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ALL-CELLULOSE COMPOSITE PRODUCTION USING AN IONIC LIQUID:

Dissolution of Wood Derived High Purity Cellulose with BmimCl

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C. Thirion

SYNOPSIS

The feasibility of producing all-cellulose composites (ACCs) films from dissolving wood pulp by partial dissolution of the cellulose was investigated. It was thought that the undissolved fraction of the cellulose fibres would have a reinforcing effect on the final product. The ionic liquid 1-butyl-3-methylimidazolium chloride (BmimCl) was used to dissolve sheets of the dissolving wood pulp on a laboratory scale.

Before the cellulose sheets could be produced, the recovery of BmimCl was considered. Reuse of the solvent was important for the process to be cost effective and environmentally benign. Since little published information existed on the rinsing process to recover the solvent, a rinsing method was developed. The rinsing was performed using sequential rinsing stages with demineralised water.

Increasing the temperature of the rinsing water was found to improve the efficiency of the rinsing stage and to accelerate the recovery of BmimCl. When the rinsing water was heated to 80 °C, approximately 30 % better recovery of BmimCl during the first rinsing stage was achieved compared to rinsing at 25 °C. When the BmimCl recovery for cellulose samples which were dissolved to different degrees was compared, it was found that a high degree of dissolution leads to slower recovery. Although the recovery was slower for the cellulose samples that were highly dissolved, the total recovery after four rinsing stages was 97.6 % (+/- 2.7 %) independent of the degree of dissolution. The concentration profiles for the duration of each rinsing stage was determined. The concentration profile of the first rinsing stage showed that more than 65 % of the BmimCl used could be recovered in 10 min when only 2.4 ml rinsing water per gram of BmimCl was used. For the 0.16 mm thick starting material films used in this study, four rinsing stages of 10 min duration each, using rinsing water at 80 °C was found to be sufficient for BmimCl recovery, independent of the dissolution conditions.

Partial dissolution was achieved for few of the dissolution conditions investigated. Complete dissolution occurred for the majority of dissolution conditions and the

produced films did not qualify as ACCs. Some of the dissolution conditions resulted not only in complete dissolution of the cellulose, but also in possible degradation and weakening of the cellulose. Especially when high concentrations of BmimCl was used, the regenerated cellulose structure had more defects and was weakened. It is recommended that shorter dissolution times and lower BmimCl concentrations be investigated.

For the samples that did show some remnants of the native cellulose fibres, the undissolved fractions did not have a reinforcing effect on the regenerated cellulose matrix. For this reason, dissolving wood pulp was not suitable for the production of ACCs by partial dissolution. It is recommended that the starting material sheets be prepared as a mixture of the dissolving wood pulp and a different, stronger, high purity cellulose source, such as cotton. If the starting material contains stronger cellulose fibres, partial dissolution might result in the desired strengthening effect.

Most of the sheets showed a large amount of variation which was suspected to be due to uneven dispersion and removal of the BmimCl through the film, the defects discussed or internal stresses resulting from the drying process. It is recommended that the process be refined to eliminate the large variation observed within each sample.

The presence of BmimCl was found to have a plasticising effect on the produced cellulose film. The BmimCl inhibited the formation of crystals, probably resulting in the plasticising effect. It was also determined that crystals did not form as soon as cellulose precipitated from solution, due to the presence of BmimCl. Only after BmimCl was removed from the cellulose structure did crystals form in the solid cellulose structure. The crystal formation in the solid phase continued as the cellulose films were allowed to age. The long term effect of BmimCl was to reduce this crystal formation in the regenerated phase over time, but an increase in crystallinity was still observed independent of the presence of BmimCl in the cellulose.

The temperature at which regeneration of the cellulose and rinsing of the regenerated material was performed visually affected the produced material. Regeneration and rinsing at 25 °C resulted in more transparent films with reduced crystallinity when

compared to the films that were regenerated and rinsed at 80 °C. The films were more plastic due to the reduced crystallinity resulting from the lower temperature.

The cellulose crystal structures also differed for the two different temperatures. Cellulose II formed if no time was allowed for regeneration, whereas an unidentified cellulose structure, possibly a paracrystallite, formed when time for regeneration before rinsing was allowed. The general effect of increased regeneration time was a reduction in crystallinity. It was hypothesised that the regeneration conditions determine the crystal structure which forms. This hypothesis explains the different cellulose types that have been reported in published literature on the crystal structures of cellulose regenerated from solution with BmimCl.

