fibres were broken into fragments quickly, dissolving in the IL. It was also observed that during the initial stage, the dissolution occurred very rapidly as the less disordered stable cellulose dissolved first. Then dissolution rate decreased, which might be the result of taking more time to dissolve the remaining of more crystalline cellulose components.

Table 4.1: Dissolution time to dissolve 5 wt% cotton in ILs

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>Dissolution time (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Room temp</td>
</tr>
<tr>
<td>AMIMCl</td>
<td>swelling</td>
</tr>
<tr>
<td>BMIMOAc</td>
<td>swelling</td>
</tr>
</tbody>
</table>

Figure 4.3: PLM images of the dissolution of cotton yarn in AMIMCl at 100°C
4.2.2 Separation of polyester/cotton blend by chemical dissolution

After verifying that both AMIMCl and BMIMOAe do not dissolve polyester, but cotton, the dissolution of polyester/cotton blend in ILs was investigated. Polyester/cotton blended yarn, used as received (polyester: cotton blend ratio 50:50) was added to AMIMCl and BMIMOAe at 100°C at 2 wt% increments up to 10 wt% (totalling up to 5 wt% of cotton). After 6 hours, the undissolved component was removed, rinsed with water and weighed. Table 4.2 shows the weights of the blend before cotton dissolution and the recovered amounts in AMIMCl. Both AMIMCl and BMIMOAe was found to have similar amounts of dissolved cellulose and undissolved polyester. The blend recovery yields obtained for BMIMOAe are given in Appendix A: Table A1. These results show that approximately 50 wt% of the blend yarn had been dissolved suggesting that indeed the cotton component of the blend was completely dissolved. On this basis, it was decided that both ILs have similar separation capabilities. In contrast, BMIMOAe was found to be less diffusive compared to AMIMCl which made polymer solutions in BMIMOAe difficult to process. (This will be discussed in Chapter 6). Therefore only the separation study with AMIMCl is discussed in this section.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Initial blend weight (mg)</th>
<th>Residue weight (mg)</th>
<th>Undissolved polyester from the blend %</th>
<th>Dissolved cotton from the blend %</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1602.25</td>
<td>803.60</td>
<td>50.15</td>
<td>49.85</td>
</tr>
<tr>
<td>B</td>
<td>1598.23</td>
<td>798.85</td>
<td>49.98</td>
<td>50.02</td>
</tr>
<tr>
<td>C</td>
<td>1600.40</td>
<td>801.72</td>
<td>50.09</td>
<td>49.91</td>
</tr>
</tbody>
</table>

The dissolved cotton was then cast into films using water as the coagulant. After the regeneration, the residual solvent was collected separately to recycle the IL. The IL was recycled by solvent evaporation as previously described [84, 98]. No difference
in the neat IL and recycled IL was detected by $^1$H NMR spectra as shown in Figure 4.4. The recycled IL was able to use in further two dissolution cycles without any noticeable degradation of the IL. There was no difference in cellulose recovery yield% and the material properties of the cellulose regenerated from the neat IL and recycled IL.

Figure 4.5 shows the general scheme for the separation of the polyester/cotton blend using AMIMCl. After the selective dissolution, the recovered polyester (undissolved component) was characterised and compared with the raw polyester as received. The dissolved cotton was regenerated in the film form using water, then characterised and compared with the cellulose regenerated from a pure cotton sample.
4.2.3 Characterisation of recovered polyester

This section explores a series of material characterisation performed for the recovered polyester in comparison to the pure polyester as received. The undissolved polyester from the blend was rinsed several times and oven dried before the characterisation.

4.2.3.1 Scanning electron microscopy

*Figure 4.6.a* shows the morphology of the 50/50 polyester/cotton blend yarn. It shows that the fibres are tightly held together by means of a twist. The cotton and polyester fibres were clearly distinguishable. The cotton fibre possesses a twisted ribbon like structure due to its convolutions present along the fibre axis [3, 57]. In contrast, the polyester fibre possesses a uniform circular structure [44, 57].

From *Figure 4.6.b*, it is observed that the fibres have been unravelled and that there is an absence of the twisted cotton fibres. Instead, a loose bundle of polyester fibres remains. This reveals that the cotton part of the polyester/cotton blend had been removed during the dissolution.
4.2.3.2 Fourier transform infrared spectroscopy

The FTIR spectrum of pure (black curve) and recovered (red curve) polyester are shown in below Figure 4.7. Both spectra show four distinguished peaks related to the polyester. The peaks which appear at 1715 cm\(^{-1}\) and 1245 cm\(^{-1}\) are due to carbonyl (C=O) stretching and (C=O)-O stretching respectively [135-139]. The CH\(_2\) wagging of the ethylene glycol segment owing to gauche-conformation and trans-conformation appeared at 1095 cm\(^{-1}\) and 724 cm\(^{-1}\) respectively [135-139]. This gauche-conformation is found only in the amorphous phase whilst the trans-conformation is found in both amorphous and crystalline phases of the polyester fibre [135, 136]. These
distinguished peaks appeared in both FTIR spectra (pure and recovered polyester) suggesting that the polyester structure was maintained after the separation process. However, there was an additional broad peak near 3300 cm\(^{-1}\) due to the presence of the OH stretching vibration which was obtained for the recovered polyester [127, 140]. This indicates that there could still be traces of cotton present in the recovered material.

4.2.3.3 \(^{13}\)Carbon nuclear magnetic resonance

Figure 4.8 shows the \(^{13}\)C NMR spectra of pure (black curve) and recovered polyester (red curve). Peak shifts for six different carbon environments present in polyester [141] could be seen in both spectra. Additionally, in the recovered polyester spectra there were new peak shifts between 60 to 110 ppm due to presence of cotton. The \(^{13}\)C NMR spectrum of cotton gives peak shifts owing to its six different carbons between 60 to 110 ppm [88, 102]. This trace amount of cotton which remained in the recovered polyester was found to be less than 2% as evidenced by the additional peaks observed.
at 60 and 110 ppm and the presence of the hydroxyl peak at 3300 cm\(^{-1}\) in the FTIR spectrum.

4.2.3.4 Thermal stability

Polyester is a thermoplastic polymer which has a melting temperature around 250\(^\circ\)C. Figure 4.9.a shows the DSC curves of pure (black curve) and recovered (red curve) polyester. Both curves displayed a single phase transition around 252\(^\circ\)C indicating the melting point. It can be seen that there was no change in the melt temperature of the recovered polyester, which is important since polyester can be recycled by melting the polyester and reshaping the polyester into a desired form (fibres, bottles, etc.). Figure 4.9.b shows the TGA curves of pure (black curve) and recovered (red curve) polyester. For both curves one thermal degradation phase was observed due to thermal decomposition indicating high purity of the recovered material as pure polyester. This again tells that the traces of cotton present in recovered polyester is negligible. Pure polyester showed an onset thermal degradation temperature at 408\(^\circ\)C while the
recovered polyester onset was at 398°C. The slight reduction of thermal stability of recovered polyester may have been caused due to the high temperature treatment experienced during the polyester/cotton blend dissolution step.

Based on these characterisations, it was verified that the polyester had been separated from the polyester/cotton blend and the thermal properties of the recovered polyester were similar to pure polyester as received.

Figure 4.9: DSC curves (4.9.a) and TGA curves (4.9.b) of pure (black curve) & recovered (red curve) polyester
4.2.4 Characterisation of regenerated cellulose

Once the undissolved polyester component was recovered, the remaining solution (cotton/AMIMCl solution) was used to regenerate cellulose using water as the coagulant. Below describes a series of material characterisation experiments performed on the cellulose regenerated from the cotton component in a polyester/cotton blend and from a pure cotton sample, by using the same IL, AMIMCl.

4.2.4.1 Scanning electron microscopy

Figure 4.10 shows SEM images of the cellulose films regenerated from a pure cotton (4.10.a) & a cotton blend (4.10.b). In both cases, a homogenous morphology without any visible phase separation and a continuous surface is observed. This verifies complete dissolution of cotton in the ionic liquid as well as the complete removal of polyester fibres from the IL solution. Additionally this suggests that the cellulose regeneration in water is not diffusion limited as expected in films with a thickness of 65 μm.

![SEM images of regenerated cellulose from pure cotton (4.10.a) & recovered cellulose (4.10.b)](image126x163to554x199)

**Figure 4.10**: SEM images of regenerated cellulose from pure cotton (4.10.a) & recovered cellulose (4.10.b)
4.2.4.2 Fourier transform infrared spectroscopy

*Figure 4.11* below shows the FTIR spectra of regenerated cellulose made from pure cotton (black curve) and recovered cellulose (red), from the polyester/cotton blend.

Both spectra were similar showing a broad peak around 3300 cm\(^{-1}\) owing to the O-H stretch vibration and the peak observed at 2900 cm\(^{-1}\) due to the C-H stretching in cellulose polymers [126, 127, 142]. Cellulose is derived from anhydroglucose units (AGU), which condense through glycosidic bonds. The multiple hydroxyl groups on the glucose residues holding the chains firmly together side-by-side via inter- and intra-molecular hydrogen bonding to form micro fibrils with high tensile strength (see *Figure 4.12*).
The O-H stretch region (3000 cm$^{-1}$ to 3600 cm$^{-1}$) in FTIR spectra could be deconvoluted to calculate the intra- and inter-molecular hydrogen bond conformations. No major change in the hydrogen bond conformation were measured which suggests that the hydrogen bond conformation of regenerated cellulose is maintained during the separation process. Deconvolution data is provided in Table 4.3.

*Figure 4.12: a.1 & a.2) Intra- and b) inter-molecular hydrogen bonds in cellulose*

*Table 4.3: Hydrogen bond conformation % in the regenerated cellulose from pure cotton & recovered cellulose*

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Intra-molecular hydrogen bonds</th>
<th>Inter-molecular hydrogen bonds</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O(2)H … O(6) (3455-3410 cm$^{-1}$)</td>
<td>O(3)H … O(5) (3375-3340 cm$^{-1}$)</td>
</tr>
<tr>
<td>Regenerated cellulose-pure</td>
<td>6.39%</td>
<td>73.05%</td>
</tr>
<tr>
<td>Regenerated cellulose-recovered</td>
<td>5.00%</td>
<td>72.09%</td>
</tr>
</tbody>
</table>
4.2.4.3 Thermal stability

Figure 4.13 shows the TGA curves of regenerated cellulose made from pure cotton (black curve), recovered cellulose (red) from the polyester/cotton blend and pure cotton as received (black dotted line). The onset thermal degradation temperature for pure cotton was 315°C and for cellulose regenerated from pure and recovered were measured to be 274°C and 277°C, respectively. Even though the thermal stability of the two regenerated cellulose samples was similar, it exhibited a lower onset degradation temperature compared to the natural cotton fibre as reported by Swatloski et al. [85]. This could be due to the breakdown of long cellulose polymer chains into shorter chain lengths during dissolution caused by high temperature and time. These short length polymer chains could therefore lower the thermal stability of regenerated cellulose.

Interestingly, the residual masses after pyrolysis of pure cotton and regenerated cellulose was about 27% and 33% respectively. Regenerated cellulose in IL gives a higher char yield (non-volatile carbonaceous material) on pyrolysis, indicated by the high residual masses after the degradation step. A similar char yield has been observed for other regenerated cellulose types; viscose and lyocell [143]. It seems that this higher char yield observed could be because the regenerated cellulose is “purer” (containing less non-carbon contents) compared to the parent cotton fibres. This will be an area of interest in the carbon fibre industry to use IL treated cellulose as low cost precursor materials [144, 145].
4.2.4.4 Dynamic Mechanical analysis

The stress-strain curves of regenerated cellulose from pure cotton (black curve) & recovered cellulose (red curve) are shown in Figure 4.14. The maximum tensile strength, elongation at break and Young’s modulus are given in Table 4.4. The tensile strength/elongation at break of regenerated cellulose from pure cotton and recovered cellulose was measured to be 54.89 MPa/4.70% and 55.66 MPa/4.48% respectively. There was not a considerable difference in the tensile properties between the two regenerated cellulose specimens. This indicates that the cellulose has been successfully recovered from the polyester/cotton blend without altering its material properties in the regenerated form. However it has been noticed that the regenerated cellulose in imidazolium based IL is very brittle in nature with poor elasticity as reported by us and others (low strain %) [70, 146-149]. The tensile strain of cellulose regenerated in imidazolium ILs were found to be in the range of 4-5% [70, 147, 148].This is considerably lower to that of regenerated cellulose fibres; viscose and lyocell where the tensile strain ranged from 8-20% [4].This phenomenon is therefore not desirable to make use of the regenerated material in applications such as spun in to fibres.
Therefore, a considerable understanding of the factors which affect the tensile properties is essential towards improving the elasticity of regenerated cellulose in IL. The tensile properties of cotton cellulose is intimately related with the degree of polymerisation (DP) of cotton. The next section explores how the processing parameters affect the DP of regenerated cellulose, thus its tensile properties.

![Stress-strain curves of regenerated cellulose from pure cotton (black curve) & recovered cellulose (red curve)](image)

**Figure 4.14: Stress-strain curves of regenerated cellulose from pure cotton (black curve) & recovered cellulose (red curve)**

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Stress at breakage (MPa)</th>
<th>Strain at breakage (%)</th>
<th>Young’s modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regenerated cellulose-pure</td>
<td>54.89 ± 4.37</td>
<td>4.70 ± 0.26</td>
<td>1.76 ± 0.11</td>
</tr>
<tr>
<td>Regenerated cellulose-recovered</td>
<td>55.66 ± 3.61</td>
<td>4.48 ± 0.34</td>
<td>1.74 ± 0.08</td>
</tr>
</tbody>
</table>

**Table 4.4: Stress-strain values of the regenerated cellulose from pure cotton & recovered cellulose**
4.2.5 Processing parameters affecting the degree of polymerisation of regenerated cellulose

After the successful separation of the polyester/cotton blend into individual components by selectively dissolving the cotton component, the dissolved cotton was regenerated. The regenerated cellulose in IL was very brittle in nature which led to poor tensile properties (low strain at break), as measured previously. The degree of polymerisation (DP), is an important polymer property which has a direct measurement on the tensile properties. This study was carried out to understand the influence of the processing conditions on the DP of regenerated cellulose as a function of cellulose concentration, ionic liquid, dissolution temperature, dissolution time and the type of coagulant. The processing parameters studied in cellulose regeneration is shown below in Figure 4.15.

In this work, how the processing conditions impacts the degree of polymerisation were investigated. Three cellulose dissolving ILs: 1-allyl-3-methylimidazolium chloride (AMIMCl), 1-butyl-3-methylimidazolium acetate (BMIMOAc), and 1-ethyl-3-methylimidazolium methylphosphonate ([EMIM][P(OCH₃)(H)O₂]) were used to completely dissolve known cellulose concentrations at different temperatures and time. The complete dissolution was verified by PLM imaging. The dissolved cellulose were then regenerated using water, methanol and iso-propanol as coagulants. Interestingly, cellulose could not be regenerated when [EMIM][P(OCH₃)(H)O₂] was used. Therefore no further studies were conducted using this IL. The intrinsic viscosity–average DP of regenerated cellulose was determined using an Ostwald
viscometer in cupri-ethylenediamine hydroxide solution (refer to Chapter 3 for the method). The intrinsic viscosity–average (DP) represents the average number of glucose units in the cellulose polymer [125].

Table 4.5 shows the DP of different grades of commercially available cellulose. It can be seen that the raw cotton used in this study has the highest DP value of 1260. When comparing the DP of the lyocell and viscose, lyocell was found to have a noticeably higher DP. The lower DP obtained by viscose in comparison to lyocell is due to the difference in the fibre formation process as well as the derivatisation of cellulose during viscose processing [4, 5, 11].

<table>
<thead>
<tr>
<th>Cellulose grade</th>
<th>DP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw cotton (used to in this study)</td>
<td>1260</td>
</tr>
<tr>
<td>Lyocell fibres</td>
<td>730</td>
</tr>
<tr>
<td>Viscose rayon</td>
<td>300-450[150]</td>
</tr>
</tbody>
</table>

Table 4.5: DP of the different types of commercial cellulose fibres

4.2.5.1 Effect of dissolution temperature and ionic liquids

The raw cotton (DP of 1260) was dissolved in IL and the DP of regenerated cellulose was measured. Figure 4.16 shows the DP of regenerated cellulose in water; as a function of temperature for cotton dissolved in AMIMCl (black) and BMIMOAc (red). The amount of cellulose dissolved at each temperature was constant at 8 wt%, however the time taken to dissolve changes with temperature such that; it took about 30 hours to dissolve at 80°C compared with 5 hours to dissolve at 130°C. When dissolution was performed at 80°C, the DP was decreased by almost half (compared to the DP of starting material 1260). Further increase of the temperature continued to reduce the DP. When dissolution was performed at 130°C, the DP is reduced to 280. A similar trend was observed when BMIMOAc was used. Interestingly, the choice of IL did not alter the DP expressively. However, it can be seen that the temperature of dissolution has a dramatic effect on the DP.
The lowered DP obtained after dissolution at high temperatures suggests that degradation (depolymerisation) of cellulose had occurred. A decrease in the DP has also been reported by others when high temperatures (above 100 °C) were employed for dissolution [87, 146]. Associated with dissolution at high temperatures was the colouration (darkening) of the solution [87]. Acid catalysed hydrolysis of cellulose in ionic liquids has been extensively studied and may have a role this degradation [140, 151, 152].

**Figure 4.16:** The change of DP of 8 wt% regenerated cellulose in AMIMCl (black) & BMIMOAc (red) at different temperatures

### 4.2.5.2 Effect of dissolution time

Next, the influence of dissolution time on the DP of the regenerated cellulose was determined. The dissolution time is temperature dependent. Therefore, the DP as a function of dissolution time was measured keeping the dissolution temperature constant at 100°C. **Figure 4.17** shows the impact of dissolution time on DP on the
regenerated cellulose. Here, time zero is when complete dissolution has occurred which was after 8 hours. The DP decreases as dissolution time increases. Over a period of additional 8 hours of dissolution, a decrease in the DP from 550 to 430 was measured. Very clearly the dissolution time does not have the same impact as dissolution temperature on the DP. It is suggested that the IL aids in the hydrolysis reaction occurring at the glycoside bond which promotes dissolution. From these results it is clear that the hydrolysis reaction is driven by the dissolution temperature.

4.2.5.3 Effect of cellulose concentration in solution

The change in DP was measured by varying the cellulose concentration dissolved in AMIMCl at 100°C. The cellulose concentration was varied from 5 to 12 wt% and the corresponding DP was increased from 535 to 560 (Figure 4.18). A slight increase in the DP at higher dissolved cellulose concentrations could be explained by a higher degree of polymer chain entanglement as the total polymer concentration increases.
Additionally, the time taken for the complete dissolution increased as the concentration increased.

**4.2.5.4 Effect of coagulant**

The impact of the coagulating solvent on the material properties of cellulose has been previously shown to be important [153, 154]. To determine the effect of coagulant on DP, 8 wt% of cotton was dissolved in AMIMCl at 100°C. The dissolved cotton was then regenerated using three different coagulants; water, methanol and iso-propanol. The DP of regenerated cellulose in these coagulants are shown in **Figure 4.19**. The DP of regenerated cellulose in methanol and iso-propanol showed a slight reduction in the DP by 5.5% compared to the cellulose regenerated in water. This could be attributed to that polarity of the coagulant favouring the hydrogen bond formation of regenerated cellulose during regeneration, which increased the DP. The hydrogen bond network of cellulose regenerated in methanol and iso-propanol is different to the cellulose regenerated in water [148], which could have caused a difference in the DP of the regenerated cellulose. Water was shown to be the best coagulant which has the highest

![Figure 4.18: The effect of cellulose concentration on DP of regenerated cellulose in AMIMCl dissolved at 100°C](image-url)
polarity among the coagulants investigated. Therefore, water seems more effective as the ideal coagulant to regenerate cellulose. Moreover, since water is the most environmentally friendly solvent, this eliminates the possibility of using volatile organic solvents in the cellulose regeneration process.

4.2.5.5 Effect of DP on material properties of regenerated cellulose

The tensile and thermal properties of the regenerated cellulose obtained at different dissolution temperatures were measured. The measured material properties are given in Table 4.6.

![Graph showing the effect of coagulant on DP of regenerated cellulose in AMIMCl dissolved at 100°C](image)

*Figure 4.19: The effect of coagulant on DP of regenerated cellulose in AMIMCl dissolved at 100°C*
Table 4.6: Tensile & thermal properties of the cellulose films regenerated at different temperatures (from a 8 wt% cotton/AMIMCl solution)

<table>
<thead>
<tr>
<th>Sample</th>
<th>DP</th>
<th>Stress at breakage (Mpa)</th>
<th>Strain at breakage (%)</th>
<th>Young’s modulus (Gpa)</th>
<th>Thermal stability (˚C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose regenerated at 80 ˚C</td>
<td>640</td>
<td>59.41 ± 5.41</td>
<td>4.13 ± 0.83</td>
<td>1.89 ± 0.22</td>
<td>306</td>
</tr>
<tr>
<td>Cellulose regenerated at 100 ˚C</td>
<td>550</td>
<td>57.98 ± 6.73</td>
<td>4.48 ± 0.95</td>
<td>1.88 ± 0.26</td>
<td>274</td>
</tr>
<tr>
<td>Cellulose regenerated at 130 ˚C</td>
<td>280</td>
<td>45.86 ± 6.20</td>
<td>3.42 ± 0.88</td>
<td>1.84 ± 0.23</td>
<td>252</td>
</tr>
</tbody>
</table>

The stress-strain curves of r cellulose (films) regenerated at different temperatures are shown in Figure 4.20. The regenerated cellulose dissolved at the highest temperature had the poorest tensile properties which correlates well with the DP data. As the dissolution temperature is increased the tensile properties reduced in line with the DP trend, a higher DP equates to improved tensile properties. By increasing the dissolution temperature from 80˚C to 130˚C, the stress at break was reduced from 59.41 MPa to 45.86 MPa which is a 22% loss. The loss of tensile properties for low DP values accounts for the reduction in inter adhesion forces between polymer chains as the length of polymer chains become shorter.
Figure 4.21 shows the TGA curves of regenerated cellulose at different temperatures. Similar to the tensile properties, the thermal properties of regenerated cellulose also reduces when the dissolution temperature is increased. By increasing the dissolution temperature from 80°C to 130°C, the onset thermal degradation temperature was reduced from 306°C to 252°C. The degradation of the cellulose chain length into shorter polymer chains at higher temperatures has led to the reduced thermal stability of the regenerated cellulose.