PREFACE

This dissertation is structured to present four areas of research relating to the production of all-cellulose composites (ACCs) using 1-butyl-3-methylimidazolium chloride (BmimCl) as solvent. The first two chapters are dedicated to the introduction of each of the areas that were researched and to provide the necessary background information. Chapter 3 explains the general method and materials used in the experiments. The refinements made to the general experimental method for each experiment is explained at the start of the following relevant chapters. Each chapter from Chapter 4 through Chapter 6 are dedicated to one of the four research areas as follows:

- Chapter 4: The recovery of ionic liquid using rinsing stages,
- Chapter 5: Different cellulose dissolution conditions,
- Chapter 6: The effect of rinsing and regeneration conditions..

Chapter 7, Chapter 8 and Chapter 9 contains a summary from the three investigations, recommendations for future research and a list of references consulted.

LIST OF ABBREVIATIONS

1,3-PDO	1,3-Propanediol
ABS	Acrylonitrile butadiene styrene
PA	Poly(amide) (Nylon)
PB	Poly(butylene)
PBS	Poly(butylene succinate)
PBSAT	Poly(butylene succinate-co-adipate terephthalate)
PBSL	Poly(butylene succinate-co-L-lactate)
PBST	Poly(butylene succinate-co-butylene terephthalate)
PBT	Poly(butylene terephthalate)
PCL	Poly(caprolactone)
PE	Poly(ethylene)
PEIT	Poly(ethylene isosorbide terephthalate)
PET	Poly(ethylene terephthalate)
PHA	Poly(hydroxyalkanoates)
PLA	Poly(lactic acid)
PO3G	Poly(oxytrimethylene)glycol
PP	Poly(propylene)
PTMAT	Poly(tetramethylene adipate terephthalate)
PTT	Poly(trimethylene terephthalate)
PUR	Poly(urethane)
PVC	Poly(vinyl chloride)
SBR	Styrene-butadiene rubber

ACC	All-cellulose composite
BmimCl	1-Butyl-3-methylimidazolium chloride
CNC	Crystalline nano-cellulose
CrI	Crystallinity index
EmimAc	1-Ethyl-3-methylimidazolium acetate
IL	Ionic liquid
LiCl/DMAc	Lithium chloride/N,N- dimethylacetamide
MCC	Micro-crystalline cellulose
NaOH	Sodium hydroxide
NFC	Nano-fibrillated cellulose

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1 INTRODUCTION

Growing environmental awareness, sustainability, environmental regulations and the prospect of petroleum resources being depleted have motivated the search for sustainable, environmentally benign materials and processes (Pinkert *et al*, 2009). One such material is cellulose and cellulose-based materials can help address the serious environmental pollution concerns caused by the accumulation of non-biodegradable plastics (Zhao *et al*, 2009).

Cellulose has a high specific strength and has been investigated for use as reinforcing component in biocomposites (Miao & Hamad, 2013). Poor compatibility of the cellulose fibres with the matrix material was a critical problem when producing composite materials containing cellulose. One approach to overcoming this incompatibility is to use chemically similar or identical cellulosic materials for both the filler phase and matrix phase of the composite material. This type of composite material will then be a monocomposite, known as an All-Cellulose Composite (ACC). These ACCs can be produced by partially dissolving the surface of cellulose fibres followed by *in situ* regeneration of the dissolved fraction to form a matrix around the undissolved fraction. (Huber *et al*, 2012)

Many of the chemicals capable of dissolving cellulose are primarily limited by their environmental toxicity, the difficulty with which they are reused, insufficient solvent power and the need for harsh conditions to achieve cellulose dissolution (Pinkert *et al*, 2009). Some ionic liquids (ILs) offer high cellulose dissolution rates and are seen as environmentally friendly due to their the low vapour pressure, making them safer to handle and easier to recover after use (Swatloski *et al*, 2002;Liebert & Heinze, 2008).

1-Butyl-3-methylimidazolium chloride (BmimCl) is the most widely used IL (Pinkert *et al,* 2009). Although tests have shown BmimCl not to be acutely toxic, (Swatloski *et al,* 2004), it is still important to recover BmimCl after use because ILs containing imidazolium salts were shown to have poor biodegradability (Romero *et al,* 2008). BmimCl can be recovered from the cellulose after use by displacement of the BmimCl from the cellulose matrix, using a coagulant (commonly demineralised water) (Duchemin, Mathew & Oksman, 2009a; Yousefi *et al,* 2011).

The following four sets of experiments were performed on a laboratory scale to improve the understanding of the processes of dissolving cellulose with BmimCl, the feasibility of recovering BmimCl after use and the possibility of producing an ACC from dissolving pulp using BmimCl.

1.1 Investigation A: The recovery of IL using rinsing stages

Although BmimCl is a very efficient cellulose solvent, it has not been investigated properly for its toxicity and biodegradability. Thus, it is essential to have sufficient BmimCl recovery after use to ensure a cost effective and environmentally benign process (Plechkova & Seddon, 2008). To recover BmimCl from the cellulose matrix, rinsing with a coagulant (rinsing water) is performed. During the rinsing, the BmimCl diffuses into the rinsing water and is displaced from the cellulose matrix by the rinsing water. The rinsing is performed in stages; each rinsing stage duration is defined as the time between the replacements of the BmimCl containing rinsing water with fresh rinsing water (Duchemin *et al*, 2009a; Yousefi *et al,* 2011).

Little information on the amount of rinsing water and the time needed for rinsing is known. The total rinsing times for the recovery of BmimCl from cellulose in published articles were 12 h and 48 h (Duchemin *et al*, 2009a; Yousefi *et al,* 2011). The objectives of the first set of experiments (Investigation A) were to determine if the recovery process could be improved by using warmer rinsing water, whether the extent to which the cellulose was dissolved would affect the BmimCl recovery and to quantify how many rinsing stages are needed and how long each rinsing stage should be.

1.2 Investigation B: Dissolution conditions

Partial dissolution of the native cellulose fibre structure is desired if the objective of the treatment is to produce ACCs (Huber et al, 2012). No information was available on the dissolution conditions required to achieve partial dissolution of high purity cellulose derived from wood when using BmimCl as solvent. The objective was to investigate the effect of different dissolution conditions on the final cellulose material with the aim of identifying optimal conditions for the production of ACCs from dissolving wood pulp.

1.3 Investigation C: The effect of rinsing and regeneration conditions

In Investigation B it was assumed that the dissolution conditions were the main contributor to the properties of the produced cellulose film. Duchemin, Newman and Staiger (2009) found the conditions under which precipitation occur during regeneration to be a determining factor of the mechanical properties of regenerated cellulose. The first objective of Investigation C was to deterine the effect that regeneration and rinsing termperure and duration had on the produced cellulose film. All known variables in the preparation of the samples for regeneration and rinsing were kept constant. Two different regeneration and rinsing temperatures, agreeing with those used to investigate BmimCl recovery in Section 1.1 were investigated. For each of these temperatures, four different regeneration times were investigated.