![Figure 4.21: The TGA curves for 8 wt% regenerated cellulose in AMIMCl at 80°C (green), 100°C (black) & 130°C (red)]](image)

4.2.5.6 Effect of storage time period

Figure 4.22 shows the change in DP for the regenerated cellulose as a function of the storage time after regeneration. Notably, after two years, the DP of the regenerated cellulose was found to have reduced remarkably from 550 to 310. Therefore, material properties of regenerated cellulose would also decrease as a function of storage time. It is postulated that, there may be trapped IL in the regenerated cellulose. It is likely that over time, the trapped IL continuously hydrolyses the glycosidic bond in the cellulose, to reduce the DP over a long period of time. Therefore it is important to remove the IL completely from the regenerated cellulose to maintain its material properties long term. A detailed study on the diffusion equilibrium was conducted to understand this phenomena which is discussed in a chapter 6.
4.3 Chapter conclusion

In this chapter, a facile route to separate polyester/cotton blend into their individual components had been discussed. This was achieved by selectively dissolving the cotton component using imidazolium ionic liquids AMIMCl and BMIMOAc. The separation capabilities of both ILs were found to be similar. The undissolved component (recovered polyester) was characterised and was found to be similar to the as received pure polyester. Therefore, it could be melt into solution and reused as spun fibres or bottles. However, the combination of $^{13}$C NMR and FTIR showed that there may be about 2% cotton traces remained in the recovered polyester. The dissolved cotton was then regenerated using water as the coagulant. After the regeneration, the IL was recycled and reused. The regenerated cellulose from the blend was characterised and found no difference to the cellulose regenerated from pure cotton as received. However, the tensile properties of regenerated cellulose were found to be inferior. The tensile properties have to be improved to make it usable in textile applications.
The degree of polymerisation (DP), is an important polymer property which has a direct influence on the tensile properties. The DPs of cellulose regenerated in AMIMCl or BMIMOAc, at different temperatures, times and coagulants were measured. Little to no difference in DP was observed when either AMIMCl or BMIMOAc was used in dissolution. It was shown that the increasing dissolution temperature and dissolution time reduced the DP of the regenerated cellulose leading to inferior material properties as measured. This was attributed to the breaking down of cellulose polymer chains into shorter chain lengths during dissolution which reduces the interfacial adhesion forces between the cellulose molecules. Water was shown to be the best coagulant for cellulose with the highest DP obtained, as it seems that the polarity of water favoured the hydrogen bond formation of regenerated cellulose. A substantial reduction in DP over a period of two years was noticed for the regenerated cellulose. This is likely due to continuous interaction between the cellulose and the trapped IL. This will be further discussed in chapter 06.

Regenerated cellulose is a material finding increased use in the textiles industry [4, 5, 28], in the carbon fibre industry as low cost precursor materials [144, 145] and as the starting material for bioethanol production [9, 155, 156]. However, this work found that the tensile properties of regenerated cellulose needs to be improved in order to be utilised for textile applications. The next chapter will be focussed on improving the tensile properties of regenerated cellulose in ILs via blending with other natural polymers.
CHAPTER 5
Exploring polymer blending: Towards improving properties of regenerated cellulose

5.1 Introduction

In the previous chapter, the tensile properties of IL regenerated cellulose films were measured and shown to be relatively poor. Our findings were consistent with previous reports suggesting that cellulose regenerated from ILs suffers from poor elasticity as measured by low elongation at break [70, 146]. Such poor properties were due to higher dissolution temperature, prolonged dissolution time as discussed in chapter 4.

This chapter is then aimed at improving the tensile properties of the IL regenerated cellulose via polymer blending using the IL; AMIMCl. AMIMCl was selected as the common dissolving media as it gave less viscous polymer solutions and better diffusive than BMIMOAc (This will be discussed in Chapter 6). Polymer blending is a well-known technique used in the polymer industry to develop new materials with improved properties [24, 28, 157]. Three different natural protein-based polymers were blended with cellulose to develop a series of novel cellulose/protein bio-composites. The selected natural protein polymers used for dissolution were wild muga silk, original merino wool and duck feathers. Silk was used as it has been used in the textile fibre industry since ancient times due to its fineness, lustre and excellent tensile properties [158]. However, regenerated silk in the film form is generally brittle [66-68]. For this reason, wool and duck feather has also been included in this polymer blending study. Wool, like silk, is used extensively in the fibre industry and is known to have higher elasticity with the ability to recover from extremely large strains due to its helical structure [38] when compared to the beta sheet structure of silk [159-161]. Duck feather is also an α-helix fibrous protein [21] and the use of duck feather as a blending material has not been previously reported.[21, 40]. The accumulation of considerable amount of silk and wool fibrous waste [69, 89] and duck feather waste in
The fabrication of bio-composite blends was carried out in two stages. The schematic of the material development is shown in Figure 5.1. At stage 1, cellulose was blended with silk (CS blends), wool (CW blends), and duck feather (CDF blends) to prepare three different bi-composite materials. Then, the best blend composition was selected as CDF blend type upon material characterisation. A range of blend ratios for CDF blend type (most promising results bi-composite) and tri-composite (cellulose/silk/wool) were prepared and characterised at stage 2 to find out the optimum blend composition and the blend ratio. A combination of DMA, FTIR, TGA, SEM and contact angle measurements have been used to characterise the material properties of newly developed bio-composites.
Figure 5.1: Flow chart of Cellulose/protein blend composites fabricated
5.2 Results and Discussion

5.2.1 Preparation of bi-composite materials

Cotton was blended with silk (CS), wool (CW) and duck feather (CDF) at a fixed polymer blend ratio to make three different bi-component composites. All the blend dissolutions were carried out at 100°C. The objective of this stage was to identify the most suitable protein polymer to blend with cellulose to improve the material properties. The fixed blend ratio of cellulose to protein polymer was selected to be 80:20. This blend ratio was selected to have a considerable amount of cellulose (cellulose domain) in the final material. The tensile strength of the final material is driven by the amount of cellulose present in the blended material. The blended polymer solutions were then regenerated using water as the coagulant. The cellulose/protein polymer composites made at this stage are shown in Table 5.1.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Natural polymer composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>C100</td>
<td>100% cellulose</td>
</tr>
<tr>
<td>S100</td>
<td>100% silk</td>
</tr>
<tr>
<td>W100</td>
<td>100% wool</td>
</tr>
<tr>
<td>DF100</td>
<td>100% duck feather</td>
</tr>
<tr>
<td>CS80</td>
<td>80% cellulose, 20% silk</td>
</tr>
<tr>
<td>CW80</td>
<td>80% cellulose, 20% wool</td>
</tr>
<tr>
<td>CDF80</td>
<td>80% cellulose, 20% duck feather</td>
</tr>
</tbody>
</table>

5.2.2 Characteristics of cellulose/protein bi-composite materials

5.2.2.1 Dynamic mechanical analysis

The mechanical properties of the regenerated cellulose/protein composite films were measured using DMA. For the films prepared above, the Young’s modulus, maximum
stress and strain at breakage are given in Table 5.2. C100 shows the highest stress, 54.89 MPa with a strain at break of 4.20%. Compared to the C100, the addition of silk or wool had reduced the tensile properties of the bio-based film with CW80 having the lowest stress and strain at breakage. It has been reported that when protein fibres such as wool and silk are regenerated, the degree of beta sheet is increased, resulting a brittle material with low strain at break [66, 68, 148]. On the other hand, addition of duck feather clearly improved the elasticity as measured by improvements in the strain at break. Interestingly, CDF80 gave the highest strain at break value, 6.30% which is an improvement of almost 50%, when compared to 100% regenerated cellulose. This is likely due to preservation of the $\alpha$-helix structure in the regenerated duck feather which will be discussed later in the next section. However, CDF80 showed a substantial decrease in the stress at break at 26.43 MPa.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Stress at breakage (MPa)</th>
<th>Strain at breakage (%)</th>
<th>Young's Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C100</td>
<td>54.89 ± 4.37</td>
<td>4.20 ± 0.26</td>
<td>1.76 ± 0.11</td>
</tr>
<tr>
<td>CS80</td>
<td>48.40 ± 5.91</td>
<td>3.07 ± 0.29</td>
<td>1.71 ± 0.02</td>
</tr>
<tr>
<td>CW80</td>
<td>42.18 ± 6.90</td>
<td>2.83 ± 0.31</td>
<td>1.61 ± 0.03</td>
</tr>
<tr>
<td>CDF80</td>
<td>26.43 ± 2.98</td>
<td>6.30 ± 0.41</td>
<td>1.64 ± 0.19</td>
</tr>
</tbody>
</table>

Table 5.2: Stress-strain values of the cellulose/protein blends

It was clear that the addition of duck feather improved the elasticity of the regenerated material. This finding eventually lead to the elimination of the brittleness of the cellulose regenerated in IL, which was the main issue identified in previous chapter. Thereafter, during the second stage, a series of cellulose/duck feather blends with different polymer blend ratios were prepared for further investigation (stage 2.2). As in the cases of cellulose/silk and cellulose/wool blending, neither improved the tensile properties. Therefore, a series of cellulose/silk/wool blends (tri-component) were prepared to investigate the properties of the tri component blend materials (stage 2.2).

The goal of this stage was to determine the optimum composition and/or blend ratio that improved the final material properties.
Stage 2.1: *Different blend ratios of cellulose: duck feather regenerated in water towards selecting the optimum blend ratio which gives best tensile properties (CDF binary system)*

Stage 2.2: *Different blend ratios of cellulose: silk: wool regenerated in different coagulants towards improving the properties (CSW tertiary system)*

5.2.3 Preparation & characteristics of cellulose/duck feather (CDF) bi-composite materials

In order to find the optimum cellulose to duck feather blend ratio regenerated in water, a range of CDF blends were prepared with varying blend ratios as shown in *Table 5.3*. Even though the CDF80 showed a remarkable improvement in strain at break, it showed a clear decrease in stress at break. Therefore, CDF blends where the cellulose component was greater than 80% were investigated.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Natural polymer composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>C100</td>
<td>100% cellulose</td>
</tr>
<tr>
<td>DF100</td>
<td>100% duck feather</td>
</tr>
<tr>
<td>CDF97.5</td>
<td>97.5% cellulose, 2.5% duck feather</td>
</tr>
<tr>
<td>CDF95</td>
<td>95% cellulose, 5% duck feather</td>
</tr>
<tr>
<td>CW90</td>
<td>90% cellulose, 10% wool</td>
</tr>
<tr>
<td>CDF80</td>
<td>80% cellulose, 20% duck feather</td>
</tr>
</tbody>
</table>

*Table 5.3: CDF blend compositions prepared in this study*

5.2.3.1 Dynamic mechanical analysis

The tensile properties of the regenerated CDF films are shown in *Table 5.4*. As expected, C100 showed the highest stress, 54.89 MPa with a strain at break of 4.20 %. The addition of duck feather noticeably improved the elasticity as measured by improvements in the strain at break. The addition of 10 wt% duck feather (CDF90) gave the greatest strain at break value, 11.63 % which is an improvement of greater than 150 %, when compared to the pure regenerated cellulose sample, C100. A small
decrease of 13 % in the stress at break was measured with the 10 wt% duck feather addition. Moreover, these results were still superior to CS80 and CW80 blends which were prepared previously. The decrease in the stress at break for CDF80 was substantially higher relative to the CDF90. This suggests that the optimum duck feather concentration was 10 wt% in the blended material. The stress-strain graphs of CDF blends are shown in Appendix A: Figure A1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Stress at breakage (MPa)</th>
<th>Strain at breakage (%)</th>
<th>Young’s Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C100</td>
<td>54.89 ± 4.37</td>
<td>4.20 ± 0.26</td>
<td>1.76 ± 0.11</td>
</tr>
<tr>
<td>CDF97.5</td>
<td>53.35 ± 3.67</td>
<td>4.48 ± 0.34</td>
<td>1.73 ± 0.15</td>
</tr>
<tr>
<td>CFD95</td>
<td>49.82 ± 2.32</td>
<td>6.17 ± 0.23</td>
<td>1.67 ± 0.20</td>
</tr>
<tr>
<td>CDF90</td>
<td>47.16 ± 3.02</td>
<td>11.63 ± 0.38</td>
<td>1.66 ± 0.22</td>
</tr>
<tr>
<td>CDF80</td>
<td>26.43 ± 2.98</td>
<td>6.30 ± 0.41</td>
<td>1.64 ± 0.19</td>
</tr>
</tbody>
</table>

Table 5.4: Stress-strain values of the CDF blends

The material properties mainly depend on the compositions in the film and the interfacial adhesion between them. It was clear that the cellulose component of the blend gave the strength to the final material. When adding low amounts of duck feather to cellulose, it improved elasticity due to its α-helix conformation. However, regenerated pure duck films (DF100) did not have good tensile strength (attempts to measure 100% regenerated duck feather films failed). Therefore, it was anticipated that at some duck feather loading, the properties of the blended material would decrease. From these measurements, at duck feather loadings greater than 10 wt%, a substantial decrease in material properties was measured.

5.2.3.2 Fourier transform infrared spectroscopy

FTIR has been used to determine what interactions were responsible for the improved elasticity with the addition of duck feather to the cellulose. Figure 5.2.a shows the FTIR spectra of native duck feather and the regenerated duck feather. The medium absorption band appeared at 3272 cm⁻¹ was due to the N-H stretching of the amide A region. A strong band appearing at 1628 cm⁻¹ was due to the C=O stretching in the
amide I region. The peak found at 1515 cm\(^{-1}\) was attributed to C-N stretching and N-H bending of the amide II region. The peak observed at 1236 cm\(^{-1}\) was related to the C-N and C-O stretching, N-H and O=C-N bending vibrations in amide III region [129, 131, 132, 162]. Here, the spectra of regenerated duck feather in AMIMCl was very similar to that of the native duck feather. Normally when natural protein fibres such as wool and silk are regenerated, the degree of beta sheet was increased, resulting in a brittle material with low strain at break [66, 68, 148]. However upon close inspection of the amide I region, shown in the insert, it clearly showed the regenerated duck feather maintained its \(\alpha\)-helix structure. Table 5.5 shows the deconvolution of the region, where a very slight decrease in helical content was observed. Figure 5.2.b shows the spectra of native and regenerated cellulose. The spectra of regenerated cellulose is similar to the native cotton with both showing a broad peak around 3300 cm\(^{-1}\) due to the O-H stretch vibration and the peak observed at 2900 cm\(^{-1}\) is due to the C-H stretching [126, 127].
Table 5.5: Secondary structure conformations of native and regenerated duck feathers

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>α-helix (1654-1658 cm(^{-1}))</th>
<th>β-sheet (1621-1630 cm(^{-1}))</th>
<th>Random coil (1646-1652 cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>DF native</td>
<td>54.14 %</td>
<td>33.88 %</td>
<td>11.98 %</td>
</tr>
<tr>
<td>DF100- AmimCl</td>
<td>46.78 %</td>
<td>46.22 %</td>
<td>7.00 %</td>
</tr>
</tbody>
</table>

Figure 5.2 a-b: FTIR spectra of native and regenerated 5.2.a) duck feather and 5.2.b) cellulose. Where native polymers are in black line, and regenerated polymers in AMIMCl in red line.
Figure 5.3 shows the FTIR spectra of the regenerated cellulose/duck feather blends. Increasing the duck feather concentration in the composite resulted in a narrowing as well as a shift of the O-H peak in the 3000 cm\(^{-1}\) -3500 cm\(^{-1}\) region. This peak could be used to understand the hydrogen bond network with a shift to lower wavenumbers suggesting an increase in the intermolecular hydrogen bonds with duck feather addition. This suggests that as the duck feather was added, a strong interaction between the cellulose and the duck feather exists. This also suggests that a homogenous blend was formed. Table 5.6 gives the deconvoluted data for this region for the various blends. The peak near 1620 cm\(^{-1}\) of the regenerated cellulose was overlapped with the amide I region. Therefore it was not possible to deconvolute the amide I region for the cellulose/duck feather blends.

**Figure 5.3: FTIR spectra of CDF blends in AMIMCl.**

Where C100 is red, CDF97.5 is green, CDF95 is purple, CDF90 is blue, CDF80 is gold and DF100 is black.
5.2.3.3 Thermal gravimetric analysis

The thermal degradation curves of the regenerated films in AMIMCl are shown in Figure 5.4.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Intra-molecular hydrogen bonds</th>
<th>Inter-molecular hydrogen bonds</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O(2)H – O(6)</td>
<td>O(3)H – O(5)</td>
</tr>
<tr>
<td></td>
<td>(3455-3410 cm⁻¹)</td>
<td>(3375-3340 cm⁻¹)</td>
</tr>
<tr>
<td>C100</td>
<td>4.28%</td>
<td>70.62%</td>
</tr>
<tr>
<td>CDF97.5</td>
<td>3.88%</td>
<td>69.40%</td>
</tr>
<tr>
<td>CDF95</td>
<td>3.72%</td>
<td>67.42%</td>
</tr>
<tr>
<td>CDF90</td>
<td>4.41%</td>
<td>63.18%</td>
</tr>
<tr>
<td>CDF80</td>
<td>4.18%</td>
<td>59.87%</td>
</tr>
</tbody>
</table>

Table 5.6: Hydrogen bond conformations of CDF blends in AmimCl

It could be seen that the blend composition played a major role in the thermal degradation temperature ($T_d$) of the films. The $T_d$ increased as the duck feather content of the blend increases, with CDF80 showing the highest $T_d$, which is 289 °C. The increase in the measured thermal stability was likely the result of the new bonding occurring between –NH groups of duck feathers and –O-H groups of cellulose in the
blend which increased the intermolecular hydrogen bonds as measured in FTIR deconvolution.

5.2.3.4 Contact angle measurements

Surface properties of the native and regenerated materials were measured from water contact angle. The average contact angles provided in Table 5.7 shows that the native duck feather is a super hydrophobic material with a water contact angle of 152.64°. Materials are classed as being super hydrophobic when their water contact angle is greater than 150° [163, 164]. In contrast, the water contact angle of regenerated duck feather was 77.97°, which indicated hydrophilicity (Hydrophilic materials have water contact angle less than 90° [39]). It is interesting that the surface of the regenerated duck feather changed from hydrophobic to hydrophilic during the regeneration. This could possibly be due to the changes of the secondary structure of duck feather during the dissolution process. Furthermore, when the dissolved duck feather was regenerated using water, the hydrophilic groups such as the amino and carboxyl groups may tend to self-assemble towards the water phase, making the surface of the regenerated duck feather more hydrophilic.

The water contact angle of the native cellulose fibres were 142.45°. This hydrophobicity was imparted due to the waxes present in the raw cellulose fibre. The cellulose used for the dissolution was not scoured to remove these waxes. The water contact angle of the regenerated cellulose was reduced to 119.70°, which means it retains hydrophobic properties. The removal of waxes during the dissolution process may account for the slight contact angle reduction.

For the regenerated cellulose/duck feather blended films, the addition of duck feather resulted in a reduction in the water contact angle. The CDF80 blended film has the most hydrophilic properties, with a contact angle of 82.07°. This phenomenon was due to the hydrophilicity imparted from the presence of the duck feather. The contact angle images are given in Appendix A: Figure A2.
5.2.3.5 Scanning electron microscopy

The surface morphologies of the CDF films regenerated are shown in *Figure 5.5*. It revealed the continuous morphology of the blend films, which suggest that there was no phase separation. That means that the cellulose was miscible with duck feather keratin. Also the film surface has become more irregular with the addition of the duck feather. This may be due to the difference in the way that cellulose and duck feather keratin coagulate in water. The difference in diffusion kinetic behaviour between the two materials may account for the rapid coagulation to form a clotted structure. The SEM observations, suggests that pure duck feather coagulates or refolds much faster than pure cotton giving it an irregular morphology. A higher magnification images are shown in *Appendix A: Figure A3*.

![Figure 5.5: SEM images of CDF blends in AMIMCl](image-url)

### Table 5.7: Contact angles of native and regenerated CDF blends in AMIMCl

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Water contact angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Duck feather native</td>
<td>152.64</td>
</tr>
<tr>
<td>Cotton native</td>
<td>142.45</td>
</tr>
<tr>
<td>C100</td>
<td>119.70</td>
</tr>
<tr>
<td>DF100</td>
<td>77.97</td>
</tr>
<tr>
<td>CDF97.5</td>
<td>117.25</td>
</tr>
<tr>
<td>CDF95</td>
<td>101.52</td>
</tr>
<tr>
<td>CDF90</td>
<td>95.52</td>
</tr>
<tr>
<td>CDF80</td>
<td>82.07</td>
</tr>
</tbody>
</table>
5.2.4 Characteristics of cellulose/silk/wool (CSW) tri-composite materials

From the material characterisation of the CDF binary blend system regenerated in water, CDF90 was shown to have best material properties. Since the bi-components of cellulose/silk and cellulose/wool did not improve the tensile properties, tri-components of cellulose/silk/wool compositions were prepared (see Figure 5.6) and material properties were investigated to observe if the properties could be improved. As the coagulant type also plays a key role in determining the final material properties, three different coagulants; water, methanol and iso-propanol were used to regenerate the tri-component composites to see the impact of the coagulant on the material properties. The bio-composites prepared in this study are shown in Table 5.8. The material properties were characterised as a function of the tri-polymer composition of the blend as well as the coagulant.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Natural polymer composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>C100</td>
<td>100% cellulose</td>
</tr>
<tr>
<td>S100</td>
<td>100% silk</td>
</tr>
<tr>
<td>W100</td>
<td>100% wool</td>
</tr>
<tr>
<td>CSW90</td>
<td>90% cellulose, 5% silk, 5% wool</td>
</tr>
<tr>
<td>CSW80</td>
<td>80% cellulose, 10% silk, 10% wool</td>
</tr>
<tr>
<td>CSW70</td>
<td>70% cellulose, 15% silk, 15% wool</td>
</tr>
<tr>
<td>CSW50</td>
<td>50% cellulose, 25% silk, 25% wool</td>
</tr>
</tbody>
</table>

Table 5.8: CSW blend compositions prepared
5.2.4.1 Fourier transform infrared spectroscopy

FTIR analysis was used to investigate the hydrogen bond interactions occurring in these bio-composite films. The amide 1 region (1590-1710 cm\(^{-1}\)) [128, 132] and the hydroxyl stretching region (3000-3500 cm\(^{-1}\))[126, 128] were investigated as a function of polymer composition and the coagulant. The full FTIR spectra of bio composite films are shown in Appendix A: Figure A4.

*Figure 5.7 (a-c)* shows the amide I region for the single and bio-composite films as a function of coagulating solvent. The amide I region is largely associated with the C=O stretching vibration which is used to characterise the secondary structure of proteins [132, 162]. Proteins with an\(\alpha\)-helix structure show a characteristic peak maximum at 1652 cm\(^{-1}\), while \(\beta\) sheet structured proteins are known to have a peak at 1620 cm\(^{-1}\) [132, 161, 162]. Wool is known to be an \(\alpha\)-helix protein and silk has a \(\beta\)-sheet protein structure [165, 166].
Figure 5.7: FTIR spectra of the amide I region for the bio-films regenerated in
5.7.a) water, 5.7.b) methanol & 5.7.c) iso-propanol

Where C100 is the blue line, S100 is black line, W100 is brown line, CSW90 is green line, CSW80 is green dashed line, CSW70 is green short dashed line, and CSW50 is green dotted line.

Figure 5.7.a shows the amide I region of the bio-composites regenerated in water. A difference in peak maximum of W100 and S100 films in the amide I region representing the differences between α-helix and β-sheet structure as expected. The peak maximum for the tri-component films did not considerably change with the increasing amounts of both silk and wool, where CSW90 showed a peak maximum at 1639 cm⁻¹ and CSW50 showed a peak maximum at 1640 cm⁻¹.
In contrast, larger differences were observed when methanol was used as the coagulant as seen in Figure 5.7.b. Here CSW90 has a peak maximum at 1648 cm\(^{-1}\), with addition of both silk and wool the peak maximum for CSW70 and CSW50 was shifted to 1620 cm\(^{-1}\). This peak shift suggests that an increased amount of $\beta$-sheet structure was present when methanol was the coagulating solvent. Figure 5.7.c shows the bio-composites regenerated in iso-propanol. The iso-propanol showed a similar trend to water with little difference in the peak maximum for the tri-component bio-films as a function of protein polymer addition. Interestingly, the regenerated single component proteins which were S100 and W100 showed little difference as a function of coagulating solvent.

Figure 5.8 a-c shows the hydroxyl stretching region of the bio-composites regenerated in water, methanol and iso-propanol. In Figure 5.8.a, C100 regenerated in water shows a single broad peak with a maximum at 3306 cm\(^{-1}\) corresponding to the O-H stretching band. Two peaks were observed for the protein polymers S100 (3271 cm\(^{-1}\) and 3069 cm\(^{-1}\)) and W100 (3270 cm\(^{-1}\) and 3060 cm\(^{-1}\)). These peaks correspond to the O-H and the N-H bands respectively [70, 126, 127]. For the tri-component bio-films, a single broad peak was observed. The intensity of this peak decreases with increasing protein content, and a slight shift in this peak was observed for the high protein sample CSW50. This is likely explained by the influence from the N-H groups of the protein polymers altering the H-bond interactions within the new bio-films.

Figure 5.8.b shows the same bio-films coagulated in methanol. Only a slight difference was observed for the single component films C100, S100 and W100 when compared with water coagulated samples as in Figure 5.8.a. However for the tri-component bio-films, noticeable differences were observed as the protein content increased. Again a decrease in the intensity of the peak was observed as the protein content increased. As the protein polymer content was increased, the shape and position of the peak changed. It was no longer a broad peak as in the case for CSW90, but shifted towards the peak positions of the single component S100 and W100 with a clear narrowing of the peak. This clearly shows the impact that the coagulating solvent has on the structure of these tri-component bio-films.
Finally, Figure 5.8.c shows the bio-films regenerated in iso-propanol. Again a slight difference in the OH stretch region was observed for the single component films, suggesting that the coagulating solvent has a minor role to play in the regeneration of single component bio-films. It is surprising then, that the coagulating solvent can impact the structure of the tri-component films. The iso-propanol coagulating tri-component bio-films again showed a difference in the OH region as the protein polymer content is increased.

Figure 5.8: FTIR spectra of the hydroxyl stretch region for the bio-films regenerated in 5.8.a) water, 5.8.b) methanol & 5.8.c) iso-propanol

Where C100 is the blue line, S100 is black line, W100 is brown line, CSW90 is green line, CSW80 is green dashed line, CSW70 is green short dashed line, and CSW50 is green dotted line.
In order to further investigate the hydrogen bond conformation within the bio-composites as noticed above, fourier self-deconvolution of the hydroxyl stretching region were performed. **Table 5.9** shows the distribution of the inter- and intra-molecular hydrogen bonds as a function of polymer composition and coagulant. The percentage of intermolecular hydrogen bonds increased with increased addition of silk and wool. This suggests as the protein polymers were added, a strong interaction between the blended polymers was occurring between the protein amide groups and cellulose hydroxyl groups. A change in the inter- and intra-molecular hydrogen bonds was also calculated as a function of coagulating solvent. A slight increase in the intramolecular hydrogen bonds was observed for the water coagulated films. This suggests that when the films were coagulated using water, the interactions between the polymers were improved. This could be due to the difference in miscibility of the IL in the different coagulating solvents - the miscibility of IL was highest in water.

**Table 5.9: Intra & inter molecular hydrogen bond conformation in CSW blends**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Intramolecular hydrogen bonding</th>
<th>Intermolecular hydrogen bonding</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Water</td>
<td>Methanol</td>
</tr>
<tr>
<td>C100</td>
<td>70.62%</td>
<td>4.28%</td>
</tr>
<tr>
<td>CSW90</td>
<td>67.44%</td>
<td>3.58%</td>
</tr>
<tr>
<td>CSW70</td>
<td>56.35%</td>
<td>3.42%</td>
</tr>
<tr>
<td>CSW50</td>
<td>51.99%</td>
<td>3.36%</td>
</tr>
</tbody>
</table>

5.2.4.2 Thermal gravimetric analysis

The thermal degradation temperature (T_d) of CSW bio-composites are shown in **Table 5.10**. The TGA graphs obtained for bio-composites are given in **Appendix A: Figure A5**. It was seen that the coagulant type played a key role in the T_d of tri-component bio-films. The T_d increased as the protein polymer content increased, for all coagulants, with CSW50 showing the highest T_d of the bio-films. The T_d for CSW50 coagulated in water was 290 °C. This increase in thermal stability measured for
CSW50 coagulated in water was likely due to the increase in the hydrogen bonds measured for this bio-film.

**Table 5.10: Thermal degradation temperature of CSW blends**

<table>
<thead>
<tr>
<th>Sample</th>
<th>C100</th>
<th>S100</th>
<th>W100</th>
<th>CSW90</th>
<th>CSW80</th>
<th>CSW70</th>
<th>CSW50</th>
<th>Coagulant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Td (°C)</td>
<td>274</td>
<td>278</td>
<td>227</td>
<td>238</td>
<td>259</td>
<td>286</td>
<td>290</td>
<td>Water</td>
</tr>
<tr>
<td>Td (°C)</td>
<td>276</td>
<td>271</td>
<td>230</td>
<td>240</td>
<td>249</td>
<td>267</td>
<td>274</td>
<td>Methanol</td>
</tr>
<tr>
<td>Td (°C)</td>
<td>274</td>
<td>269</td>
<td>232</td>
<td>242</td>
<td>245</td>
<td>263</td>
<td>272</td>
<td>Iso-propanol</td>
</tr>
</tbody>
</table>

**5.2.4.3 Dynamic mechanical analysis**

For CSW bio-films coagulated in water, the Young’s modulus, maximum stress and strain at breakage are given in **Table 5.11**. The addition of silk and wool fibres were found to reduce the tensile properties of the bio-film, with CSW50 having the lowest stress and strain values at breakage. The stress-strain graphs of the CSW blends are given in **Appendix A: Figure A6 & A7**.

**Table 5.11: Stress-strain values of CSW blends**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Stress at breakage (MPa)</th>
<th>Strain at breakage ( % )</th>
<th>Young’s Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C100</td>
<td>54.89 ± 4.37</td>
<td>4.20 ± 0.26</td>
<td>1.76 ± 0.11</td>
</tr>
<tr>
<td>CSW90</td>
<td>47.53 ± 5.43</td>
<td>3.31 ± 0.26</td>
<td>1.79 ± 0.01</td>
</tr>
<tr>
<td>CSW80</td>
<td>45.87 ± 7.06</td>
<td>2.98 ± 0.34</td>
<td>1.77 ± 0.03</td>
</tr>
<tr>
<td>CSW70</td>
<td>28.42 ± 7.45</td>
<td>1.54 ± 0.38</td>
<td>1.76 ± 0.03</td>
</tr>
<tr>
<td>CSW50</td>
<td>22.94 ± 6.68</td>
<td>1.49 ± 0.47</td>
<td>1.70 ± 0.05</td>
</tr>
</tbody>
</table>

**Table 5.12** shows the stress-strain values of the CSW70 bio-film coagulated in water, methanol and *iso*-propanol. CSW70 coagulated in water had the highest stress at strain, with CSW70 coagulated in methanol having a 16% decrease in stress at breakage and a reduction in the strain at breakage. This could be due to the enhanced β-sheet as revealed by the FTIR measurements. Although β-sheet is linked to high strength, it can also induce an increased brittleness to the films. *Iso*-propanol coagulated CSW70, also
performed similar to methanol with a loss in the material properties relative to water coagulation.

Table 5.12: Stress-strain values of CSW70 coagulated in water, methanol & iso propanol

<table>
<thead>
<tr>
<th>Sample</th>
<th>Stress at breakage (MPa)</th>
<th>Strain at breakage ( % )</th>
<th>Young's Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSW70 in water</td>
<td>28.42 ± 7.45</td>
<td>1.54 ± 0.38</td>
<td>1.76 ± 0.03</td>
</tr>
<tr>
<td>CSW70 in Methanol</td>
<td>25.44 ± 4.34</td>
<td>1.32 ± 0.26</td>
<td>1.73 ± 0.05</td>
</tr>
<tr>
<td>CSW70 in Iso-propanol</td>
<td>26.63 ± 5.13</td>
<td>1.44 ± 0.30</td>
<td>1.75 ± 0.04</td>
</tr>
</tbody>
</table>

5.2.4.4 Scanning electron microscopy

Figure 5.9 shows SEM images of the CSW bio-films regenerated in different coagulants. For all coagulants a homogenous morphology without any visible phase separation and a continuous surface was observed. This verified complete dissolution of the natural fibres in the IL and suggests that coagulation was not diffusion limited, as expected in films with thickness of 65 μm.

Figure 5.9: SEM images of CSW blends regenerated in different coagulants
5.3 Chapter conclusion

In this chapter, a comprehensive study was carried out to develop a novel regenerated cellulose composite material with improved tensile properties. Silk, wool and duck feather in the fibrous waste form were used to blend with cellulose in AMIMCl. Firstly, bi-component cellulose blends with silk, wool and duck feather at a fixed blend ratio were regenerated in water. Blending silk or wool with cellulose did not improve the tensile properties. Interestingly, cellulose/duck feather bi-component showed a remarkable improvement in elasticity properties measured as strain at break.

Secondly, a series of cellulose/duck feather compositions were regenerated in water to explore the optimum blend ratio that offered the best material properties. The new CDF (bi-component) blended films showed enhanced elastic properties as well as thermal stability in comparison with the 100% cellulose (C100) regenerated in AMIMCl. The CDF90 film showed the highest elasticity properties whereas CDF80 was shown to have the highest thermal degradation temperature. The amount of α-helix in the blend film accounted for improved elastic properties and the increase in intermolecular hydrogen bonds for the increase in thermal degradation.

The blends of cellulose/silk or cellulose/wool regenerated in water did not improve the tensile properties compared to C100. Therefore, cellulose/silk/wool (CSW) tri-component blends were regenerated in water, methanol and iso-propanol to investigate the material properties. Again, the CSW blends showed enhanced thermal stability compared with the regenerated single component films. However, tri-component blends did not improve the tensile properties compared to C100. The choice of the coagulant was shown to considerably impact the material properties of the tri component bio films. Methanol was shown to enhance the formation of β-sheet structure but as a consequence a reduced strain at breakage was measured. While water was shown to coagulate films with the best material properties, the CSW50 bio-film was shown to have the highest thermal degradation temperature. The increase in
hydrogen bonds for the bio-films likely accounted for the increase in thermal degradation.

Based on this study, a novel cellulose bio-composite material has been developed by regenerating dissolved cellulose/duck feather blend in water. The ideal cellulose to duck feather blend ratio was found to be 90:10 (CDF90), which gave the best material properties. CDF90 bio-composite showed a stress at break 47.16 MPa, strain at break 11.63% and thermal degradation temperature at 284°C whereas regenerated cellulose have stress at break 54.89 MPa, strain at break 4.20% and thermal degradation temperature at 274°C.

Clearly, blending of 10 wt% duck feather with cellulose (CDF90) has improved the elasticity greater than 150% compared to 100% regenerated cellulose (C100). This work demonstrated the use of non-fibrous waste materials to develop a novel cellulose-based composite material with improved elasticity.

The work presented in this chapter shows that, the addition of 10% duck feather to cellulose improves the elastic properties of the final composite in the film form. The next chapter will be focused towards developing a novel regenerated fibre from the above mentioned composite that could potentially be used in textile applications.
CHAPTER 6
Towards developing an improved regenerated cellulose fibre

6.1 Introduction

This chapter seeks to understand the “spin ability” of cellulose (C100) and cellulose/duck feather solution (CDF90) towards developing a new regenerated cellulose based composite fibre using IL. As outlined in the literature review, wet spinning is a well-established method for spinning cellulose-based solutions. In wet spinning, many parameters can influence the final properties of the fibre. Figure 6.1 highlights the parameters investigated in this chapter.

Figure 6.1: Schematic of the fibre development stage
The rheological properties of the spinning solution have a major influence on the fibre shaping, structure formation and final properties of the fibre. This is because of the change in the elastic behaviour of the polymer solutions when the shear is exerted during spinning. Therefore, the elastic behaviour of the polymers under shear was analysed by rheological measurements. Diffusion kinetics of the IL during fibre formation is an important parameter to understand, as the IL can have an affinity with the cellulose and often trapped IL remains in the regenerated cellulose material. It was therefore important to characterise this. The stretch ratio of the new fibres was also investigated, as stretch fibres during formation is known to improve crystallinity and therefore material properties. Finally, the tensile properties of the fibres produced were measured towards establishing a structure-property relationship for the regenerated fibres.

6.2 Results and Discussion

6.2.1 Characterisation of solution state properties of the polymers dissolved in IL

The experimental results of two important solution state properties, namely; the IL diffusion during polymer regeneration and the rheology properties of the polymer solutions are discussed in this section.

6.2.1.1 Diffusion of IL during polymer regeneration

To date, the diffusion dynamics of IL in cellulose solutions have not been studied. Only the diffusion dynamics in Polyacrylonitrile (PAN) fibre formation in Dimethyl sulfoxide (DMSO), Dimethylacetamide (DMAc) and IL (BMIMCl) were reported [110, 111, 167]. It is well known that higher diffusion rate has a faster diffusion, which leads to the formation of a non-uniform fibre. On the other hand, a slower diffusion rate has a slower diffusion which causes insufficient coagulation of the fibre. Therefore, a moderate diffusion is important to obtain a fibre with the desired
properties [110]. This work will investigate how the diffusion dynamics affect, as a function of IL, polymer concentration, dissolution temperature and cellulose/duck feather composition.

6.2.1.1.1 Effect of IL on diffusion

Both AMIMCl and BMIMOAc were used to investigate the diffusion in cellulose-IL solutions by dissolving raw cotton at 100ºC. Figure 6.2 shows the diffusion equilibrium with the coagulation time for the two ILs investigated.

![Figure 6.2: Change of diffusion dynamics as a function of IL, where AMIMCl is the black line, and BMIMOAc is the red line.](image)

It could be seen that for both ILs, the IL content in the fibre decreased rapidly in the initial coagulation. With increasing coagulation time, the residual IL content in the fibre reached a constant value. Interestingly, some residual IL remained in the fibre for both ILs.

The AMIMCl showed a higher diffusion rate reaching an equilibrium position in around 8 minutes of coagulation. After the equilibrium, the trapped IL (AMIMCl) in
the fibre was measured to be 2.9% of the weight of the fibre. BMIMOAc showed a slower diffusion rate, reaching equilibrium in around 15 minutes of coagulation. The amount of trapped IL for BMIMOAc dissolved cotton is almost double that of the fibre regenerated from AMIMCl dissolved cotton (This finding of trapped IL then could be related to the decrease of tensile properties of the regenerated cellulose over time, as shown in chapter 4.

To further investigate the diffusion of IL from cellulose to water, the chemical shift as measured by $^1$H NMR of the water peak was used. Since cellulose precipitates in water, it was not possible to use it in this experiment. Therefore, glucose was used as a model. *Figure 6.3* shows how the water peak shift changes with the water content in the IL-glucose system.

*Figure 6.3: Change in water peak shift as a function of water content in IL-glucose system, where AMIMCl in black line, and BMIMOAc in red line*
The peak shifts indicate that the addition of water considerably disrupts the hydrogen bonding between IL and the glucose. For the AMIMCl-glucose system, the peak shift was changing more up field when the water was added. In contrast, for BMIMOAc, the peak shift was changing from downfield when the water was added. From this clear peak shift change directions, it can be seen that the BMIMOAc-glucose interaction was less affected by the addition of water and maintains more hydrogen bonds with glucose compared to the AMIMCl-glucose interactions. These data are correlated with the anion-dependent hydrogen bond acceptor (HBA) properties of the ILs, determined using \(^1\)H NMR chemical shift of ethanol in equimolar ethanol-ILs mixtures by Sellin et al. \[168\]. The HBA properties of the OAc anion was measured to be greater than the Cl anion, irrespective of the IL cation present \[168\]. Therefore, it is anticipated that the slow diffusion of BMIMOAc into water during cellulose regeneration is due to the strong hydrogen bond interaction between BMIMOAc and cellulose. Furthermore, the larger molecular size of the BMIMOAc compared to AMIMCl must have resulted in slow down the diffusion further because the large size diffusion entities possess relatively low diffusion coefficients \[118\].

Based on the above result, it was shown that the slow diffusion in BMIMOAc to water in cellulose regeneration is due to the strong hydrogen bond interaction between the BMIMOAc and cellulose. As a result, cellulose regeneration in BMIMOAc leads to a higher equilibrium time and trapped IL compared to cellulose in AMIMCl solution. Furthermore, corresponding AMIMCl regenerated cellulose had a higher DP of 550 compared to the DP value of 535 for BMIMOAc regenerated cellulose, as discussed in chapter 4. Hence, AMIMCl was selected as the spinning solvent over the BMIMOAc due to having relatively less equilibrium time and trapped IL.

6.2.1.1.2 Effect of polymer concentration and composition on diffusion

Before adding the duck feather, cellulose (raw cotton) dissolved in AMIMCl at 100°C at different concentrations were used to investigate the diffusion dynamics as a function of polymer concentration as seen in Figure 6.4. Figure 6.5 shows how the diffusion changed when 10% duck feather was added to the cellulose solution in the
total weight of 8 wt% polymer concentration. Since the 90% cotton: 10% duck feather composition (CDF90) had the best elastic properties, as shown in chapter 5, only this composition was considered for the diffusion study. For future work, it is suggested to study the diffusion dynamics as a function of duck feather: cellulose composition ratio.