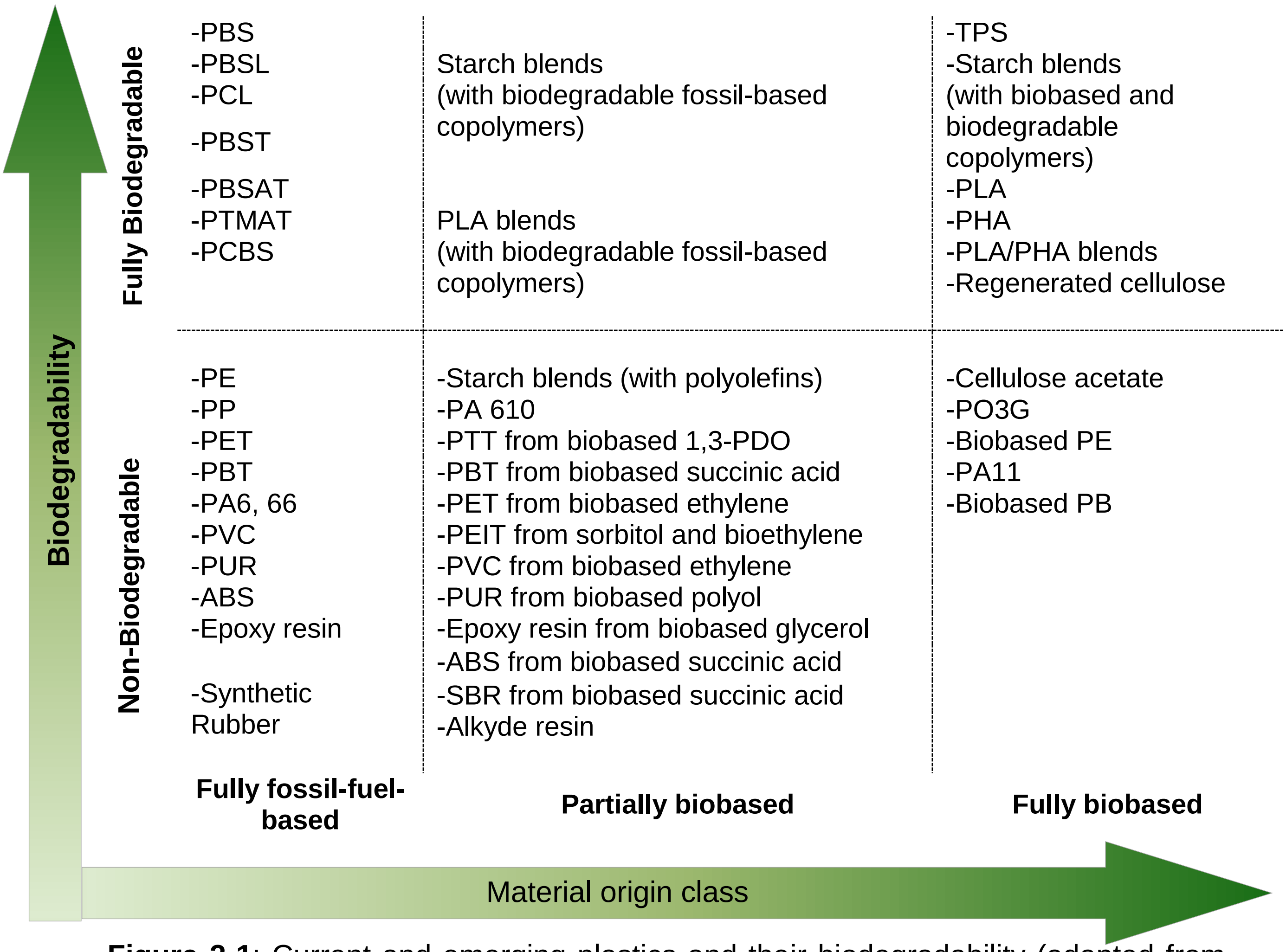
Although the recovery of BmimCl is desirable for the reasons mentioned in Section 1.1, it is important to know what the effect of BmimCl that could remain in the cellulose matrix would have on the properties of the film. Hence, the second objective of Investigation C was to determine the effect of BmimCl on regenerated cellulose and to quantify the amount of BmimCl remaining in the cellulose film if removal of the BmimCl was only performed partially. Partial rinsing, based on the rinsing method developed from Section 1.1, was performed for samples prepared using two different dissolution conditions.

2 LITERATURE

Environmental concerns surrounding petroleum based materials, the need for sustainable technologies and the abundance of available plant material (Miao & Hamad, 2013) have resulted in renewed interest in the first commercially processed polymer: cellulose. Approximately 80 % of the current polymer market is based on non-renewable petroleum resources (Faruk *et al*, 2012), but the next generation of materials, products and processes will most likely be directed by sustainability, industrial ecology, eco-efficiency and green chemistry (Pinkert *et al,* 2009).

One strategy for the reduction of the amount of petroleum based, synthetic polymers needed per finished product is to composite the synthetic polymer with natural cellulose fibres to produce short fibre composites. These composites can be processed by a method similar to that of the neat matrix. The fibres offer strengthening to the material, are lightweight and have good sound dampening properties. Disadvantages of these composite materials include large variation in the properties of natural fibres, the hydrophilic nature of natural fibres which can result in swelling or inefficient fibre dispersion in the matrix and processing temperatures being limited to 200 °C, due to the low degradation temperature of natural fibres (230 °C). (Miao & Hamad, 2013)

Natural fibres are much weaker than their microfibril building blocks due to the presence of amorphous cellulose and other components such as hemicellulose (Miao & Hamad, 2013). To utilise more of the potential strength that cellulose has to offer, natural fibres can be disintegrated into microfibrils before being used to produce a composite material. As shown in Figure 2-1 composites of natural fibres or microfibrils and polymers based on fossil fuels have been investigated for a variety of polymer matrices. Some of these composites have found applications, especially in Europe where car manufacturers need to comply with strict legislation regarding end-of-life recycling (Kanari, Pineau & Shallari*,* 2003; Ashori, 2008). Compositing of natural fibres with a biodegradable matrix is needed to achieve complete biodegradability of the composite and many have been investigated (Figure 2-1). When both the fibre and matrix are biobased and biodegradable, the composites are often only of modest strength (Gindl & Keckes, 2005).



	Fully fossil-fuel-based	Partially biobased	Fully biobased
Fully Biodegradable	-PBS -PBSL -PCL -PBST -PBSAT -PTMAT -PCBS	Starch blends (with biodegradable fossil-based copolymers) PLA blends (with biodegradable fossil-based copolymers)	-TPS -Starch blends (with biobased and biodegradable copolymers) -PLA -PHA -PLA/PHA blends -Regenerated cellulose
Non-Biodegradable	-PE -PP -PET -PBT -PA6, 66 -PVC -PUR -ABS -Epoxy resin -Synthetic Rubber	-Starch blends (with polyolefins) -PA 610 -PTT from biobased 1,3-PDO -PBT from biobased succinic acid -PET from biobased ethylene -PEIT from sorbitol and bioethylene -PVC from biobased ethylene -PUR from biobased polyol -Epoxy resin from biobased glycerol -ABS from biobased succinic acid -SBR from biobased succinic acid -Alkyde resin	-Cellulose acetate -PO3G -Biobased PE -PA11 -Biobased PB

Figure 2-1: Current and emerging plastics and their biodegradability (adapted from Shen, Haufe & Patel, (2009)).

Since more of the inherent strength of cellulose can be harnessed if sub-components of the plant fibre are isolated for use in composites (Miao & Hamad, 2013), it is important to review the macro, micro and nano structure of cellulose fibres.

2.1 Structure of Cellulose

Cellulose is a polysaccharide of linearly linked glucose units, with two glucose molecules forming a cellubiose repeat unit (Brandt *et al*, 2013). The cellulose chains are structured in amorphous and crystalline regions and native wood has a cellulose crystallinity ranging between 50 % and 70 % (Biermann, 1996: 32). The crystalline region of cellulose is particularly resistant to chemical attack and degradation, due to the difficulty with which crystallinities are penetrated by chemicals (Biermann, 1996: 33). Hydroxyl groups can assume different positions on the glucose unit, determining whether the native cellulose crystals will form triclinic (cellulose I_α) or monoclinic (cellulose I_β) unit cells (Huber *et al,* 2012). The crystalline structure of cellulose I is a mixture of cellulose I_α and cellulose I_β, with cellulose I_β being dominant in higher plants (Park *et al,* 2010).

The polymer chains are packed into elemental fibrils or nanofibrils, which contain both crystalline and amorphous regions. These elemental fibrils are often referred to as microfibrils, but when the diameters of the fibrils are under 100 nm, the use of the term nanofibrils might be more correct (Klemm *et al*, 2011; Miao & Hamad, 2013) and will be used in this study. The nanofibrils have a diameter of approximately 3.5 nm (Biermann, 1996: 33). These Nanofibrillated cellulose particles (NFC) has been investigated for reinforcing properties (Miao & Hamad, 2013). Dissolution of the amourphous domains in the elemental fibril results in the production of crystalline nano-cellulose (CNC) (Dufresne, 2013). The elemental fibrils aggregate (Klemm *et al,* 2011) to form microfibrils. The dimensions of CNC, nanofibrils, and microfibrils depend on their cellulose source (Klemm *et al,* 2011). These cellulose microfibrils are present in the secondary cell wall of all plants and aggregate to form fibres which are embedded in hemicellulose and lignin (Huber *et al,* 2012) (Figure 2-2).

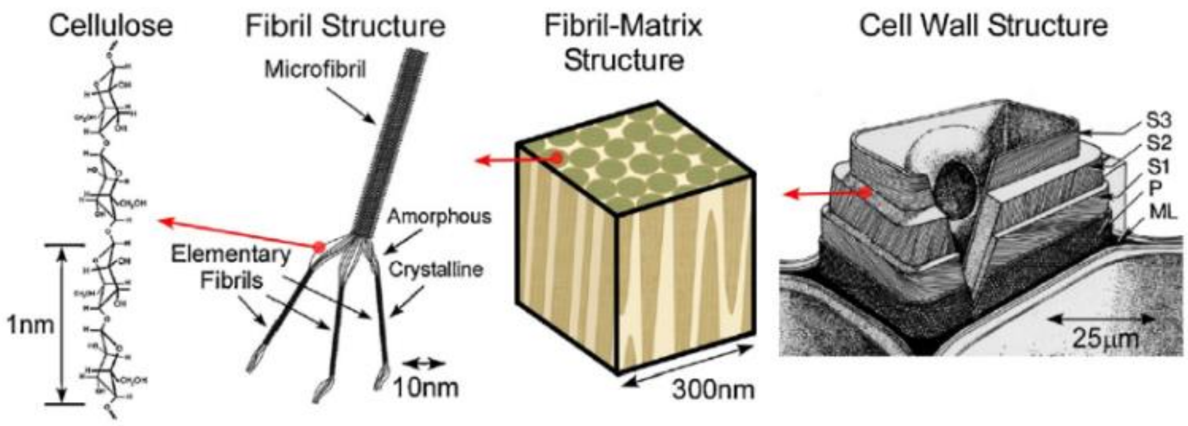


Figure 2-2: Hierarchical structure of a wood fibre (Moon in Dufresne (2013)).