Figure 6.4: Change of diffusion dynamics as a function polymer concentration, Where 5% in red line, 8% in black line & 10% in green line

Figure 6.5: Change of diffusion dynamics in C100 (black) & CDF90 (red) at total of 8 % polymer concentration
From *Figure 6.4*, it is seen for all cellulose concentrations, the diffusion rate of the IL into the water was higher at the beginning of the coagulation. This is expected due to the larger concentration gradient of the IL between the cellulose filament and the water bath. After a sufficient coagulation time, the IL concentration difference between cellulose fibre and water bath was decreased, thus resulted a diffusion equilibrium. It can be seen that the diffusion rate is reduced when the cellulose concentration is increased in the IL solution. Even though the concentration difference between cellulose fibre and water bath is the key factor to stimulate the IL diffusion from cellulose fibre to water bath, the higher viscosity of cellulose/AMIMCl solutions has depressed the diffusion of AMIMCl as the cellulose concentration is increased. At higher cellulose concentrations, the higher viscosity reduce the driving force of IL molecular diffusion in to the water bath. This result is comparable with the diffusion studies of cellulose in 1-butyl-3-methylimidazolium chloride (BMIMCl) solution reported by Jiang et al. [120] where the diffusion coefficient of BMIMCl was reduced with the increase of solution viscosity at higher cellulose concentrations. Furthermore, higher cellulose concentration in solution could substantially form a larger gelatinous regenerated cellulose network during coagulation, which is considered as the main resistance to further diffusion [117]. Further, this result correlates with the diffusion kinetics of cellulose/NMNO solutions [119, 121] and cellulose/NaOH solutions [118, 122] as the diffusion of the solvent is decreased rapidly with increasing the cellulose concentration in all the studies reported.

*Figure 6.5* shows the diffusion equilibrium curves for the pure cellulose (C100) and the cellulose 90: duck feather 10 blended composition (CDF90) dissolved at 100°C. It could be seen that the diffusion rate markedly increased at the CDF90 solution. The average equilibrium time was reduced to 5 minutes from the 8 minutes when the duck feather was introduced to the solution (see *Table 6.1*). A reduction in the solution viscosity (will be shown in rheology experiments later in this chapter) was observed for the cellulose/duck feather blends. Notably, as in the case of diffusion of different cellulose concentrations, the reduced viscosity of the polymer blend must have increased the diffusion rate. The average time took to reach diffusion equilibrium,
trapped IL % and the corresponding DP of the regenerated cotton are given in Table 6.1.

Table 6.1: Diffusion dynamics & DP data of different cellulose concentrations, where C100- 100% cotton, CDF90-90% cotton: 10% duck feather

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average time to equilibrium (min)</th>
<th>Trapped IL (°)</th>
<th>DP</th>
</tr>
</thead>
<tbody>
<tr>
<td>5% C100 in AMIMCl</td>
<td>6.5</td>
<td>1.89±0.03</td>
<td>535</td>
</tr>
<tr>
<td>8% C100 in AMIMCl</td>
<td>8.0</td>
<td>2.89±0.05</td>
<td>550</td>
</tr>
<tr>
<td>10% C100 in AMIMCl</td>
<td>8.0</td>
<td>4.54±0.06</td>
<td>555</td>
</tr>
<tr>
<td>8% CDF90 in AMIMCl</td>
<td>5.0</td>
<td>2.44 ± 0.05</td>
<td>-</td>
</tr>
<tr>
<td>8% C100 in BMIMOAc</td>
<td>15.0</td>
<td>3.78 ± 0.04</td>
<td>535</td>
</tr>
</tbody>
</table>

Even though the DP is increased with the cellulose concentration, the trapped IL % as well as the equilibrium time also increased. For 10 wt% cellulose, the trapped IL% was measured to be 4.54%, which is relatively higher. Despite the higher DP value of 555, such a high amount of trapped IL could degrade the regenerated cellulose to reduce the tensile properties, as shown in chapter 04, as the measured DP reduction over a period of two years after the regeneration. Therefore, a polymer concentration of 8 wt% was selected as the optimum polymer concentration for the fibre formation. For CDF 90, no great difference was noticed in the trapped IL compared to the C100 in total 8 wt% polymer concentration.

6.2.1.2 Rheology of the polymers in IL solutions

Once the IL was chosen, polymer concentration and the cellulose/duck feather composition was established based on the previous experiments, the rheological behaviour was investigated to determine the spinning ability of the selected polymer solutions.
It is well known that the formation and the properties of spun fibres are largely influenced by the rheological properties of the spinning solutions [11, 106]. Cellulose solution in IL possesses a clear elastic behaviour, which could be quantified via rheological measurements similar to polymer melts. As far as fibre spinning is concerned, the spinning solutions can be appropriately characterised using two rheological experiments, namely the flow sweep test and frequency sweep test. Before adding the duck feather, the rheology of pure cellulose solution was characterised as a function of polymer concentration and temperature. The spinning parameters were established based on rheological and diffusion data. The rheology of cellulose/duck feather compositions was characterised under these defined spinning parameters.

6.2.1.2.1 Flow sweep analysis of polymer solutions in IL

The flow sweep analysis of cellulose in AMIMCl solutions have been previously reported only for a lower shear rates up to 100 s\(^{-1}\) [169, 170]. In general, the shear rate that would apply during the fibre spinning stage usually occurred at a higher range. Therefore, the flow sweep analysis of cellulose solutions were investigated over a wide range of shear rates up to 5000 s\(^{-1}\).

*Figure 6.6* illustrates how the dynamic viscosity of solutions of different cellulose concentrations dissolved in IL (AMIMCl) changes when increasing the shear rate at 25°C. For 8 wt% cellulose in AMIMCl, *Figure 6.7* shows the change of viscosity with the increase of shear rate.
Figure 6.6: Dynamic viscosity as a function of shear rate for solutions at different cellulose concentrations in AMIMCl at 25°C, Where 5% in red line, 8% in black line & 10% in green line.

Figure 6.7: Dynamic viscosity as a function of shear rate for 8% cellulose solution at different temperatures, where 25°C in black solid line, 40°C in black dashed line & 60°C in black dotted line.
For all curves, a Newtonian behaviour at lower shear rates and a typical shear thinning behaviour (reduction in viscosity) were observed when the shear rate is increased. The shear thinning of the polymer solutions is mainly caused by the alignment of the polymer chains in the direction of the shear filed and the disentanglements of the long polymer chains when the shear rate is increased [171]. With the increase of cellulose concentration in AMIMCl, the dynamic viscosity was also increased intensively as seen in Figure 6.6. This has been attributed to the increase of solution viscosity with the increase of dissolved cellulose concentration, which increases the entanglements of dissolved cellulose macromolecules in solution. This study suggests that at higher cellulose concentrations, an increased in the aggregation of cellulose chains occurs causing a higher degree of entanglements and leading to a higher viscosity. Such increase of solution viscosity is not desirable for the spinning process.

The change of dynamic viscosity of 8 wt% cellulose solution with the temperature was then tested. It was clearly noticed that the viscosity drops dramatically when the temperature was increased, as shown in Figure 6.7. This could be attributed to the enhancement of the polymer chain mobility due to the reduction in polymer chain entanglements when the temperature was increased.

The zero shear viscosity can be approximated by fitting the flow sweep data over a wide range of shear rate using the three parameter cross model [172]. The cross model is given below in Equation 1 where \( \eta_a \) is the apparent viscosity, \( \eta_\infty \) is the infinite shear viscosity, \( \eta_0 \) is the zero shear viscosity, \( \dot{\gamma} \) is the shear rate, and \( \alpha_c \) and \( m \) are time constants related to the polymer relaxation time in solution.

\[
\eta_a = \eta_\infty + \frac{\eta_0 - \eta_\infty}{1 + (\alpha_c \dot{\gamma})^m}
\]

Equation 1: The full cross model used to calculate zero shear viscosity
Figure 6.8 shows the range of zero shear viscosities of these cellulose solutions as a function of cellulose concentration and temperature. It could be noticed that the viscosity of the polymer solution can be manipulated either from polymer concentration or temperature within a broad range of around 2.8 – 760 Pa.s. This is important in giving more flexibility in the fibre spinning in terms of changing the solution viscosity.

![Figure 6.8: Range of zero shear viscosities as a function of cellulose concentration and temperature, Where 5% in red line, 8% in black line & 10% in green line](image)

In this work, 8 wt% polymer concentration was chosen as the suitable concentration for spinning, considering the DP and the diffusion data. However, at room temperature, 8 wt% cellulose concentration was not able to spin due to having a higher viscosity. Since the increased temperature favoured in reducing the solution viscosity, 40°C was selected as the spinning temperature. The selected cellulose/duck feather composition (CDF90) in AMIMCl solution was characterised and shown in Figure 6.9.
It can be seen that the viscosity was further reduced by adding the duck feather into solution. It was reported that silk solution in AMIMCl behave as a Newtonian fluid which belongs to a dilute solution region, unlike the cellulose solution in AMIMCl [12]. Therefore it is anticipated that the duck feather solution in AMIMCl also behave in the dilute solution region as silk since both polymers are keratin based proteins. The reduction in zero shear viscosity was calculated to be by around 70% compared to the viscosity of C100. Such overall reduction in solution viscosity due to both elevated temperature and duck feather were desirable in terms of the spinning process. Further exploration of reducing the viscosity as a function of duck feather in CDF blends is recommended for future studies.

Figure 6.9: Dynamic viscosity of C100 (black dashed line) & CDF90 (red dashed line) as a function of shear rate for 8% polymer solution at 40 °C
6.2.1.2.2 Frequency sweep analysis of polymer solutions in IL

Frequency sweep test was performed by measuring the shear moduli G’ and G” as a function of the frequency in an oscillation experiment. The storage (G’) and loss (G”) moduli as functions of frequency for different cellulose concentrations at 25°C are shown in Figure 6.10. Next, Figure 6.11 illustrates the shear moduli as a function of frequency for 8 wt% cellulose solution at different temperatures. Finally, the selected cellulose/duck feather composition (CDF90) in AMIMCl solution (8 wt%) was characterised at 40°C as seen in Figure 6.12.

Figure 6.10: Storage (G’) and loss (G”) moduli of different cellulose concentrations as a function of frequency, where dashed lines: G’, solid lines: G” and 5% in red lines, 8% in black lines & 10% in green lines
Figure 6.11: Storage ($G'$) and loss ($G''$) moduli 8% cellulose as a function of frequency for different temperatures, where dashed lines: $G'$, solid lines: $G''$ and 25°C in black lines, 40°C in green lines & 60°C in red lines.

Figure 6.12: Storage ($G'$) and loss ($G''$) moduli of C100 (black lines) & CDF90 (red lines) as a function of frequency for 8% polymer solution at 40°C, Where dashed lines: $G'$, solid lines: $G''$. 
From Figure 6.10, it could be seen that the viscoelastic behaviour of solution was increased with the increase of cellulose concentration as expected. For 8 and 10 wt% cellulose concentrations, a cross over point was found, which is the frequency at the $G''$-$G'$ intersection point which is also known as the gelation point. Here, the region before the cross over point (where $G'' > G'$), the solution is considered as a fluid, while after the cross over point is considered as a gel. At the cellulose concentration of 5 wt%, a cross over point was not found and the solution behaved as a fluid. When the concentration was increased to 8 and 10 wt%, the viscous region ($G''$) has become narrower and the elastic region ($G'$) has become wider. As a result, a cross over point was found for both these concentrations at 25°C which implied both fluid and gel regions were occurring. This means, with the increase of concentration, the polymer solution behaves like an elastic solid (gel) at higher frequency. This also suggests that higher concentrations would improve the formation of temporary network between cellulose and IL molecules which favoured to behave as elastic solids [171]. Further it is suggested this elastic behaviour caused by the fact that the tight molecular entanglements between cellulose chains at higher concentrations.

When the temperature of the 8 wt% cellulose solution was increased, the viscoelastic behaviour of the solution was shifted to the opposite trend compared to when the cellulose concentration was increasing as seen in Figure 6.11. Therefore, this is in a good agreement to optimise the solution properties by increasing the concentration while reducing the viscosity by increasing the temperature. It can be seen that both shear moduli shifted to lower values when the temperature was increased. This is mainly due to lowering the molecular chain entanglements at higher temperature. At 60°C, a cross over point was not found, which indicates no gelation was occurred.

Finally, the selected cellulose/duck feather composition (CDF90) in AMIMCl solution (8 wt% total polymer concentration) was characterised at 40°C as seen in Figure 6.12. The cross over point was shifted to a higher frequency and a lower modulus when the duck feather was added to the cellulose in solution.
Further, it was reported that the average molecular weight, branching degree and molecular weight distribution could be qualitatively understood by the location of this cross over point [12]. The crossover point shifts to a higher frequency means that the average molecular weight and the branching degree of the polymer solution is lowered. This was attributed to the fact that the short cellulose chains remain in motion at high frequency, but the long and the highly branched chains cannot move any more. The lower the modulus at the cross over point, the broader the molecular weight distribution [40, 124]. The cross over points for the polymer solutions are given in Table 6.2.

Table 6.2: Cross over point location of polymer solutions, Where C100-100% cellulose, CDF90-90% cellulose: 10% duck feather

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cross over point</th>
<th>Frequency (Hz)</th>
<th>Modulus (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5% C100 at 25°C</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>8% C100 at 25°C</td>
<td>11.83</td>
<td>11,200</td>
<td></td>
</tr>
<tr>
<td>10% C100 at 25°C</td>
<td>2.25</td>
<td>8490</td>
<td></td>
</tr>
<tr>
<td>8% C100 at 40°C</td>
<td>33.84</td>
<td>6420</td>
<td></td>
</tr>
<tr>
<td>8% C100 at 60°C</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>8% CDF90 at 40°C</td>
<td>54.12</td>
<td>3820</td>
<td></td>
</tr>
</tbody>
</table>

In the frequency sweep analysis of the polymer solutions, different crossover points (gel points) were observed for the spinning solutions containing 8% and 10% cellulose, and for the solutions at 25 and 40 °C. It was then suggested that the differences in their crossover points were originated from, or directly correlated to, their differences in the molecular weight, branching degree and molecular weight distribution. The cross over point was shifted to a higher frequency and a lower modulus when the duck feather was added to the 8 wt% cellulose in solution at 40°C. This shift suggests that the average molecular weight of the cellulose/duck feather solution may have been lowered and the molecular weight distribution has become broader. Although the
changes in molecular weight, branching degree and molecular weight distribution can lead to a change in the crossover point (gel point), this does not necessarily imply that any crossover point change in a polymer solution is due to the changes in the polymer’s molecular weight, branching degree and molecular weight distribution.

Based on above diffusion and rheological experiments, some of the parameters were selected for the fibre spinning. The chosen IL for spinning was AMIMCl. The polymer blend concentration in solution was selected as 8 wt%. The moderate DP value, residual IL% trapped in the fibre and coagulation time for equilibrium have been considered for this selection. The spinning temperature was selected as 40°C due to lowering the dynamic viscosity of the polymer solution which favoured the spinning process. Additionally, the increased temperature also helped in broadening the molecular weight distribution in the solution during spinning. A broader molecular weight distribution in solution state is essential to maintain a uniform molecular weight distribution along the fibre during spinning which give rise to good material properties. Next section will discuss the spinning process of the polymer blends using wet spinning technique.

6.2.2 Characteristics of the new fibre regenerated

This section will explore some of the important characteristics of the fibres regenerated. Following spinning dope parameters and spinning conditions given in the Table 6.3 have been selected based on the previous experimental results described earlier.
After the spinning solution was prepared, the solution was extruded through a 25G needle (internal diameter of 0.260 mm) into a water bath at a given flow rate. Fibres were spun at two different flow rates. The shear rate exerted on polymer solution during spinning could be approximated by assuming the polymer solution behaved as a Newtonian fluid flowing in a thin pipe[173]. The formula of this calculation is given in Equation 2 where (γ̇) is shear rate, (Q) is volumetric flow rate and (r) is internal radius of the needle. Corresponding shear rates exerted in each spinning condition is given in Table 6.4.

\[
\dot{\gamma} = \frac{4Q}{\pi r^3}
\]

*Equation 2: Formula to calculate the shear rate in a fluid flow*
Table 6.4: Approximated shear rate applied in spinning

<table>
<thead>
<tr>
<th>Flow rate (ml/hour)</th>
<th>Shear rate (S⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>4830</td>
</tr>
<tr>
<td>60 (maximum flow rate)</td>
<td>9660</td>
</tr>
</tbody>
</table>

Clearly, it could be seen that the spinning was occurred at the shear thinning region (>1000 s⁻¹) of the polymer solutions which further reduction in solution viscosity occurred that essentially favoured the spinning process. It was apparent that, such higher shear rates are expected when forming very thin fibres using very fine needles. However rheological behaviour of the solutions at higher shear rates above 5000 s⁻¹ was not possible to characterise due to the limitation of the instrument.

After the desired coagulation time was reached in the water bath, the fibres were manually drawn to produce fibres at four different stretch ratios. Stretch ratios (%) of the fibres produced are shown in Table 6.5.

Table 6.5: Different stretch % of the fibres produced

<table>
<thead>
<tr>
<th>Sample</th>
<th>Stretch (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0 (no stretch)</td>
</tr>
<tr>
<td>2</td>
<td>6.66</td>
</tr>
<tr>
<td>3</td>
<td>13.33</td>
</tr>
<tr>
<td>4</td>
<td>20.00</td>
</tr>
<tr>
<td>5</td>
<td>26.66</td>
</tr>
</tbody>
</table>

6.2.2.1 Scanning electron microscopy

Figure 6.13 shows the SEM images of the regenerated fibres both no stretch and stretched, spun at the flow rate of 60 ml/h. Different surface morphologies for C100 and CDF90 were clearly noticed as in the film form which was discussed in chapter 05. The surface of the CDF90 was having a more irregular surface compared to C100
fibre. This could be due to the clear difference in the diffusion kinetic behaviour as measured by the time to reach the diffusion equilibrium. That indicates cellulose and duck feather keratin coagulate in water differently. Such difference in diffusion equilibrium between the two polymers may account for the faster coagulation to form a clotted structure. However, in the stretched fibres, this irregularity was no longer evident. For both C100 and CDF90 fibres, a more even and smoother surface with a streaky appearance was obtained after the stretching. This suggests that the stretching has improved the molecular orientation for some extent. Further, it was noticed a reduction in the fibre thickness as seen in Figure 6.13, when the stretch was applied. The calculated avg. fibre diameters are displayed in Figure 6.14. When the duck feather was added, a slight change in the fibre diameter was not noticed. However, the increase of the flow rate has resulted in increasing the fibre diameter marginally.

Figure 6.13: SEM images of fibres C100-no stretch (a), C100-13.33% stretch (b), CDF90-no stretch (c) & CDF90-13.33% stretch (d) spun at a flow rate 60ml/h
Figure 6.14: Avg. fibre diameters of fibres as a function of stretch ratio, where
Blue bar: C100 at flow rate 30ml/h, Blue line bar: C100 at flow rate 60ml/h and
Red line bar: CDF90 at flow rate 60ml/h
6.2.2.2 Tensile properties of the regenerated fibres

Some of the tensile properties of the regenerated fibres are given in Figure 6.15 (a-c). The single fibre stress-strain graphs are shown in Appendix A: Figure A8.
Figure 6.15.a shows the tensile stress of the fibres produced as a function of stretch ratio. With the increase of stretch ratio, the tensile stress of the fibres was increased to a maximum and then decreased. For all fibres, maximum tensile stress was achieved at the 13.33% stretch ratio. Such trend of the tensile stress profile could be stipulated to the change in the degree of amorphous orientation along the fibres. In general, tensile properties of regenerated fibres are directly related to the amorphous orientation of the fibres. The tensile stress was increased with the stretch ratio due to the increase of the orientation. However, when the stretch ratio was closer to the fibre breaking stretch, it might have caused some internal fractures on the fibre which reduced the tensile properties. For C100 and CDF90 fibres produced at flow rate of 60 ml/h the maximum tensile stress was obtained at 141.32 and 131.57 MPa respectively. As
similar to the tensile profile of the films discussed in chapter 05, the addition of duck feather reduced the tensile stress slightly.

The tensile strain of the fibres produced are shown in Figure 6.15.b. Again the trend was similar to the tensile stress profile where maximum tensile stain was achieved at the 13.33 % stretch. As expected, the addition of duck feather was able to increase the elasticity of the blended fibre. The improvement in elasticity of the fibre was measure to be 66.5%.

Figure 6.15.c shows the young’s modulus of the fibres produced. Even though it exhibited the same trend with the increase of the stretch ratio, the maximum values for all fibres were obtained at the 6.66% stretch ratio.

6.3 Chapter conclusion

In this chapter, spin ability of polymer solutions (C100 and CDF90) in IL was investigated towards producing a new regenerated cellulose/duck feather composite fibre (CDF90). A novel regenerated fibre was produced by blending cellulose and duck feathers in IL solution and tensile properties were characterised and compared with the 100% regenerated cellulose fibre (C100). Some of the key parameters to prepare the spinning solution were determined by characterising the solution state of the polymer solutions. Although a higher polymer concentration in solution is expected to give a higher DP value, the diffusion experiments revealed that the higher polymer concentration could slow down to reach to the diffusion equilibrium as well as trapping more IL inside the regenerated fibre. Further, the addition of duck feather has increased the diffusion of the IL by reaching to the equilibrium position much faster. It was found that the coagulation time should allow sufficient time to reach this equilibrium position and removing the most of the IL from the regenerated fibre.
In wet spinning operation, it is also essential to obtain a spinning dope with suitable rheology properties, i.e. viscosity and gel point, and this can be achieved by adjusting the dope concentration and temperature as revealed by the rheology experiments. The induced changes in the viscosity and gel point can be solely attributed to the change in the degree of polymer chain entanglements. Every effort would be made to avoid changes in the polymer molecular structure (molecular weight and distribution etc.) during the spinning operation.

Finally, the fibres were produced at two different flow rates by varying the stretch ratio. The tensile properties of the fibres were increased first and then reduced when the stretch ratio was increasing. The highest tensile stress and strain values for the fibres were obtained at 13.33% stretch ratio, while the highest Young’s modules values achieved at 6.66% stretch ratio. The increase of the amorphous orientation of the fibres was responsible in improving the tensile properties when the stretch was applied. As expected, the addition of the duck feather to cellulose improved the elastic properties of the final fibre. As a result of both addition of duck feather and applying 13.33% stretch ratio, the elasticity was enhanced by 66.5% of the blended CDF90 fibre regenerated in IL.