The terminology surrounding nanocellulose has developed over the years resulting in multiple terms to describe the sub-categories. CNC has been referred to as nanocrystalline cellulose, cellulose crystallites, cellulose whiskers and cellulose microcrystals (Figure 2-3). (Klemm *et al,* 2011).

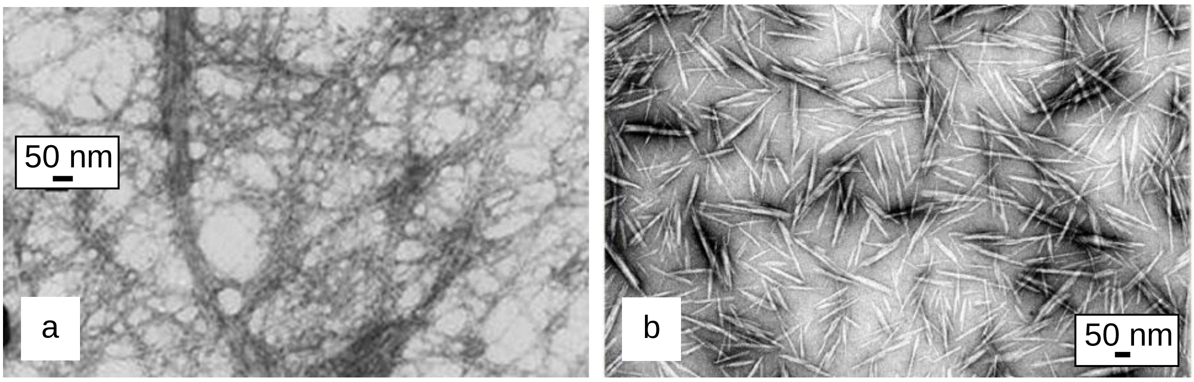


Figure 2-3: TEM images of a) NFC (Miao & Hamad, 2013) and b) CNC (Dufresne, 2013)

Amorphous cellulose forms spherical aggregates (Ioelovich, 2012; Ioelovich, 2013) that are distinctly different from the shape of native fibrils and acicular nanocrystals (Figure 2-4).

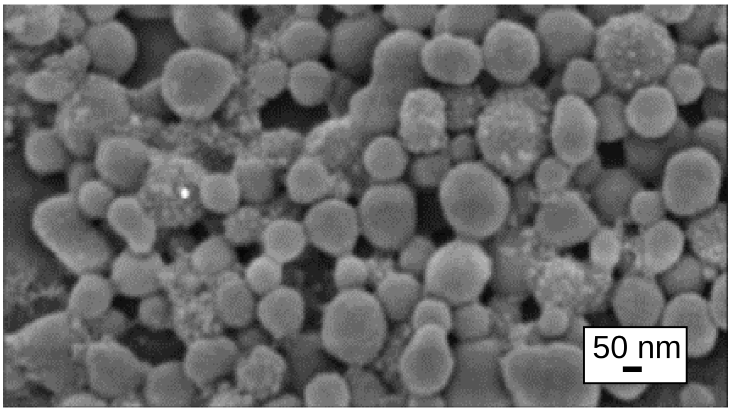


Figure 2-4: SEM image showing the spherical nature of aggregates of amorphous cellulose (Ioelovich, 2013).

Although the intrinsic strength of cellulose has attracted interest, harnessing this strength remains a challenge. The poor surface adhesion between the two phases remains critical problem when a composite is made between components from hydrophilic natural fibres and hydrophobic polymers (Huber *et al,* 2012). Proper interface adhesion between the two phases is one of the most important determining factors of the properties of the composite material (Mohanty, Misra & Drzal, 2001).

Compatibility of the surface interactions of the two phases will help to overcome poor dispersion of the filler and poor interface adhesion between the phases.