The next chapter will briefly summarise the key outcomes of this research and recommendations for further studies.
7.1 Conclusions

The work in this thesis has demonstrated the potential of recycling a common textile blend waste, polyester/cotton blend, and regenerating cellulose from the recovered cellulose into different forms such as films and fibres. Further, it has shown that the material properties of the regenerated cellulose are improved by blending it with duck feathers. The schematic in Figure 7.1 shows schematically the outcome from this thesis. Key outcomes for each chapter of the thesis are summarised below.

Figure 7.1: Schematic of the project outcomes
7.1.1 Chapter 4: Key outcomes

In this chapter, a simple route to separate polyester/cotton blend into their individual components was developed. This was achieved by selectively dissolving the cotton component of the blend, using the imidazolium based ionic liquids AMIMCl and BMIMOAc. Undissolved polyester was removed, washed and characterised. It was found that the recovered polyester was similar to native polyester as received.

Dissolved cotton was regenerated using water as the coagulant. The characteristics of regenerated cellulose from the blend were similar to the cellulose regenerated from pure cotton as received. However, the tensile properties of regenerated cellulose were found to be inferior.

It was shown that the higher dissolution temperature and prolonged dissolution time reduced the degree of polymerisation (DP) of the regenerated cellulose leading to inferior tensile properties as measured. Additionally, it was noticed that the DP of regenerated cellulose decreased as a function of storage time over a period of two years. The likelihood of trapped ionic liquid in regenerated cellulose has been proven by the diffusion kinetics experiment. The implications of this trapped ionic liquid on the DP were shown with a considerable lowering of the DP as a function of storage time.

7.1.2 Chapter 5: Key outcomes

Since the tensile properties of the regenerated cellulose was inferior, it was sought to improve the properties to make it usable in textile applications. This chapter focused on the methods for improving the material properties of the regenerated cellulose via blending with different natural protein polymers.

The cellulose was blended with silk, wool and duck feather in solution state and a range of bio-composite films were regenerated. The new cellulose/duck feather blended films showed enhanced elastic properties, as well as thermal stability, in
comparison with other blend types investigated. The selected cellulose: duck feather blend ratio was 90:10 (CDF90). The amount of $\alpha$-helix in the blend film accounted for the improvement in the elastic properties and the increase in intermolecular hydrogen bonds for the increase in thermal degradation as measured.

7.1.3 Chapter 6: Key outcomes

Since the tensile properties of the regenerated cellulose in the film form were improved by blending with duck feather, this work was extended towards developing a new regenerated cellulose/duck feather blended fibre using wet spinning. The diffusion kinetics experiments and the rheological characteristics of the polymer solutions were used to determine the ‘spin ability’ of the polymer solutions. The spinning domain was defined based on the diffusion kinetics and rheological behaviour of the polymer solutions.

After defining the spinning domain, both 100% cellulose and cellulose/duck feather blend (CDF90) fibres were produced at different stretch ratios. The tensile properties of the fibres were increased initially and then reduced when the stretch ratio was increasing. The increase of the fibre orientation was responsible for the improvement in the tensile properties when the stretch was applied. As expected, CDF90 fibres showed the highest elastic properties compared to 100% cellulose fibres. This improvement was further enhanced when the stretch was applied to the fibre. Finally, as a result of both the addition of duck feather and the application of the 13.33% stretch ratio, elasticity was enhanced by 66.5% of the blended CDF90 fibre regenerated in IL.

Overall, this work has shown potential for the development of a new regenerated cellulose/duck feather blend fibre, and it is a good platform for recycling polyester/cotton blend materials by effectively separating the blend into its pure forms chemically. As far as these two areas are concerned, the below future work is recommended for further studies.
7.2 Future work

Since this project was focused on two aspects, future work suggested for each area is outlined separately.

7.2.1 Towards an ionic solution to recycle textile wastes

- Recycling polyester/cotton blends is a broader aspect in textile recycling. In this context, only 50/50 polyester/cotton blend was investigated. Since there are so many varieties available in this blend type, a proper sorting technique could be established. Some parameters which can be considered would be the polyester/cotton blend ratio, type of the material (yarn or fabric), and the colour of the material (type of dye).

- The proposed chemical method in this work can be implemented in various types of polyester/cotton blends towards investigating the recyclability of different polyester/cotton blends and properties of the regenerated cellulose. Various processing parameters, such as the choice of IL, dissolution method and processing temperature, may have to be optimised to obtain the maximum efficiency of the process.

- This separation method could be extended to investigations on other polymer blend types present in the textile market. For example, cotton/nylon, cotton/spandex blends.

- Finally, scaling up of this technique could be combined with a proper sorting technique and defined processing parameters.
7.2.2 Spinning the waste: From waste to fibres

- The rheology and diffusion experiments were carried out on one cellulose/duck feather composition (CDF90), which was shown to be the best composition in the regenerated film form. However, a comprehensive study on rheology and diffusion dynamics by varying the duck feather composition in the blend solution is recommended.

- It is also recommended to produce fibres with different duck feather compositions in order to verify the best cellulose/duck feather composition that provide the best properties in the fibre form.

- The rheological analysis showed that the spinning domain can be broadened by increasing the polymer concentration of the spinning dope and the spinning temperature. Therefore, it is suggested to investigate the fibre properties spun at higher polymer concentrations as a function of spinning temperature.

- In this study, the fibres were drawn manually, it is recommended that a complete wet spinning set up could be used which includes drawing and winding. This would improve the fibre properties further.

- Further characterisations of the regenerated fibres, such as crystallinity, molecular orientation could be determined using WAXD and SAXS.

- Finally, this spinning process could be up-scaled towards spinning a new regenerated cellulose/duck feather fibre that can be used in textile applications.
APPENDIX A

Supplementary graphs

Table A1: Dissolved cotton % and undissolved polyester of the blend samples in BMIMOAc

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Initial blend weight (mg)</th>
<th>Residue weight (mg)</th>
<th>Undissolved polyester from the blend %</th>
<th>Dissolved cotton from the blend %</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>1601.60</td>
<td>805.55</td>
<td>50.30</td>
<td>49.70</td>
</tr>
<tr>
<td>F</td>
<td>1600.10</td>
<td>796.21</td>
<td>49.76</td>
<td>50.24</td>
</tr>
<tr>
<td>E</td>
<td>1599.54</td>
<td>800.56</td>
<td>50.05</td>
<td>49.95</td>
</tr>
</tbody>
</table>

Figure A1: Stress-strain curves of cellulose/duck feather blends regenerated in water

Where C100 is red, CDF97.5 is green, CDF95 is purple, CDF90 is blue, CDF80 is gold and DF100 is black.
Figure A2: Water contact angle of native DF (a), regenerated DF (b), native cotton (c), regenerated cellulose (d), CDF97.5 (e), CDF95 (f), CDF90 (g) & CDF80 (h)
Figure A3: SEM images of higher magnification (1μm) of the cellulose/duck feather blend films regenerated
Figure A4: FTIR spectra of CSW blends regenerated in water (a), methanol (b) & iso-propanol (c)

Where C100 is the blue line, S100 is black line, W100 is brown line, CSW90 is green line, CSW80 is green dashed line, CSW70 is green short dashed line, and CSW50 is green dotted line.
Figure A5: TGA curves of CSW blends regenerated in water (a), methanol (b) & iso-propanol (c)

Where C100 is the blue line, S100 is black line, W100 is brown line, CSW90 is green line, CSW80 is green dashed line, CSW70 is green short dashed line, and CSW50 is green dotted line.
Figure A6: Stress-strain curves of CSW blends regenerated in water  
Where C100 is the black line, CSW90 is green line, CSW80 is red line, CSW70 is blue line, and CSW50 is purple line.

Figure A7: Stress-strain curves of CSW70 blend film regenerated in water (blue), methanol (green) & iso-propanol (red)
Figure A8: Stress-strain curves of C100 (a) & CDF90 blend fibres (b) regenerated at different flow rates and stretch ratios.

Where dotted lines are C100 spun at 30ml/h (in figure a), solid lines are C100 spun at 60ml/h (in figure a & b) & dashed lines are CDF90 spun at 60ml/h (in figure b).

Black is no stretch, red is 6.6% stretch, green is 13.33% stretch, purple is 20% stretch, & orange is 26.66% stretch.
APPENDIX B

Publications
Cellulose regeneration in ionic liquids: factors controlling the degree of polymerisation

Rasike De Silva · Kylie Vongsanga · Xungai Wang · Nolene Byrne

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Abstract The degree of polymerisation (DP), is an important polymer property which has a direct influence on the mechanical properties such as tensile strength. Here we measure the degree of polymerisation of regenerated cellulose dissolved in the ionic liquids 1-butyl-3-methylimidazolium acetate (BMI-MOAc) and 1-allyl-3-methylimidazolium chloride (AMIMCl), at different dissolution temperatures, times and coagulants. We show that dissolution temperature has a dramatic impact on the DP of the regenerated cellulose. The DP of cellulose dissolved at 130 °C was measured at 230 while the DP of cellulose dissolved at 80 °C was measured at 650. We also show that ionic liquid remains trapped in the regenerated cellulose and over a period of 2 years a significant reduction in DP was measured. This is likely due to the continued interaction between the cellulose and the trapped ionic liquid.

Keywords Regenerated cellulose · Ionic liquids · Degree of polymerisation

Introduction

Cotton is the most popular cellulosic fibre used in textiles, however cotton crops consume large amounts of land, and water. As such regenerated cellulose fibres have become increasingly more popular. Regenerated cellulose fibres are produced by dissolving wood pulp in a solvent (Kotek 2007; Woodings 2000). To date, there are only two classes of regenerated cellulose fibres commercially available; with viscose currently being the most commonly used. In the viscose process, the cellulose is converted into sodium cellulose xanthate using carbon disulfide, which makes the cellulose soluble in NaOH, the fibre is then wet spun from the NaOH solution (Gibril and Yue 2012; Klemm et al. 2005; Kotek 2007). A major disadvantage of this process is the use of carbon disulfide (CS₂), a volatile and toxic gas, which is harmful to both the environment and human health (Heinze and Liebert 2001; Zhu et al. 2006; SIGMA-ALDRICH 2013). In the Lyocell process, cellulose is directly dissolved in N-methyl-morpholine-N-oxide (NMMO) and dry-jet spun from the NMMO solution (Fink et al. 2001; Kotek 2007; Woodings 2000). This method suffers from long processing times and the formation of by-products due to the degradation of both NMMO and cellulose (Kotek 2007; Woodings 2000). The main by-products formed in the process have been N-methyl-morpholine (NMM), morpholine (M), and chromophores...
which cause severe discoloration of the solution (Kotek 2007; Woodings 2000; Roseneu et al. 2001).

To make the Lyocell as commercially competitive as the viscose process, more optimisation is required with respect to solvent recovery and reduction of by-product formation. Great progress in optimisation is therefore required to make the Lyocell process more efficient and sustainable.

Due to such limitations in current cellulose regeneration methods, new solvents for cellulose processing are constantly being sought. One relatively new and growing class of cellulose solvents is ionic liquids (ILs). The dissolution of cellulose, in ILs was first reported by Swatloski et al. (2002). Since then, many researchers have focused on IL design to increase the amount of cellulose which can be dissolved by the IL (Kosan et al. 2008; Pinkert et al. 2009; Xie et al. 2005; Zakrzewska et al. 2010; Zavrel et al. 2009; Zhu et al. 2006). Generally, ILs consisting of an imidazolium cation coupled with either the chloride or acetate anions have been investigated for dissolving cellulose (Swatloski et al. 2002; Vitz et al. 2010a; Zhang et al. 2005; Goujon et al. 2013; Phillips et al. 2004; Li and Wang 2013; Xie et al. 2005). It has been reported by us and others that cellulose films regenerated from ILs suffer from poor mechanical properties. It is likely that these poor mechanical properties are linked to the dissolution temperature used. We show that there was a significant impact on the degree of polymerisation and thus the mechanical properties (Cao et al. 2010; Hameed and Guo 2009, 2010; De Silva et al. 2013, 2015). The degree of polymerisation (DP) is an important polymer property which can impact the mechanical properties of the resulting polymer. The DP is directly linked to the molecular weight of cellulose, defined as the number of anhydroglucose units (AGU) in the cellulose polymer chain (Klemm et al. 2005; Wakelyn et al. 2007; Fink et al. 2001).

Results and discussion

In this work, we have investigated how the processing conditions including dissolution time and temperature as well as coagulant, impacts the degree of polymerisation. We have selected three cellulose dissolving ionic liquids: 1-butyl-3-methylimidazolium acetate (BMIMOAc), 1-allyl-3-methylimidazolium chloride (AMIMCl), and 1-ethyl-3-methylimidazolium methylphosphonate ([EMIM] [P(OCH3)(H)O2]) (Zhang et al. 2005; Zhu et al. 2006; Fukaya et al. 2008). The dissolved cellulose were regenerated using water, methanol and isopropanol as coagulants. Interestingly, we could not regenerate cellulose when [EMIM][P(OCH3)(H)O2] was used therefore no further studies were conducted using this IL. The DP was determined using an Ostwald viscometer in cupri-ethylenediamine hydroxide solution (complete experimental details provided in supplementary information file) (Standard Test Method for Intrinsic Viscosity of Cellulose). The intrinsic viscosity–average (DP) represents the average number of glucose units in the cellulose polymer (Standard Test Method for Intrinsic Viscosity of Cellulose). Table 1 shows the DP of different grades of commercially available cellulose. It can be seen that raw cotton has the highest DP value of 1260. Comparing the DP of the Lyocell and viscose fibres shows that Lyocell has a significantly higher DP. The lower DP obtained by viscose in comparison to Lyocell is due to the difference in the fibre formation process as well the derivatisation of cellulose during viscose processing (Fink et al. 2001; Kotek 2007; Woodings 2000).

Next we measured the DP of regenerated cellulose (A) dissolved in BMIMOAc and AMIMCl. Figure 1a, b shows the DP of regenerated cellulose as a function of dissolution temperature and the dissolution time respectively for cotton dissolved in BMIMOAc and AMIMCl. It can be seen from Fig. 1a, that the temperature of dissolution has a dramatic effect on the DP. When dissolution of raw cotton was performed at 80 °C, a DP of 650 is measured, this compares to a DP of 280 when the temperature is increased to 130 °C. Interestingly, the choice of IL did not alter the DP significantly. Figure 1b shows the influence of dissolution time on the DP. Over a period of 8 h, a decrease in the DP from 550 to 430 was measured. It has been proposed that the IL aids in the hydrolysis reaction occurring at the glycoside bond which promotes dissolution, from our results its clear that the hydrolysis reaction is driven by temperature.

The lowered DP obtained after dissolution at high temperatures suggests that degradation (depolymerisation) of cellulose had occurred. A decrease in the DP has also been reported by others when high temperatures (above 100 °C) were employed for dissolution.
dissolution at high temperatures was the colouration (darkening) of the solution (Vitz et al. 2010b). Acid catalysed hydrolysis of cellulose in ionic liquids has been extensively studied and may have a role in this degradation (Amarasekara and Owereh 2009; Amarasekara and Wiredu 2012; Rinaldi et al. 2010).

Next the amount of dissolved cellulose and the change in DP was measured. The cellulose concentration was varied from 5 to 12 % and the corresponding DP was changed from 535 to 560 (Data shown in supplementary information file). A slight increase in the DP at higher dissolved cellulose concentrations is explained by a higher degree of polymer chain entanglement as the total polymer concentration increases.

The DP can directly impact the mechanical properties of the polymer therefore we measured the tensile properties of the regenerated cellulose as a function of dissolution time at different dissolution temperatures (the stress–strain curves are shown in supplementary data file). The mechanical properties of the various samples is given in Table 2. The regenerated cellulose dissolved at the higher temperature had the poorest tensile properties which correlates well with the DP data. As the dissolution temperature is reduced the tensile properties increase in line with the DP trend, a higher DP equates to improved mechanical properties. By reducing the dissolution temperature from 130 to 80 °C, the stress at break was improved by 33.33 %.

Previously we showed that cellulose coagulated using either methanol or iso-propanol had inferior material properties when compared to cellulose films coagulated using water (De Silva et al. 2013). The impact of the coagulating solvent on the material properties of cellulose has been previously shown to be important (Lu and Wu 2008; Cho et al. 1989). To determine if the coagulant solvent has any significant impact on the DP, we measured the DP of regenerated cellulose coagulated in methanol and iso-propanol (data shown in supplementary information file) and found a small difference. A slight reduction of 5.5 % was noted when compared to using water as the coagulant. This could likely by due to differences in the alignment and formation of the cellulose chains, we have previously shown that the hydrogen bond network of cellulose regenerated in these two alcohols is different to water regenerated cellulose. (De Silva et al. 2013).

Figure 2 shows the change in DP for the regenerated cellulose as a function of the time after regeneration. Notably, after 2 years, the DP of the regenerated cellulose has changed slightly.

<table>
<thead>
<tr>
<th>Cellulose grade</th>
<th>DP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw cotton yarn (cellulose A)</td>
<td>1260</td>
</tr>
<tr>
<td>Lyocell fibres (regenerated in NMMO)</td>
<td>730</td>
</tr>
</tbody>
</table>
| Viscose rayon (regenerated in NaOH/CS₂)             | 300–450   | (Kadolph 2010)
cellulose was found to have reduced quiet significantly from 550 to 310. The probability of trapped ionic liquid in the fibre is a possible explanation for the reduction in the DP over time. To investigate this, we have measured the coagulation kinetics for cellulose regeneration. Figure 3 shows the coagulation equilibrium curve of 10% cellulose-90% AMIMCl solution in water. The diffusion of the IL from cellulose into water was found to be very slow to reach equilibrium. Even after 15 min of coagulation, only approximately 87% of IL was removed. Therefore in a completely regenerated cellulose fibre using water, 3% of IL remains. It is likely that the trapped IL continuously hydrolyses the glycoside bond in the regenerated cellulose polymer chains. This in turn resulted in a gradual decrease in the DP over the storage time of the material. The mechanical properties would also decrease as a function of time. Therefore the complete removal of the ionic liquid is critical to maintain the long term mechanical properties of the regenerated cellulose fibres.

**Conclusion**

We have shown that the higher dissolution temperature and prolonged dissolution time reduced the DP of the regenerated cellulose leading to inferior material properties. The probability of trapped ionic liquid in regenerated cellulose products has been proven by the diffusion kinetics experiment. The implications of this trapped ionic liquid on the DP was shown to significantly lower the DP as a function of time.

**Acknowledgments**

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**Compliance with ethical standards**

**Conflict of interest**

The authors wish to confirm that there are no known conflicts of interest associated with this publication.

**References**


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**Table 2** Mechanical properties of 8 wt% regenerated cellulose (A) in AMIMCl at various temperatures

<table>
<thead>
<tr>
<th>Sample described</th>
<th>Measured DP</th>
<th>Stress at breakage (Mpa)</th>
<th>Strain at breakage (%)</th>
<th>Young’s modulus (Gpa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose regenerated from 80 °C</td>
<td>640</td>
<td>59.41 ± 5.41</td>
<td>4.13 ± 0.83</td>
<td>1.89 ± 0.22</td>
</tr>
<tr>
<td>Cellulose regenerated from 100 °C</td>
<td>550</td>
<td>57.98 ± 6.73</td>
<td>4.48 ± 0.95</td>
<td>1.88 ± 0.26</td>
</tr>
<tr>
<td>Cellulose regenerated from 130 °C</td>
<td>280</td>
<td>45.86 ± 6.20</td>
<td>3.42 ± 0.88</td>
<td>1.84 ± 0.23</td>
</tr>
</tbody>
</table>


Vitz J, Erdmenger T, Schubert US (2010b) Imidazolium based ionic liquids as solvents for cellulose chemistry. 1033:299–317. doi:10.1021/bk-2010-1033.ch017


Development of a novel regenerated cellulose composite material

Rasike De Silva, Kylie Vongsanga, Xungai Wang, Nolene Byrne *
Institute for Frontier Materials, Deakin University, Piddons Road, Waurn Ponds, 3216 Victoria, Australia

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ABSTRACT

We report for the first time on a new natural composite material achieved by blending cotton and duck feather using an ionic liquid. The addition of duck feather was found to improve the elasticity, strain at break, by 50% when compared to regenerated cellulose alone. This is a significant finding since regenerated cotton using ionic liquids often suffers from poor elasticity. The improved elasticity is likely due to the regenerated duck feather maintaining its helical structure. The new regenerated cellulose composites were characterized using a combination of dynamic mechanical analysis, Fourier transform infrared spectroscopy, thermal gravimetric analysis, contact angle measurements and scanning electron microscopy.