Mia & Hamad (2013) summarised that to this end physical, physico-chemical and chemical surface treatments of the natural materials have been investigated. They mentioned that treatments should be limited to the surface of the cellulose material to preserve the desirable mechanical strength and that large amounts of surfactant are needed to surface treat nanocellulose. The additional step of surface treatment adds cost and complexity to the production of biocomposites (Huber *et al,* 2012). One alternative approach to utilise celluloses attractive properties is to use a compatible matrix of cellulose, to produce an all-cellulose composite (Huber *et al,* 2012; Miao & Hamad, 2013).

2.2 All-Cellulose Composites (ACCs)

ACCs are monocomposites; so-called single polymer composites or self-reinforced polymer composites (Soykeabkaew, Nishino & Peijs, 2009). ACCs consist of a single chemical component (cellulose), but the composite phases usually have different morphological and/ or structural characteristics (Miao & Hamad, 2013). For example, an ACC could have crystalline nanocellulose as the filler phase and regenerated wood pulp as the matrix phase. Theoretically, this approach would result in an chemically interfaceless composite, reducing the need for intensive energy fibre treatments or coupling agents (Huber *et al,* 2012).

There are two distinct strategies for the production of ACCs: the two-step and one-step method (Figure 2-5). The two step method was first reported by Nishino, Matsuda & Hirao (2004). This method involves the complete dissolution of cellulose in a solvent and the regeneration of this cellulose in the presence of undissolved cellulose. The two-step method allows the regenerated and undissolved fractions of cellulose to be of different natural origin and to undergo different treatments before combination (Yousefi *et al,* 2011).

The one-step method is also known as the partial-dissolution method, because cellulose is only partially dissolved and regenerated in-situ to form a regenerated cellulose matrix around the undissolved cellulose fraction (Huber *et al,* 2012). This method has also been referred to as nanowelding (Yousefi *et al,* 2011) and surface selective dissolution (Soykeabkaew *et al,* 2009). Gindl & Keckes (2005) were the first to report the efficacy of the one-step method (Huber *et al,* 2012; Miao & Hamad, 2013).

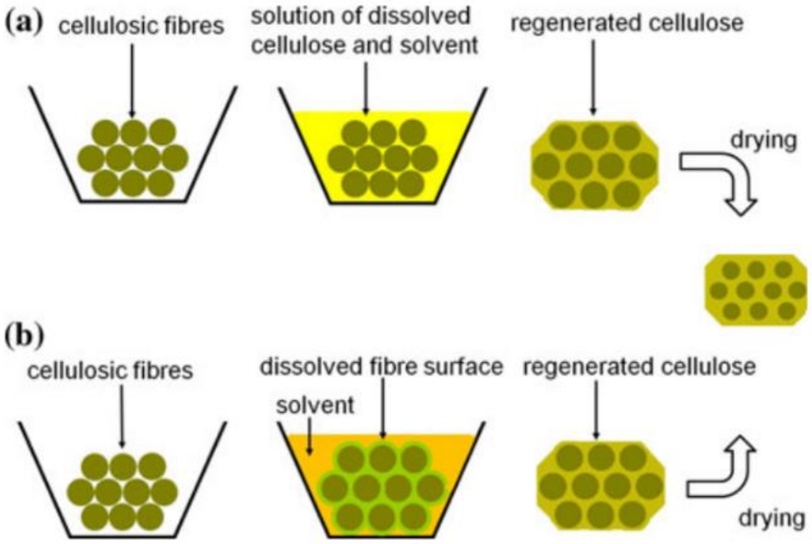


Figure 2-5: The one-step (a) and two-step (b) methods for ACC production (Huber *et al,* 2012)

Some of the advantages that the one-step method holds over the two-step method is its simplicity (Duchemin *et al,* 2009a) and improved fibre/matrix adhesion due to the absence of a distinct fibre/matrix interface (Soykeabkaew *et al,* 2009).

Far better properties were reported for ACCs compared to traditional biocomposites, with tensile strengths of 480 MPa reported for ACCs prepared by both one-step and two step methods (Huber *et al*, 2012). To produce the cellulose matrix, dissolution and regeneration of cellulose is needed and for this purpose a variety of cellulose solvents are known.