1. Introduction

Cellulose, the structural component of plant walls, is the most abundant raw material on Earth, with millions of pounds of this biopolymer produced every year (Wakelyn et al., 2007; Wang & Zhang, 2009). Given that cellulose is biodegradable, bio-compatible, thermally and chemically stable, plentiful and inexpensive, it makes for a versatile and valuable resource (Belgacem & Gandini, 2008; Klemm, Heublein, Fink, & Bohn, 2005; Morton & Hearle, 2008; Nettavali, Huang, & Mizuta, 2007; Wakelyn et al., 2007). Due to the recalcitrance of cellulose to both chemical and enzymatic processing, the development of new materials often encounters disadvantages such as long reaction times, harsh conditions or the use of toxic chemicals. Regenerated cellulose fibres can be achieved in a variety of different ways, which ultimately depends on the processing solvent. The most common methods for the preparation of regenerated cellulose are the viscose rayon along with non-viscose rayon methods (Kotek, 2007; Woodings, 2000). In the viscose method, the cellulose is converted into sodium cellulose xanthate, which is soluble in NaOH making it possible to wet-spin the polymer into a fibre or film (Gibril & Yue, 2012; Klemm et al., 2005; Kotek, 2007). The major disadvantage of this process is the use of carbon disulfide (CS₂), a volatile and toxic gas, which is harmful to both the environment and human health (Heinze & Liebert, 2001; SIGMA-ALDRICH, 2013; Zhu et al., 2006). In the non-viscose rayon processes the cellulose is not modified but directly dissolved in a solvent system, such as N-methylmorpholine-N-oxide (NMNO)/H₂O system or N,N-dimethylacetamide (DMA)/lithium chloride (LiCl) (Fink, Weigel, Purz, & Ganster, 2001; Heinze & Koschella, 2005; Heinze & Liebert, 2001; Kotek, 2007). Again, these processes suffer from long treatment times, high temperatures and have environmental concerns associated with effluent waste entering waterway. In recent times, ionic liquids (ILs) have been used for the dissolution of cellulose (Gibril & Yue, 2012; Heinze & Koschella, 2005; Kosan, Michels, & Meister, 2008; Swatloski, Spear, Holbrey, & Rogers, 2002; Vitz, Erdmenger, & Schubert, 2010) as direct solvents. Ionic liquids are composed entirely of ions with numerous possibilities for cation and anion combinations (Marsh, Boxall, & Lichtenthaler, 2004; Matsumoto et al., 2000; Rogers & Seddon, 2003; Zhu et al., 2006). The dissolution of cellulose, along with other polymers, in ionic liquid is ever expanding, with increasing numbers of ionic liquids capable of dissolving cellulose reported (Kosan et al., 2008; Pinkert, Marsh, Pang, & Staiger, 2009; Xie, Li, & Zhang, 2005; Zakrzewska, Bogel-Lukasik, & Bogel-Lukasik, 2010; Zavrel, Bross, Funke, Büchs, & Spiess, 2009; Zhu et al., 2006). The impact of ionic liquids in cellulose dissolution has expanded so greatly that companies such as BASF have even developed a pilot line utilizing 1-ethyl-3-methylimidazolium acetate (EmimOAc) as the solvent to regenerate cellulose (Hermanutz, Meister, & Uerdingen, 2006).

The material properties of regenerated cellulose can depend greatly on the processing methods, however in general, cellulose regenerated using ionic liquids suffers from poor elasticity (Cao, Li, Zhang, Zhang, & He, 2010; De Silva, Wang, & Byrne, 2013; Hameed & Guo, 2010). Therefore, in this study we have sought to improve the properties of regenerated cellulose by blending.

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Polymer blending is a well-known technique used in the polymer industry to develop new materials with improved properties (Wang & Zhang, 2009; Yu, 2009; Yu, Dean, & Li, 2006). The blending of natural polymers using ionic liquids has been previously reported by us and others (De Silva et al., 2013; Hameed & Guo, 2009, 2010), however as is the case with any polymer blending, the selection of the starting materials ultimately impacts the material properties of the final polymer. We found that using wool or silk blended with cellulose did not significantly improve the material properties of the regenerated cellulose. The use of duck feather as a blending material has not been previously reported (Idris et al., 2013; Zhao et al., 2010). Duck feathers are a keratin based protein material consist about 90% keratin which contains about 7% cysteine (Idris et al., 2013; Sun, Liu, & Liu, 2009; Ullah, Vasanthan, Bressler, Elias, & Wu, 2011). It is considered largely to be a waste material (Idris et al., 2013; Zhao et al., 2010). Only a small quantity is utilized in the textile industry for the manufacture of manchester (i.e. beddings and pillows) (Ullah et al., 2011) and duck feathers are also used in the shuttlecock for the sport badminton (Li, Mao, & Yaniv, 2007). Duck feather is under-utilized as it is a difficult material to solubilize due to the tight arrangement of the α-helix and β-sheet in the polypeptide chain (Idris et al., 2013; Sun et al., 2009; Ullah et al., 2011). Therefore, to utilize these natural polymers by converting them into suitable materials, there is a need for alternative common solvents which are efficient in dissolving both cellulose and duck feather keratin.

It was recently shown that ionic liquids can dissolve duck feather however the material properties were not measured. Here we blend cotton, which was previously separated from polyester–cotton blend wastes (De Silva, Wang, & Byrne, 2014) with duck feather and show a significant improvement in the strain properties of the composite material. In this report the new bio-composites are characterized using a combination of dynamic mechanical analysis (DMA), fourier transform infrared spectroscopy (FTIR), thermal gravimetric analysis (TGA), contact angle measurements, and scanning electron microscopy (SEM).

2. Experimental method

2.1. Dissolution of natural polymers

Single and blended natural polymer solutions of 10 wt% of the total polymer content were made using dried 1-allyl-3-methylimidazolium chloride (AmimCl) (purchased from Sigma–Aldrich, NSW, Australia) in 20 mL vials under inert N2 atmosphere. Other cellulose dissolving ionic liquids such as 1-butyl-3-methylimidazolium acetate (BMIMOAc) can be used as a solvent to blend natural polymers. Duck feather obtained from purchases duck feather pillows from spotlight, Australia. The cellulose based materials (yarns) were obtained from Leading Textiles, VIC, Australia. These yarns have not been pre-treated such as scouring or bleaching. The degree of polymerization (DP) of the starting material was measured to be 1260.

Ionic liquids were dried under reduced pressure at 85 °C for 10 h to remove water before dissolution of the polymers was carried out. The water content of the ionic liquid was measured to be less than 0.2% by Karl Fisher titration. The dissolution process was carried out using a pre-heated heating block with a thermometer at 100 °C. The cotton and duck feathers were oven dried for 24 h at 105 °C. The polymers were added at increments of 1 wt% under magnetic stirring. After total polymer dissolution, a clear and viscous bio-polymer solution was obtained. The complete dissolution was observed and verified using a Nikon 80i eclipse polarizing light microscope (PLM). A dissolved solution was obtained when no crystallinities in the polymer solution were detected.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Polymer blend composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>C100</td>
<td>100% cotton</td>
</tr>
<tr>
<td>DF100</td>
<td>100% duck feather</td>
</tr>
<tr>
<td>CDF97.5</td>
<td>97.5% cotton; 2.5% duck feather</td>
</tr>
<tr>
<td>CDF95</td>
<td>95% cotton; 5% duck feather</td>
</tr>
<tr>
<td>CDF90</td>
<td>90% cotton; 10% duck feather</td>
</tr>
<tr>
<td>CDF80</td>
<td>80% cotton; 20% duck feather</td>
</tr>
</tbody>
</table>

Measurements of regenerated polymer blends.

2.2. Preparation of regenerated films

The dissolved polymer solution (approximately 1 mL) was spread evenly between two glass slides and immersed in water for 10 min. This was repeated 3 times to ensure removal of the IL from the film. During immersion in the 2nd and 3rd bath, the film was removed from between the glass slides. After which, the film was again immersed in water for 24 h and dried for 48 h at room temperature. The measured film thickness was 65 µm. After film preparation, the residual solvent was collected separately to recycle the IL. The IL was recycled by water evaporation as described (Cao et al., 2009; Wu, Wang, Wang, Bian, & Li, 2009). No difference in the neat IL and recycled IL was detected in 1H NMR spectra (1H NMR spectra are shown in the supplementary graph document). Additionally, the recycled IL was used for further dissolution studies. The regenerated films prepared in this study are shown in Table 1.

2.3. DMA measurements

The stress–strain properties of the regenerated films were measured using dynamic mechanical analysis. Tensile properties of films were measured on a TA Q800 DMA testing machine in tensile mode, with a maximum load capacity of 18 N. Stress–strain curves for the thin rectangular bio-film strips having the dimension of 25 mm × 5 mm × 0.065 mm were obtained at room temperature at a controlled force rate of 0.25 N/min. DMA measurement were repeated with 5 specimens of each sample type. Young’s modulus was obtained from calculating the gradient of the linear part of the stress–strain curve.

2.4. FTIR spectroscopy

FTIR spectra of the regenerated films were measured on a Bruker LUMOS FTIR microscope. Firstly, samples were scanned in the frequency range of 600–4000 cm⁻¹ at the scan resolution of 4 cm⁻¹ with a background and sample scan time of 64 scans. Then the samples were again scanned in the regions of interest in the OH stretch region in 2900–3600 cm⁻¹ and amide I region in 1590–1710 cm⁻¹ for the deconvolution. FTIR measurement was repeated 3 times, taken over 3 places on the same film.

The hydroxyl region (2900–3600 cm⁻¹) was deconvoluted, and the curve was fitted adopting Gaussian model using OPUS 7 software. Deconvolution was carried out adopting a Lorentzian model using a deconvolution factor of 2 and noise reduction factor 0.3. A straight baseline correction of FSD spectrum was performed followed by curve fitting using a Gaussian model. Deconvoluted spectra were automatically adjusted by the autofit programme using a local least square algorithm. Band positions were determined based on fixed number bands determined according to the second derivatives of the original spectra. Three peaks were found in the hydroxyl region which represent inter- and intramolecular hydrogen bonding of the regenerated films. The intramolecular hydrogen bonds for O(2)H···O(6), and O(3)H···O(5) (endocyclic oxygen) and the inter-molecular hydrogen bonds for O(6)H···O(3) in the cellulose of the bio-films appeared between

Table 1

Polymer blends prepared.

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3455–3410, 3375–3340 and 3310–3230 cm\(^{-1}\) respectively (Fan, Dai, & Huang, 2012; Griffiths & De Haseth, 2007; Kondo & Sawatari, 1996; Schwanninger, Rodrigues, Pereira, & Hinterstoissier, 2004).

Finally, the spectrum was area normalized to obtain percentage conformations of three bands which represent inter-molecular and intra-molecular hydrogen bonding of the regenerated films.

The amide I region (1595–1705 cm\(^{-1}\)) was deconvoluted, and the curve was fitted as described above. Three peaks were found in the amide I region in 1654–1658 cm\(^{-1}\) (α-helix), 1621–1630 cm\(^{-1}\) (β-sheet) and 1646–1652 cm\(^{-1}\) (random coils) (Barth, 2007; Kong & Yu, 2007; Marshall, Orwin, & Gillespie, 1991; Wojciechowska, Włochowicz, & Wesełucha-Birczyńska, 1999).

2.5. TGA measurements

Thermal stability of the samples were measured using Thermogravimetric analyses (TGA) on a Netzsch STA 409 Thermogravimetric analyzer. Measurements were performed using 5–8 mg of the samples. The specimens were heated from 30 °C to 500 °C at a heating rate of 10 °C/min under N\(_2\) atmosphere. The thermal degradation temperature at which the weight loss begins (\(T_d\)) was calculated as the onset.

2.6. SEM images

The morphologies of bio-films were observed using a Zeiss Supra 55VP scanning electron microscope (SEM) at an accelerating voltage of 5.00 kV. The surface of the bio-film was gold coated before observation.

2.7. Contact angle measurements

The contact angle of the regenerated films was measured using a Malvern contact angle measurement instrument.

3. Results and discussion

The material properties of the regenerated films were measured using DMA. For the films prepared in AmimCl, the Young’s modulus, maximum stress and strain at breakage are given in Table 2 (stress–strain curves are shown in the supplementary graph document). C100 shows the highest stress, 54.89 MPa with a strain at break of 4.20% breakage. The addition of duck feather significantly improved the elasticity as measured by improvements in the strain at break. The addition of 10 wt% duck feather gives the greatest strain at break value, 11.63% which is an improvement of greater than 50%, when compared to the 100% regenerated cellulose sample, C100. A small decrease of 13% in the stress at break is measured with the 10 wt% duck feather addition, interestingly with the addition of 20 wt% duck feather, a significant decrease in the stress at break is measured while a decrease in the strain at break (relative to the 10 wt% duck feather sample) is also measured. This suggests that the optimum duck feather concentration is 10 wt%.

The material properties mainly depend on compositions in the film since it is likely that the cellulose component of the blend gives the strength to the material. At low amounts the addition of the duck feather to the cotton improves elasticity due to its α-helix conformation, regenerated duck films do not have good tensile strength (attempts to measure 100% regenerated duck feather films failed). Therefore, it completely predictable to anticipate that at some duck feather loading the properties of the blended material will decrease, from our measurements at duck feather loadings beyond 10 wt% a significant decrease in material properties is measured.

To determine what interactions are responsible for the improved elasticity with the addition of duck feather to the cellulose, we used FTIR to measure the structural interactions. Fig. 1a shows the FTIR spectra of native duck feather and the regenerated duck feather. The medium absorption band appeared at 3272 cm\(^{-1}\) is due to the N–H stretching of the amide A region. A strong band appearing at 1628 cm\(^{-1}\) is due to the C=O stretching in the amide I region. The peak found at 1515 cm\(^{-1}\) was attributed to C=O stretching and N–H bending of the amide II region. The peak observed at 1236 cm\(^{-1}\) relates to C–N and C–O stretching, N–H and O=C–N bending vibrations in amide III region (Barth, 2007; Kong & Yu, 2007; Pribic, Vanstokkum, Chapman, Haris, & Bloemendal, 1993;
Table 3
Secondary structure conformations of native and regenerated duck feathers.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>α-helix (%)</th>
<th>β-sheet (%)</th>
<th>Random coil (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DF native</td>
<td>54.14</td>
<td>33.88</td>
<td>11.98</td>
</tr>
<tr>
<td>DF100-AmimCl</td>
<td>46.78</td>
<td>46.22</td>
<td>7.00</td>
</tr>
<tr>
<td>DF100-BmimOAc</td>
<td>44.81</td>
<td>35.13</td>
<td>15.06</td>
</tr>
</tbody>
</table>

Fig. 2. FTIR spectra of regenerated films in AmimCl. Where C100 is red, CDF97.5 is green, CDF95 is purple, CDF90 is blue, CDF80 is gold and DF100 is black. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 4
Hydrogen bond conformations of regenerated cotton/duck feather blends in AmimCl.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Intra-molecular hydrogen bonds</th>
<th>Inter-molecular hydrogen bonds</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O(2)H...O(6) (3455–3410 cm⁻¹)</td>
<td>O(3)H...O(5) (3375–3340 cm⁻¹)</td>
</tr>
<tr>
<td>C100</td>
<td>4.28%</td>
<td>70.62%</td>
</tr>
<tr>
<td>CDF97.5</td>
<td>3.88%</td>
<td>69.40%</td>
</tr>
<tr>
<td>CDF95</td>
<td>3.72%</td>
<td>67.42%</td>
</tr>
<tr>
<td>CDF90</td>
<td>4.41%</td>
<td>63.18%</td>
</tr>
<tr>
<td>CDF80</td>
<td>4.18%</td>
<td>59.87%</td>
</tr>
</tbody>
</table>

Table 5
Contact angles of native and regenerated cotton/duck feather blends in AmimCl.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Water contact angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DF native</td>
<td>152.64</td>
</tr>
<tr>
<td>Cotton native</td>
<td>142.45</td>
</tr>
<tr>
<td>C100</td>
<td>119.70</td>
</tr>
<tr>
<td>DF100</td>
<td>77.97</td>
</tr>
<tr>
<td>CDF97.5</td>
<td>117.25</td>
</tr>
<tr>
<td>CDF95</td>
<td>101.52</td>
</tr>
<tr>
<td>CDF90</td>
<td>95.52</td>
</tr>
<tr>
<td>CDF80</td>
<td>82.07</td>
</tr>
</tbody>
</table>

$T_d$ increases as the duck feather content of the blend increases, with CDF80 showing the highest $T_d$, which is 289°C.

The increase in the measured thermal stability is likely due the result of the new bonding occurred between – NH groups of duck feathers and – OH groups of cellulose in the blend which increased the intermolecular hydrogen bonds as measured in FTIR deconvolution.

Surface properties of the native and regenerated materials were measured from water contact angle (contact angle images are shown in the supplementary graph document). The contact angle averages provided in Table 5 shows that the native duck feather is a super hydrophobic material with a water contact angle of 152.64°. The super hydrophobic materials have a water contact angle greater than 150° (Liu, Liang, Zhou, & Liu, 2012; Neinhuis & Barthlott, 1997). Therefore duck feather may act as hydrophobic materials such as crude oil. In contrast, the water contact angle of regenerated duck feather was 77.97°, which indicates hydrophilicity (hydrophilic materials have water contact angle less than 90° Sun et al., 2009). It is interesting that the surface of the regenerated duck feather changed from hydrophobic to hydrophilic during the regeneration. This could possibly be due to the changes of the secondary structure of duck feather during the dissolution process. Furthermore,
when the dissolved duck feather is regenerated using water, the hydrophilic groups such as the amino and carboxyl groups may tend to self-assemble towards the water phase, making the surface of the regenerated duck feather hydrophilic.

The water contact angle of the native cotton fibres was 142.45°. This hydrophobicity is imparted due to the waxes present in the raw cotton fibre. The cotton used for the dissolution was not scoured to remove these waxes. The water contact angle of the regenerated cotton was reduced to 119.70°, which means it retains hydrophobic properties. The removal of waxes during the dissolution process may account for the slight contact angle reduction.

For the regenerated cotton/duck feather blended films, the addition of duck feather resulted in a reduction in the water contact angle. The CDF80 blended film has the most hydrophilic properties, with a contact angle of 82.07°. This phenomenon is due to the hydrophilicity imparted from the presence of the duck feather.

The surface morphologies of the regenerated films in AmimCl are shown in Fig. 4. It reveals the continuous morphology of the blend films, which suggest that there was no phase separation. That means that the cellulose is miscible with duck feather keratin. Also the film surface becomes more irregular with the addition of the duck feather. This may be due to the difference in the way that cellulose and duck feather keratin coagulate in water. The difference in diffusion kinetic behaviour between the two materials may account for the rapid coagulation to form a clotted structure. The SEM observations, suggests that pure duck feather coagulates or refolds much faster than pure cotton giving it an irregular morphology. Interestingly, the surface of the films regenerated in BmimOAc (SEM images are shown in the supplementary graph document) were different to the films regenerated in AmimCl. This is likely driven by the different diffusion kinetics, which occurred due to the different ionic liquid–water interactions caused by the anions, acetate and chloride in BmimOAc and AmimCl. The acetate anion interaction with water is stronger than that of the chloride anion. Thus BmimOAc removal from the polymer into the water phase was easier than the removal of AmimCl during the coagulation resulting in different diffusion kinetics. Future work will be explored to understand the diffusion kinetics to explain this phenomenon.

4. Conclusion

We successfully regenerated new cotton/duck feather blended materials using two imidazolium based ionic liquids as the blending solvent. The new blended films showed enhanced elastic properties as well as thermal stability in comparison with the component films regenerated in ionic liquids. The CDF90 film showed the highest elasticity properties whereas CDF80 was shown to have the highest thermal degradation temperature. The amount of α-helix in the blend film accounts to improve the elastic properties and the increase in intermolecular hydrogen bonds for the increase in thermal degradation as measured. The choice of the ionic liquid did not impact the material properties of the films apart from their different surface morphologies observed from SEM. That could possibly be due to the different diffusion kinetics present with the choice of ionic liquid. Current work is in progress to understand this diffusion kinetics in coagulation process and to develop new cotton/duck feather blend fibres using wet spinning technology.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2014.12.018.

References


Recycling textiles: the use of ionic liquids in the separation of cotton polyester blends†

Rasike De Silva, Xungai Wang and Nolene Byrne*

Textiles are commonly made from intimate blends of polyester and cotton, which makes recycling very difficult. We report for the first time the use of ionic liquid in the separation of polyester cotton blends. By selective dissolution of the cotton component, the polyester component can be separated and recovered in high yield. This finding presents an environmentally benign approach to recycling textile waste.

Introduction

One of the challenges facing society today is the recycling of textiles. It has been reported that the United States generates 25 billion pounds of textiles per year and only 15% of this is recycled with 85% being sent to landfills.1–3 The U.S. EPA estimates that textile waste occupies 5% of land fill mass.1,2 As such, many campaigns exist to improve the consumers’ awareness towards recycling textiles. While donating or selling clothing has resulted in a decrease in the disposal of textiles this is not a complete recycling solution. Currently, only 15% of all textiles material is recycled back into the original form.5–7 A significant limitation associated with the recycling of clothing back into the original fibres is that the majority of clothing is comprised of blended fibres.1 The most common blend used in clothing is a polyester/cotton blend.2,5,6 While the individual components, cotton and polyester, can be easily recycled, mechanical separation techniques cannot be used for intimately mixed polyester/cotton blends.3–5,6 Limited attempts have been made to separate these blends chemically, however polyester is only soluble in very harsh solvents such as hexafluoropropanol15 and phenol/tetrachloroethane.16 High concentration acid solutions have also been investigated, such as 70–75% aqueous sulphuric acid17 and 85% aqueous phosphoric acid.18 However these are not environmentally sustainable solutions and the acid solutions promotes hydrolysis of the glycosidic linkage of the cellulose chain resulting in the degradation of the cotton fibre.19

Here we use ionic liquids, ILs, as environmentally friendly processing solvents for the chemical separation of polyester/cotton blends. The IL selected for this study is the cellulose dissolving 1-allyl-3-methylimidazolium chloride (AMIMCl).20 The benefit of using ILs in this process is the ease with which the polyester and cotton can be separated. The AMIMCI selectively dissolves the cotton component, with the added advantage that the IL can be recycled and reused. We show that the polyester is recovered in high yield and that the cotton can be regenerated into various forms, such as wet spun into fibres or cast as films. In 2012, 88.5 million tonnes of fibres were produced,21 and this amount is expected to continue to increase with demand from developing countries. This technology reported here shows a facile route to the recycling of clothing in the form of polyester/cotton blends. We measure the material properties of the recovered polyester and cotton and show that no significant differences can be seen between the recovered polymers and the as received 100% polymers.

Materials and methods

Dissolution studies

1-allyl-3-methylimidazolium chloride AMIMCl and 1-butyl-3-methylimidazolium acetate BMIMAc where purchased from Sigma Aldrich and vacuum dried for 6 hours at 80 °C prior to each dissolution experiments. The water content of the ionic liquid (IL) was measured to be less than 0.2% by Karl Fisher titration. To determine if this IL would dissolve polyester, 100% polyester as received was submerged in the AMIMCl at 80 °C and monitored using polarising optical microscopy. Over a 48 hour period, no dissolution was observed.

Separation of cotton and polyester

All the yarn specimens were oven dried at 105 °C for 24 hours prior to dissolution to remove the moisture in yarns. All the yarn samples were obtained from Leading Textiles, Australia. The yarn was added to AMIMCl at 80 °C at 2 wt% increments up to 10 wt%. After 6 hours, the undissolved component was removed, rinsed with water and weighed. Table 1 shows the weight of the blend before cotton dissolution and the recovered amount. The IL was able to be recovered and recycled as previously reported as water is the coagulating solution.22,23

Institute for Frontier Materials, Deakin University, Piddons Road, Waurn Ponds, Victoria, Australia, 3217. E-mail: Nolene.byrne@deakin.edu.au; Fax: +61 3 5227 1103
† Electronic supplementary information (ESI) available. See DOI: 10.1039/c4ra04306e
Characterization of recovered polyester and regenerated cellulose

FTIR. FTIR spectra of the samples were measured on Bruker Alpha FT-IR spectrometer. Samples were scanned in the frequency range of 600 cm\(^{-1}\) to 4000 cm\(^{-1}\) at the scan resolution of 4 cm\(^{-1}\) and background and sample scan time of 64 scans. FTIR measurement was repeated 3 times, taking over 3 places on the test specimen.

For the cotton films regenerated, the hydroxyl region 2990–3900 cm\(^{-1}\) was deconvoluted, and curve was fitted adopting Gaussian model using OPUS 5.5 software. Finally, auto fitted spectrum was area normalized to obtain percentage conformations of three bands which represent inter molecular and intra molecular hydrogen bonding of the cotton films regenerated.

The intra-molecular hydrogen bonds for O(2)H⋯O(6), and O(3)H⋯O(5) (endocyclic oxygen) and the inter-molecular hydrogen bonds for O(6)H⋯O(3) in the cellulose of the bio films were appeared in 3455–3410, 3375–3340 and 3310–3230 cm\(^{-1}\) respectively.\(^{24,25}\)

\(^{13}\)C-CP-NMR. The solid state of \(^{13}\)C NMR spectra of the samples were recorded on Bruker AVANCE III 300 MHz Wide Bore using 4.00 mm MAS HX probe. The experiments were carried out at the spinning rate of 12.5 kHz at 25°C for 5677 scans.

SEM. The morphology of samples was observed using Zeiss Supra 55VP scanning electron microscope (SEM) at an accelerating voltage of 5.00 kV. The sample surface was gold coated before observation.

Table 1 Dissolved cotton % and undissolved polyester of the blend samples in AMIMCl

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Initial blend weight (mg)</th>
<th>Residue weight (mg)</th>
<th>Undissolved polyester from the blend %</th>
<th>Dissolved cotton from the blend %</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1602.25</td>
<td>803.60</td>
<td>50.15</td>
<td>49.85</td>
</tr>
<tr>
<td>B</td>
<td>1598.23</td>
<td>798.85</td>
<td>49.98</td>
<td>50.02</td>
</tr>
<tr>
<td>C</td>
<td>1600.40</td>
<td>801.72</td>
<td>50.09</td>
<td>49.91</td>
</tr>
</tbody>
</table>

DSC. The DSC experiments were performed on TA DSC Q 200 differential scanning calorimetry using 4–6 mg of the sample. Firstly the samples were heated to 100°C at a heating rate of 10°C min\(^{-1}\) under N\(_2\) atmosphere. Then the samples were held at 100°C for 5 minutes to delete the thermal history. The samples were cooled down 0°C at a cooling rate of 10°C min\(^{-1}\) and held for 5 minutes. Subsequently, the samples were heated from 0°C to 300°C at a heating rate of 10°C min\(^{-1}\) (second scan). The second scans of the samples are shown.

TGA. The samples were subjected to thermogravimetric analyses (TGA) on Netzsch STA 409 thermogravimetric analyser. Test was performed using 5–8 mg of the samples. The specimens were heated from 25°C to 600°C at a heating rate of 10°C min\(^{-1}\) under N\(_2\) atmosphere. The decomposition temperature at which the weight loss begins (\(T_d\)) calculated as the onset.

Results and discussion

Fig. 1 shows the general scheme for the separation of the cotton/polyester blend using AMIMCl. The IL was able to be recovered and recycled as previously reported as water is the coagulating solution.\(^{22,23}\)

For this process we have studied both AMIMCl and BMIMAc, these ILs have been selected on the basics of their cellulose dissolving capabilities, both ILs show some of the highest cellulose dissolving capabilities.\(^{26}\) Little difference in the separation capabilities was noted under the conditions investigated here. We also studied the impact of temperature on the separation process and found little difference in the time it took to

![Fig. 1 Separation and utilisation of polyester/cotton blends using AMIMCl.](image-url)
dissolve the cotton component in either BMIMAc or AMIMCl at 80 °C, 100 °C and 120 °C. The dissolution of the cotton was considerably faster at 120 °C for both ILs as expected (see Table 1, ESI†).

Fig. 2a shows scanning electron image of the polyester cotton blend; prior to separation both cotton and polyester fibres can be observed. Fig. 2b shows the recovered polyester, only polyester fibres are observed.

We also characterized the structure of the recovered polyester, using a combination of DSC, TGA, NMR and FTIR shown in Fig. 3a–d. For comparison we include the as received 100% polyester. It can be seen that no change in the melt temperature of the recovered polyester is measured, which is important since polyester can be recycled by melting the polyester and reshaping the polyester into the desired form (fibres, bottles, etc.). The 13C NMR spectrum and FTIR do indicate that some small amount (less than 2%) of cotton may remain with the recovered polyester as evidenced by the additional peaks observed at 60 and 110 ppm,27,28 and the presence of the hydroxyl peak at 3300 cm−1 (ref. 25 and 29) in the FTIR spectrum.

We now turn our attention to the regenerated cotton. We show that fibres and/or films can easily be prepared from the cotton/AMIMCl solution. Regenerated cellulose fibres have a considerable market share and are growing in popularity, common regenerated cellulosic fibres are viscose, rayon and lyocell.30,31 Fig. 4a–c shows a series of material characterization experiments performed on the recovered cotton from the blend compared with as received cotton dissolved and regenerated from the same IL, AMIMCl. As can be seen no difference in the tensile properties are observed between the two cotton samples (Fig 4a, stress and strain at breakage and Young’s modules provided in Table 2 ESI†). Similarly the thermal degradation...
temperature and FTIR show no appreciable differences (deconvolution of the OH region provided in Table 3 ESI†).

Here we described the facile and efficient separation of polyester/cotton blends into their individual components. This was achieved by selective dissolution of the cotton component using the ionic liquid AMIMCl. We showed that the cotton could be regenerated using water as the coagulated solvent. Regenerated cotton is a material finding increased use in the textiles industry,30–32 in the carbon fibre industry as low cost precursor materials33,34 and as the starting material for bio-ethanol production.20,35,36

References


Fig. 4 (a–c) Characterization of the recovered cotton (red curve) compared with as received cotton (black curve) (a) DMA curves (b) TGA curves, (c) FTIR, all show little to no difference between the two cotton samples. Both samples are regenerated cotton.


Tri-component bio-composite materials prepared using an eco-friendly processing route

Rasike De Silva · Xungai Wang · Nolene Byrne

Abstract We report on the blending of three natural polymers, raw cotton, silk and wool, using ionic liquids as the dissolving media. We find that with increased content of wool and silk the thermal degradation temperature of the new bio films increases. This is due to an increase in the hydrogen bond network between the blended polymers. We also investigated the role of the coagulating solvent by coagulating the bio films using water, methanol or isopropanol. Again, we find the coagulating solvent impacts the final properties of the bio films with water shown to coagulated films with the best material properties.

Keywords Natural polymers · Polymer blending · Ionic liquids · Coagulation

Introduction

Polymer blending is a technique commonly used in the polymer industry to produce novel materials (Belgacem and Gandini 2008; Mohanty et al. 2000; Belgacem and Gandini 2008; Mohanty et al. 2002). The blending of natural polymers is an eco-friendly approach to the development of new natural polymers aimed at reducing our dependence on petroleum based polymers (Netravali et al. 2007; Mohanty et al. 2000; Belgacem and Gandini 2008; Mohanty et al. 2002). For this reason, we used cotton in its raw form, not processed in any way. Cotton like many other biopolymers (Lee et al. 2010; Heinze and Koschella 2005) can be extremely difficult to dissolve making blending difficult and often resulting in the use of harsh volatile solvents (Köhler and Heinze 2007; Maia et al. 1981). Indeed, even processing raw cotton to the more soluble form, cellulose acetate, has a significant environmental footprint due to the high energy costs and use of aggressive and volatile solvents (Carr 1995; Handbook of Fiber Chemistry 2006; Morton and Hearle 1993). Almost, all natural polymer studies involve the use of cellulose acetate as opposed to raw cotton. In this report, we describe the use of ionic liquids as recyclable, environmentally benign solvents for the dissolution of raw cotton and the subsequent blending of natural polymers.

Ionic liquids ILs, once considered niche solvents are now finding application in a variety of fields (Kokorin 2011; Rogers and Seddon 2003; Welton 2011). The ability to tailor the properties of the ionic liquid supports the wide diversity of applications that benefit from ionic liquid use (Gibril and Yue 2012; Heinze and Koschella 2005). In the context of green chemistry, ionic liquids are taking centre stage, with the processing of biopolymer being one application (Cao et al. 2009; Swatloski et al. 2002; Goujon et al. 2012), which has greatly benefiting from using ionic
liquids. Generally, ionic liquids consisting of the imidazolium cation and either the acetate or the chloride anion have been used for dissolving natural polymers (Vitz et al. 2010).

In this study, we have used 1-allyl-3-methylimidazolium chloride (AMIMCl) to create new tri-composite bio-films. At present, only few solvent systems have been found for cellulose and protein fibres. For example, LiCl/N,N-dimethylacetamide system, NaOH/(thio)urea aqueous solution, N-methylmorpholine-N-oxide monohydrate have used to dissolve cellulose and cuoxam solution to dissolve silk fibroin (Kadokawa et al. 2012; Wendler et al. 2010; Shang et al. 2011). However, drawbacks of these methods include environmental concerns such as undesirable organic waste solution, toxicity and complexity and limited dissolution in the process. (Shang et al. 2011).

In contrast, ionic liquids, especially imidazolium salts which are chemical and thermal stable, non-flammable and immeasurable low vapour pressure shows a promising alternative to overcome these limitations. (Shang et al. 2011; Stefanescu et al. 2012). The three natural polymers used here are, cotton (raw), wild type silk and wool. Cotton was selected as cellulose and cellulose based materials are key bio based polymer alternatives to petroleum derived polymers. Silk has been used in the textiles industry since ancient times due to its fineness, luster and excellent mechanical properties (Kaplan et al. 1994). However, regenerated in the film form silk is generally brittle (Du et al. 2009; Jin et al. 2004; Kweon et al. 2001). For this reason, wool has been included into the blend. Wool is also used extensively in the textile industry and is known to have increased elasticity with the ability to recover from extremely large strains (Onions and Wilfred 1962) due to its helical structure when compared to the beta sheet structure of silk (Hu et al. 2012; Phillips et al. 2004; Li and Wang 2012). The accumulation of waste wool, silk and cellulose products that are generated annually by the textiles and paper industries also drove the selection of these three natural polymers (Hameed and Guo 2010; Isci and Demirer 2007; Xie et al. 2005).

The role of the coagulating solvent has a unique and important role in the processing of polymers. This is particularly true for protein based polymers as the coagulation usually requires some degree of protein refolding in an effort to recapture the native properties of the protein polymer. Generally speaking regenerated silk and wool have inferior material properties when compared to the native form (Phillips et al. 2004; Li and Wang 2012).

In this work we have used a combination of FTIR, DMA, TGA and SEM to investigate the impact different coagulating solvents have on the structure and morphology of the tri component bio-films produced in this study.

**Experimental method**

**Dissolution of bio-polymers**

Multi component and single bio-polymer solutions of 10 wt% total polymer content were made using dried AMIMCl (purchased from Sigma Aldrich, Sydney, Australia, AMIMCl was vacuum dried at 85 °C for 6 h, water content measured to by karl fisher to be 50 ppm.) in two necked round bottom flask under inert N₂ atmosphere. AMIMCl was selected as the dissolving solvent as all three polymers were found to be soluble in this ionic liquid. The temperature of the dissolution process was controlled by automatic hot plate at 105 °C. Cotton, Silk and Wool fibres (original merino wool 18.5 μm) were oven dried for 24 h at 105 °C prior to dissolution.

**Preparation of regenerated films**

The bio-polymer solution was spreaded evenly between two glass slides and immersed in the co-solvent for 10 min. This was repeated 3 times to remove ionic liquid from the film. For immersion in the 2nd and 3rd bath the film was removed from between the glass slides. Films were dried at room temperature for 48 h, The measured film thickness was 0.065 mm. Water methanol and iso-propanol were used as co-solvents. No residual IL exists in the film as measured using solid state ¹H NMR; we do not detect any IL peaks.

After making bio films, residue solvent was collected separately to recycle the ionic liquid. The AMIMCl was recycled by evaporating water as described (Cao et al. 2009; Wu et al. 2009). No difference in the ¹H NMR spectrum of fresh AMIMCl and recycled ¹H NMR was detected, additionally recycled AMIMCl was used for further dissolution studies. No difference in the dissolution kinetics of the biopolymers detected between fresh and recycled AMIMCl. Water content of the recycled and dried
AMIMCI was measured to be 60 ppm. Bio films prepared in this study are shown in Table 1. Figure 1 shows the films prepared in this study, as the protein polymer content increases the films are no longer transparent. This is likely due to the wild type silk which is a brown colour.

Measurements of regenerated bio-polymer films

FTIR spectroscopy

FTIR spectra of bio films were measured on Bruker Alpha FT-IR spectrometer. Firstly, samples were scanned in the frequency range of 400–4,000 cm⁻¹ at the scan resolution of 4 cm⁻¹ and background and sample scan time of 64 scans. Then the samples were again scanned in the regions of interest in the OH stretch region in 3,000–3,500 cm⁻¹ and amide I region in 1,590–1,710 cm⁻¹. FTIR measurement was repeated 3 times, taking over 3 places on the same bio film. The hydroxyl region 2,990–3,900 cm⁻¹ was deconvoluted, and curve was fitted adopting Gaussian model using OPUS 5.5 software. The intra molecular hydrogen bonds for O(2)H--O(6) and the intermolecular hydrogen bonds for O(6)H--O(3) in the cellulose of the bio films were appeared in 3,455–3,410 and 3,310–3,230 cm⁻¹ respectively (Kondo and Sawatari 1996; Schwanninger et al. 2004). Finally, auto fitted spectrum was area normalized to obtain percentage conformations of two bands represent inter molecular and intra molecular hydrogen bonding.

TGA measurements

Regenerated bio films were subjected to Thermogravimetric analyses (TGA) on Netzsch STA 409 Thermogravimetric analyzer. Test was performed using 8–10 mg of the bio film sample. Samples were heated from 30 to 350 °C at a heating rate of 10 °C min⁻¹ under N₂ atmosphere. T_d calculated as the onset.

DMA measurements

Tensile properties of bio films were measured on TA Q800 DMA testing machine in tensile mode with a maximum load capacity of 18 N. Stress–strain curves for the thin rectangular bio film strips were obtained at room temperature at a controlled force rate of 0.5 N min⁻¹. DMA measurement where repeated with 5 specimens of each sample type. Young’s modulus was obtained from calculating the gradient of the linear part of the stress–strain curve.

SEM images

The morphology of bio films were observed using Zeiss Supra 55VP scanning electron microscope (SEM) at an accelerating voltage of 5.00 kV. The surface of the bio film was gold coated before observation.

Results and discussion

To investigate the hydrogen bond interactions occurring in the bio-films and the impact of the coagulating solvent we used FTIR. We investigated the amide 1 region (1,590–1,710 cm⁻¹) (Griffiths and De Haseth 2007; Kong and Yu 2007) and the hydroxyl stretching

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Bio-polymer composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>C100</td>
<td>100 % cotton</td>
</tr>
<tr>
<td>S100</td>
<td>100 % silk</td>
</tr>
<tr>
<td>W100</td>
<td>100 % wool</td>
</tr>
<tr>
<td>CS80</td>
<td>80 % cotton, 20 % silk</td>
</tr>
<tr>
<td>CW80</td>
<td>80 % cotton, 20 % wool</td>
</tr>
<tr>
<td>CSW90</td>
<td>90 % cotton, 5 % silk, 5 % wool</td>
</tr>
<tr>
<td>CSW80</td>
<td>80 % cotton, 10 % silk, 10 % wool</td>
</tr>
<tr>
<td>CSW70</td>
<td>70 % cotton, 15 % silk, 15 % wool</td>
</tr>
<tr>
<td>CSW50</td>
<td>50 % cotton, 25 % silk, 25 % wool</td>
</tr>
</tbody>
</table>
region (3,000–3,500 cm\(^{-1}\)) (Griffiths and De Haseth 2007; Kondo and Sawatari 1996). Figure 2a–c shows the amide I region for the single and multi-component bio-films as a function of coagulating solvent. The amide I region is largely associated with the C=O stretching vibration and for proteins is used to characterize the secondary structure (Kong and Yu 2007; Pribic et al. 1993). Proteins with a helical structure show a peak maximum at 1,652 cm\(^{-1}\), while β-sheet structured proteins are known to have a peak at 1,620 cm\(^{-1}\) (Kong and Yu 2007; Pribic et al. 1993; Li and Wang 2012). Wool is known to be a helical protein and silk has a β sheet structure (Handbook of fiber chemistry 2006; Morton and Hearle 1993). Figure 2a shows the amide I region for the bio-films regenerated in water. A difference in peak maximum for the W100 and S100 films in the amide I region representing the differences between helical and β sheet structure as expected. The double component bio films CS80 and CW80 again show clear differences in the peak maximum with CW80 having a peak maximum at 1,648 cm\(^{-1}\) and CS80 having a peak maximum at 1,634 cm\(^{-1}\). These differences are again likely driven by the different protein structures adopted by the wool and silk representatively. The peak maximum for the tri-component films does not significantly change with the increased addition of both wool and silk, CSW90 shows a peak maximum at 1,639 cm\(^{-1}\) and CSW50 shows a peak maximum at 1,640 cm\(^{-1}\). Larger differences can be observed in Fig. 2b where methanol was used as the coagulating solvent. Here CSW90 has a peak maximum at 1,648 cm\(^{-1}\), with addition of both silk and wool the peak maximum for CSW70 and CSW50 is shifted to 1,620 cm\(^{-1}\). This shift suggests that an increased amount of β sheet structure is present when methanol is the coagulating solvent. Figure 2c, shows the bio films regenerated in isopropanol. The isopropanol shows a similar trend to water with little different in the peak maximum for the tri-component bio-films as a function of protein polymer addition. Interestingly the regenerated single component proteins i.e. S100 and W100 showed little difference as a function of coagulating solvent (FTIR graphs are shown in the supplementary graph document).

Figure 3a–c shows the hydroxyl stretching region for the water, methanol and isopropanol regenerated biofilms respectively. C100 regenerated in water shows a single broad peak with a maximum at 3,306 cm\(^{-1}\) corresponding to the O–H stretching band. Two peaks are observed for the protein polymers S100 (3,271 and 3,069 cm\(^{-1}\)) and W100 (3,270 and 3,060 cm\(^{-1}\)). These peaks correspond to the O–H and the N–H bands, respectively (Hameed and Guo 2010; Kondo and Sawatari 1996; Schwanninger et al. 2004). For the tri component bio-films a single broad peak is observed. The intensity of this peak decreases with increasing
protein content and a slight shift in this peak is observed for the high protein sample CSW50. This is likely explained by an influence from the N–H groups of the protein polymers altering the H-bond interactions within the new bio-films. The bi component bio-films CS80 and CW80 also show a single broad peak in this hydroxyl stretching region. Figure 3b shows the same bio-films coagulated using methanol, little difference is observed for the single component films C100, S100 and W100 when compared with Fig. 3a water coagulated. However for the tri-component bio films significant differences can be seen as the protein content increases. Again a decrease in the intensity of the peak is observed as the protein content increases. As the protein polymer content is increased the shape and position of the peak changes. It no longer is a broad peak as in the case for CSW90 but shifts to the peak position of the single component S100 and W100 with a clear narrowing of the peak. This clearly shows the impact coagulating solvent has on the structure of these tri component bio films. Finally, Fig. 3c shows the bio-films regenerated using isopropanol. Again little difference is observed for the single component films, suggesting that the coagulating solvent as a minor role to play in the coagulation of single component bio films. It is surprising than, that the coagulating solvent can impact the structure of the tri component films. The isopropanol coagulating tri component bio films again shows difference in the OH region as the protein polymer content is increased.

Deconvolution of the hydroxyl stretching region for the bio films (Table 2) shows a change in the distribution of the inter and intra molecular hydrogen bonds as a function of silk and wool content. The percentage of intra molecular hydrogen bonds increased with increased addition of silk and wool. This suggests as the protein polymers are added a strong interaction between the blended polymers is occurring. A change in the inter and intra molecular hydrogen bonds is also calculated as a function of coagulating solvent. A slight increase in the intra molecular hydrogen bonds is observed for the water coagulated films this suggests the when the films are coagulated using water the interactions between the polymers is improved. This maybe due to the solubility of the IL in the different coagulating solvents—the solubility is highest in water.

The thermal degradation temperature of the new bio-films is shown in Table 3. TGA curves are shown in the supplementary graph document.

From Table 3 it can be seen that that coagulating solvent plays a significant role in the thermal degradiation temperature, $T_d$ of tri composite bio-films. The $T_d$ increases as the protein content of the composite increases, for all coagulating solvents, with CSW50 showing the highest $T_d$ of the composite bio-films. The $T_d$ for CSW50 coagulated in water is 290 °C. This is higher than any of the single
component regenerated films and is even higher than native cotton fibers which was measured to have a Td of 280 °C. This increase in thermal stability measured for CSW50 coagulated in water is likely due to the increase in the intra molecular bonds measured for this bio film.

The material properties of the regenerated bio-films were measured using dynamic mechanical analysis. For bio films coagulated in water, the Young’s modulus, maximum stress and strain at breakage are given in Table 4 (stress–strain curves shown in the supplementary data). C100 shows the highest stress (57.98 MPa), strain (4.48 %) at breakage and Young’s modulus (1.88 GPa). The addition of silk and wool fibres reduces the mechanical properties of the bio film with CSW50 have the lowest stress at breakage. However these bio films still have superior material properties when compared to collagen based bio materials (Matthews et al. 2002).

Table 4 Stress-strain values of bio films coagulated in water

<table>
<thead>
<tr>
<th>Sample</th>
<th>Stress at breakage (MPa)</th>
<th>Strain at breakage (%)</th>
<th>Young’s modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C100</td>
<td>57.98</td>
<td>4.48</td>
<td>1.88</td>
</tr>
<tr>
<td>CSW90</td>
<td>47.53</td>
<td>3.31</td>
<td>1.79</td>
</tr>
<tr>
<td>CSW80</td>
<td>45.87</td>
<td>2.98</td>
<td>1.77</td>
</tr>
<tr>
<td>CSW70</td>
<td>30.42</td>
<td>1.56</td>
<td>1.76</td>
</tr>
<tr>
<td>CSW50</td>
<td>28.94</td>
<td>1.6</td>
<td>1.70</td>
</tr>
<tr>
<td>CS80</td>
<td>48.40</td>
<td>3.07</td>
<td>1.71</td>
</tr>
<tr>
<td>CW80</td>
<td>42.18</td>
<td>2.83</td>
<td>1.61</td>
</tr>
</tbody>
</table>

Table 5 Stress-strain values of CSW70 bio film coagulated in water, methanol and isopropanol

<table>
<thead>
<tr>
<th>Sample</th>
<th>Stress at breakage (MPa)</th>
<th>Strain at breakage (%)</th>
<th>Young’s modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C70 in water</td>
<td>30.42</td>
<td>1.56</td>
<td>1.76</td>
</tr>
<tr>
<td>C70 in methanol</td>
<td>25.44</td>
<td>1.32</td>
<td>1.73</td>
</tr>
<tr>
<td>C70 in iso propanol</td>
<td>26.63</td>
<td>1.44</td>
<td>1.75</td>
</tr>
</tbody>
</table>
suggests that coagulation is not diffusion limited, as expected in films with thickness of 0.065 mm.

**Conclusion**

We successfully developed tri-composite bio films using ionic liquids as the blending solvent. The new bio composite films showed enhanced thermal stability compared with the single component films. The impact of the coagulating solvent was shown to significantly impact the material properties of the tri component bio films. Methanol was shown to enhance the formation of β-sheet structure but as a consequence a reduced strain at breakage was measured. While water was shown to coagulate films with the best material properties and the CSW50 bio film was shown to have a higher thermal degradation temperature than the raw cotton and the native silk and wool fibers. The increase in intra molecular hydrogen bonds for the bio films likely accounts for the increase in thermal degradation as measured.

**References**


Silk scaffolds achieved using Pickering high internal phase emulsion templating and ionic liquids†

Nolene Byrne,*a Rasike DeSilva,a Catherine P. Whitbyb and Xungai Wangac

We describe a convenient route to the preparation of silk scaffolds that do not require silk fiber dissolution and regeneration. We prepare the silk scaffolds via a single step Pickering-high internal phase emulsion (HIPE) method. Additionally, we find that the use of biocompatible ionic liquids significantly improves the compressive properties of the HIPEs.

Silk as a biomaterial has gained significant interest due to its biocompatibility and excellent mechanical properties. However, normally silk to be produced into a scaffold needs to be dissolved and regenerated. The dissolution of silk involves the use of harsh solvents and multiple processing steps. The typical procedure for native silk fiber dissolution is to boil in alkaline pH to remove the sericin, dissolve the silk fiber in 9MLiBr, dialyse to remove the salt and solubilize the amorphous silk in either formic acid or hexafluoroisopropanol, although ionic liquids (ILs) have been shown to directly dissolve silk cocoons. The regeneration of silk is also a complex process, with many different solvents and processing techniques being investigated currently. The major disadvantage with the dissolution and regeneration of silk, apart from the complexity and time involved, is the loss of the native silk fiber structure which impacts the material properties of the regenerated silk.

In this communication, we describe the preparation of novel silk scaffolds using a Pickering emulsion – HIPE process.

High internal phase emulsions (HIPEs) are defined as having an internal phase volume (ϕ) of 0.74 or greater. HIPEs find use in numerous applications including food preparation, fuels, oil recovery, cosmetics and recently as templates in material science. Often HIPEs require surfactants or particles to enhance stabilization and prevent coalescence or sedimentation. Recently ionic liquids have been successfully used as surfactant materials as well as to form emulsions. In addition, ionic liquids, ILs, have been shown to enhance protein stability against aggregation as well as being biocompatible crosslinking agents for collagen proteins. For these reasons, we have explored the impact of using biocompatible ionic liquids in the preparation of the silk particle stabilized HIPEs. We studied 3 different biocompatible ILs, cholineTa, cholineLa and EOALa. The choline salts were selected as they have recently been shown to cross link collagen as well as stabilize proteins, while EOALa is a simple protic ionic liquid known to possess amphiphilic properties.

High internal phase emulsions were achieved via a single step process at 10 wt% silk (Fig. 1). Briefly the ball milled silk particles were dispersed in the aqueous phase, the required amount of oil was added and the solution homogenised for 1 minute. The oil used was the biocompatible dodecane. We found that by using the 2 step process, lower silk wt% could be used to achieve a HIPE (see Table S1 in ESI†). We achieved HIPEs with internal volumes of up to 87% without the use of a surfactant. The influence of ionic liquid addition on the HIPEs was investigated at concentrations of 0.5 M, 1 M and 2.5 M. The IL was dissolved in the aqueous phase prior to the silk particles being added. Addition of IL resulted in a decrease in the internal volume fraction of the HIPEs to 80%. Fig. 2a–d shows...
the optical images of the HIPEs formed at 0 M, 0.5 M, 1.0 M and 2.5 M cholineTA. As the IL concentration is increased the droplet size increases, and at IL concentrations of 2.5 M no HIPE formation was achieved in any of the ILs studied here (see Table S2 in ESI†). This was a surprising result and suggests that the IL is likely absorbed onto the surface of the silk particle changing the surface properties, resulting in the lower internal volumes. Fig. 2e–h shows the corresponding fluorescent microscope images.

Next, we explored the rheological properties of the HIPEs. Fig. 3a shows the storage ($G'$) and loss modulus ($G''$) of the HIPEs as a function of frequency at 1.0 M IL. It can clearly be seen that all HIPEs are in the "gel" form, even in the absence of IL. However, the addition of the IL has improved the gel properties. Creating HIPEs with 1.0 M cholineTA resulted in a 3 fold improvement in the gel properties. Fig. 3b shows the impact of varying the strain rate, again the use of IL improves the HIPEs response to strain. The compressive strength of the HIPEs without IL was measured to be 32 ± 0.012 kPa and compressive strain at failure of 52%. The addition of the IL further improves both the compressive strength and the compressive strain of the HIPEs. HIPEs prepared with 1.0 M cholineTA had a compressive strength of 48 ± 0.026 kPa and a compressive strain at failure of 62% (Stress–strain curves in ESI†). This suggests that the IL, in particular the cholineTA, is enhancing the inter-particle binding, accounting for the significant improvement in material properties of the scaffolds. Interestingly, cholineTA also showed the best crosslinking capabilities for collagen when compared to other choline salts. Its likely the hydrogen bond capability of this anion, both acceptor and donor sites available, is responsible for the improvement.

Finally, we explored the morphology of the HIPEs. Fig. 4a–d shows the SEM images of the HIPEs without IL and at 1.0 M of
EOALa, cholineLa and cholineTa respectively. Significant differences in the matrix can be observed between the different HIPEs. Clear binding and/or partial dissolution of the silk particles can be observed for HIPEs prepared with 1.0 M cholineLa and cholineLa. The improved binding of the silk particles in the presence of the IL further suggests the IL is modifying the silk particle surface, this likely explains the lower internal volume fraction obtained with the IL. However, it would be interesting to study the impact of a more traditional surfactant like ionic liquid such as a long chain imidazolium. The inability for crosslinking to occur in the presence of the protic IL EOALa suggests that the unique hydrogen bond network of the protic ionic liquid, which is different to the aprotic ionic liquid, limits this IL’s ability to bind the silk particles.

Conclusions

We have shown that silk scaffolds can be prepared using a Pickering – HIPE process, thus eliminating the need to dissolve and regenerate the silk fiber. Additionally, using biocompatible ionic liquids a significant improvement in the scaffold material properties was measured. The improved compressibility is likely due to improved binding between the silk particles due either increased hydrogen bonding or particle silk particle dissolution. The improved interface properties was observed by SEM. CholineTa was shown to improve the material properties the most, this anion has multiple hydrogen sites. Future works will explore the mechanism of ionic liquid improvement as well as other methods to improved interfacial contact.

Acknowledgements

NB and XW acknowledge funding from the Australian Research Council through a discovery project. CPW acknowledges receipt of an Australian Research Council Future Fellowship. The authors thank Dr Rajkhowa for the silk particles.

Notes and references

APPENDIX C

Featured articles
Australian project claims near total recovery rates

In 2015, we interviewed researchers in Australia who told us they had used ionic liquids – salt in a liquid state – to successfully separate polyester/cotton blended textiles, with polyester recovery rates claimed to be in the region of 99.5 per cent.

Subsequently, work is now also underway to use this technology to spin new regenerated cotton fibres which – claim the researchers – are competitive with both viscose and lyocell.

The scientists involved in the work told us their work represented “a new environmentally friendly and convenient approach,” and, crucially, also suggested that, “the material properties of the recovered polyester and cotton show that no significant differences can be seen between the recovered polymers.”

Rasike De Silva, lead researcher on the project, told us: “We believe our breakthrough is game changing. From our research, we find that the separation of the polyester from the cotton is 99.5 per cent. We recover the polyester unmodified, and have been working on spinning a new regenerated cellulose fibre which is competitive with viscose and lyocell fibres.

“After recovering the undisolved polyester part, we have used the dissolved cotton to spin a new regenerated cellulose fibre. The cellulose fibre we spin, due to the non derivatising nature of the ionic liquid has a higher degree of polymerisation than the current commercially used viscose fibre. This makes this fibre not only suitable for the textile industry but as a new precursor for carbon fibre. After the fibre regeneration, the ionic liquid can be recycled and reused by a simple evaporation method.

“Since our solvent is recyclable and reusable we anticipate that the cost should not be significantly higher and potentially lower than current viscose fibre formation.”

Ionic liquids, said De Silva, mean polyester and cotton can be easily separated, adding: “The ionic liquid selectively dissolves the cotton component, with the added advantage that the liquid can then be recycled and reused.

“This cotton can then be regenerated into various forms, such as spun into fibres or cast as cellulose films, like cellophane.” It was also claimed that the recovered polyester can also be recycled by melting and reshaping it into other forms, such as plastic bottles or fibres. Again, this opens the possibility extending closing the loop between the textile industry and other industries.”
Chemical solutions attempting to separate cotton and polyester blends have, until now, been unviable both economically and environmentally. However, using an ionic liquid (a salt in a liquid state), researchers at Deakin’s Institute for Frontier Materials have developed a simple process to separate polyester/cotton blends into their individual components.

“A significant hurdle to recycling waste clothing and other textiles back into their original fibres is that most of this material is composed of blended fibres – the most common being polyester/cotton blends,” says PhD student Rasike De Silva who is working with Professor Xungai Wang and Dr Nolene Byrne at Deakin.

“Unlike harsh solvents which have previously been used to dissolve polyester, the ionic liquids we are using provide an environmentally friendly alternative; another benefit of using ionic liquids is the ease with which the polyester and cotton can be separated.

“The ionic liquid selectively dissolves the cotton component, with the added advantage that the liquid can then be recycled and reused.

“This cotton can then be regenerated into various forms, such as spun into fibres or cast as cellulose films, like cellophane.”

Regenerated cotton is also increasingly being used as a low-cost precursor in the carbon fibre industry and as the starting material for bioethanol production.

The recovered polyester can also be recycled by melting and reshaping it into other forms, such as plastic bottles or fibres. The researchers say the new process is not limited to textile recycling but can also be applied to recycling any type of bio-composite material, including those used in the automotive industry. Regenerated cellulose fibres such as viscose, rayon and lyocell have a considerable market share and are growing in popularity.

**Environmental credibility**

The environmental credibility of this new research lies in the development of a complete recycling solution for textile waste materials. Currently, solvents used are considerably more toxic and harmful than the solvents in this method. The environmental impact is also lessened by reduced water and energy use compared to current recycling methods.

“As significant amounts of textiles are discarded to landfill each year, our proposed recycling process will alleviate this problem. While we have not undertaken a detailed study; we also think this will have a positive impact on the life cycle assessment of cotton and cotton blended textiles and this is important for consumer satisfaction,” Rasike said.

A textile engineer from Sri Lanka, Rasike is working at the Institute for Frontier Materials with Dr Nolene Byrne and Professor Xungai Wang. He carried out the project as part of his PhD research into separation and utilisation of polymer fibre blends using environmentally friendly approaches.

**WHAT A WASTE**

Each year, masses of material from unwanted clothing and other sources are deposited in landfill. By example, the United States generates more than 11 billion kilograms of textile waste each year with only 15 percent recycled and an estimated more than nine billion kilograms being sent to landfill, according to the US Council for Textile Recycling.

The US EPA estimates that textile waste occupies five per cent of landfill mass.
Australian 'breakthrough' in recycling textile and other waste

August 07, 2015 by Ian Martin

Australia: Researchers at Deakin University in the Australian state of Victoria have found a way to separate blends of cotton-polyester material, hailing this as 'a major breakthrough' for recycling textile and other waste.
A significant hurdle to recycling waste clothing and other textiles into their original fibres is that most of this material is composed of blended fibres - the most common being polyester/cotton blends. While it is easy to recycle cotton and polyester individually, it is not possible to mechanically separate the blends where the fibres are closely bonded together.

Chemical solutions attempted to date have not been viable economically or environmentally, it is explained. However, researchers at Deakin’s Institute for Frontier Materials - Dr Nolene Byrne and PhD student Rasike De Silva - have developed a simple process to separate polyester-cotton blends into their individual components using an ionic liquid, or a salt in a liquid state.

Unlike harsh solvents which have previously been used to dissolve polyester, ionic liquids ‘provide an environmentally friendly solvent’ to chemically separate polyester/cotton blends. Another benefit of using ionic liquids, says De Silva, is the ease with which the polyester and cotton can be separated.

‘The ionic liquid selectively dissolves the cotton component, with the added advantage that the liquid can then be recycled and reused,’ he explains. ‘This cotton can then be regenerated into various forms, such as spun into fibres or cast as cellulose films, like cellophane.’

The recovered polyester can also be recycled by melting and reshaping it into other forms, such as plastic bottles or fibres. Regenerated cellulose fibres such as viscose, rayon and lyocell have a considerable market share and are growing in popularity, it is
noted.

Regenerated cotton is also increasingly being used as a low-cost precursor in the carbon fibre industry and as the starting material for bioethanol production.

The new process is not limited to textile recycling but can also be applied to the recycling of any type of biocomposite material - including those used in the automotive industry, according to the researchers.

A textile engineer from Sri Lanka, De Silva has carried out the project as part of his PhD research into separation and utilisation of polymer fibre blends using environmentally-friendly approaches.

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Recycling International - For professionals, by professionals

Source URL: http://www.recyclinginternational.com/node/8935
Bangladesh study reveals pollution concerns

DHAKA – The high price being paid by Bangladesh for the rapid growth of its textile dyeing and finishing sector is illustrated in new findings from researchers in Dhaka who discovered high levels of the heavy metals Cr (chromium) and Cd (cadmium) in textile effluent samples. The cadmium, collected from the Savar, Ashulia and Tongi areas in the North West of the capital, exceeded permissible World Health Organisation levels. The researchers sounded a particularly ominous warning about the “huge amount of cadmium entering into the fresh water” in the studied areas, noting that “since, it has previously been reported that the ... weekly uptake (absorption) of cadmium by rice is very high in Bangladesh, such incidence may cause serious health problems in near future.”

Cadmium entering into the fresh water can be rapidly absorbed by plant and animal life, with ingestion by humans of any significant amount leading to risks of poisoning and damage to vital organs (liver/kidneys). Cadmium also has a potential carcinogenic effect.

The researchers noted that the effluent samples were “blue in colour, which indicate that [textile effluent] is not treated properly before its release from the industry.”

High levels of TDS (total dissolved solids), BOD (biological oxygen demand) and COD (chemical oxygen demand) were also discovered, which “revealed high load of pollution incidence”, and would “severely effect” plant and animal life in the tested areas.

Bio-Geo-Chemical Characterisation of Bangladeshi Textile Effluents was written by researchers from the Department of Microbiology, Jahangirnagar University, Dhaka, Bangladesh.
Web: http://bit.ly/1Ah7RyO

ZDHC appoints executive director

AMSTERDAM – The Zero Discharge of Hazardous Chemicals (ZDHC) Group has officially appointed Frank Michel as its first executive director.

Michel, who brings in a broad range of chemical and product compliance experience working in consumer goods, will lead the recently established legal entity, which is based in Amsterdam. The aim of the ZDHC is to eliminate the use of hazardous chemicals in the textile supply chain by 2020.

Michel noted: “This is an exciting time for the ZDHC Group. Significant collaboration and engagement with organisations around the world during the past 3 years has set the group on a solid path toward their ambitious goal.”

As the former global director of regulation and sustainability management for 1WorldSync, Michel has a wide range of chemical and product compliance experience where he has helped to create transparent supply chains and advanced environmental sustainability.

The ZDHC Group now has brand members including adidas Group, Gap Inc., H&M, Inditex, Jack Wolfskin, Levi Strauss & Co., M&S, and PVH Corp., associate members including the Association of the German Sporting Goods Industry (BSI), European Outdoor Group (EOG), and the Stockholm International Water Institute (SIWI), and a diverse group of stakeholders.

Ionic liquids used to recycle poly/cotton textiles

GEELONG – Researchers in Australia have used ionic liquids to successfully separate polyester – cotton blended textiles, with polyester recovery rates claimed to be in the region of 99.5 per cent. Subsequently, work is now also underway to use this technology to spin new regenerated cotton fibres that are competitive with both viscose and lyocell.

The new technique is said to be ‘a new environmentally friendly and convenient approach,’ to the separation of polyester and cotton blended fabrics. Ionic liquids are used to dissolve cotton fibres which are later regenerated into new cellulosic materials.

Speaking to Ecotextile News, lead researcher Rasike De Silva explained: “We believe our breakthrough is game changing. From our research, we find that the separation of the polyester from the cotton is 99.5 per cent. We recover the polyester unmodified, and have been working on spinning a new regenerated cellulose fibre which is competitive with viscose and lyocell fibres.

“Since our solvent is recyclable and reusable we anticipate that the cost should not be significantly higher and potentially lower than current viscose fibre formation,” she added.

De Silva said the team were ‘very keen’ to further develop the technology: “There will be a potential, that this method can be explored for other blends. We plan to extend this into recycling natural fibre based automotive components also,” she said.

The scientists say that ionic liquids (basically a salt in the liquid state) were used because they are easily recovered and recycled and water is used as the coagulating solvent to recover the cotton.
Web: www.dro.deakin.edu.au
REFERENCES


REFERENCES


REFERENCES


REFERENCES


REFERENCES


REFERENCES


[94] Y. Fukaya, A. Sugimoto, and H. Ohno, "Superior Solubility of Polysaccharides in Low Viscosity, Polar, and Halogen-Free 1,3-


REFERENCES


[124] X. Li, N. Li, J. Xu, X. Duan, Y. Sun, and Q. Zhao, "Cellulose fibers from cellulose/1-ethyl-3-methylimidazolium acetate solution by wet spinning with increasing spinning speeds," *Journal of Applied Polymer Science*, vol. 131, pp. n/a-n/a, 2014.
REFERENCES


[140] A. S. Amarasekara and B. Wiredu, "Brönsted Acidic Ionic Liquid 1-(1-Propylsulfonic)-3-methylimidazolium-Chloride Catalyzed Hydrolysisof D-
REFERENCES


REFERENCES


REFERENCES