2.3 Cellulose dissolution

The dissolution and regeneration of cellulose is an old and well-known technology. The viscose process is the most used method, accounting for 95 % of annual production volumes (Hermanutz *et al*, 2008) of cellophane films and manmade cellulose fibres such as Byocell (Miao & Hamad, 2013). Cellulose solvents are classified as derivatising or nonderivatising solvents depending on the interaction of the solvent molecules with the polysaccharide. Derivatising solvents react chemically with the cellulose hydroxyl groups and form intermediates, whereas nonderivatising solvents do not form covalent bonds with the cellulose. (Pinkert *et al*, 2009) The viscose process is a derivatising process in which cellulose is reacted with carbon bisulphate to form cellulose xanthate and thereafter dissolved in sodium hydroxide (NaOH) and regenerated, often using sulphuric acid (Bredereck & Hermanutz, 2005). The viscose process uses large amounts of water and only 70 % to 75 % of the carbon bisulphate is recyclable (Hermanutz *et al*, 2008).

The high environmental cost of the viscose process motivated research in a direct solution and disulphite-free processes resulting in the development of the Lyocell process, which is a nonderivatising process with N-methylmorpholine-N-oxide (NMMO) as solvent (Bredereck & Hermanutz, 2005). For the viscose process, the cellulose concentration in solution is in the range of 8 % to 12 % and for the Lyocell process 10 % to 15 % cellulose solution is used (Hermanutz *et al*, 2008). There is significant interest in the development of alternative methods for the modification of cellulose, because legislation for the recovery of sodium salts, zinc salts, hydrogen sulphite and carbon disulphide gases from effluent water and gas streams have become cost determining for the viscose process (Bredereck & Hermanutz, 2005). Also, the thermally unstable nature of NMMO results in major investment in safety technology for the Lyocell process (Hermanutz *et al*, 2008).

A variety of other solvents, not applied industrially, have the ability to dissolve cellulose. Lithium chloride/N,N-dimethylacetamide (LiCl/DMAc), sodium hydroxide with additives and the IL, 1-butyl-3-methylimidazolium chloride (BmimCl) are the solvents that have most widely been used to investigate ACCs. However, most of these solvents have limited potential for use on an industrial scale, because of slow dissolution rates, toxicity and non-recyclability. (Huber *et al*, 2012)

LiCl/DMAc has mostly been used in investigations that followed the one-step ACC production route (Huber, et al., 2012), but environmental concerns limit the use of LiCl/DMAc to academic studies (Duchemin *et al*, 2009a). An advantage of using the LiCl/DMAc is that the extent of selective dissolution can be controlled by the pre-treatment step that forms part of the solvent system (Nishino *et al,* 2004).

To dissolve cellulose using an aqueous NaOH solution by addition of either urea (Qi *et al,* 2009) or polyethylene glycol (PEG) (Han & Yan, 2010) requires cooling of the solvent to sub-zero temperatures. Gelling of cellulose is achieved by reheating the solvent to room temperature.

ILs have attracted attention as a solvent for the preparation of ACCs. ILs possess many desirable properties such as negligible vapour pressure, thermal stability, its capacity to completely dissolve a broad range of cellulose without pre-treatment or activation and relative ease of recycling (Miao & Hamad, 2013).

2.4 Ionic liquids (ILs)

The use of salt-like solvents for the dissolution of cellulose was first reported in 1934 by Greanacher (1934), who applied N-alkylpyridinium salts to dissolve cellulose. In 1969, Husemann and Siefert homogeneously dissolved cellulose using N-ethylpyridinium and throughout the 1990s publications on the use of molten inorganic salt hydrates as cellulose solvents appeared (Fischer, Voigt & Fischer, 1999). Since then these salts have been termed ILs and 1-alkyl-3-methylimidazolium salts have become the most promising IL type for cellulose modification (Liebert & Heinze, 2008). The cellulose community only became interested in this class of solvents when Swatloski *et al* (2002) reported using ILs for the dissolution and regeneration of cellulose (Pinkert *et al,* 2009). Of all the ILs that Swatloski *et al* (2002) studied, BmimCl was the solvent with the highest cellulose solubility. Since their investigation, BmimCl has been one of the most widely studied ILs for the dissolution of cellulose (Pinkert *et al,* 2009).

ILs are most often defined as salts (containing a large organic cation and anion) with melting temperatures under 100 °C. The significance of 100 °C has been challenged and a general description that ILs are salts with a low melting temperature might be more fitting (Plechkova & Seddon, 2008). The low melting temperature of ILs is attributed to the large volume of the organic ions they contain. ILs are considered to be nonderivatising solvents for cellulose (Heinze *et al*, 2005), although it has been observed that BmimCl can act as a derivatising solvent for cellulose at 120 °C (Iguchi *et al*, 2013). Interest in ILs has grown considerably in the past twenty years (Figure 2-6) and they will likely continue to attract attention (Pinkert *et al,* 2009).

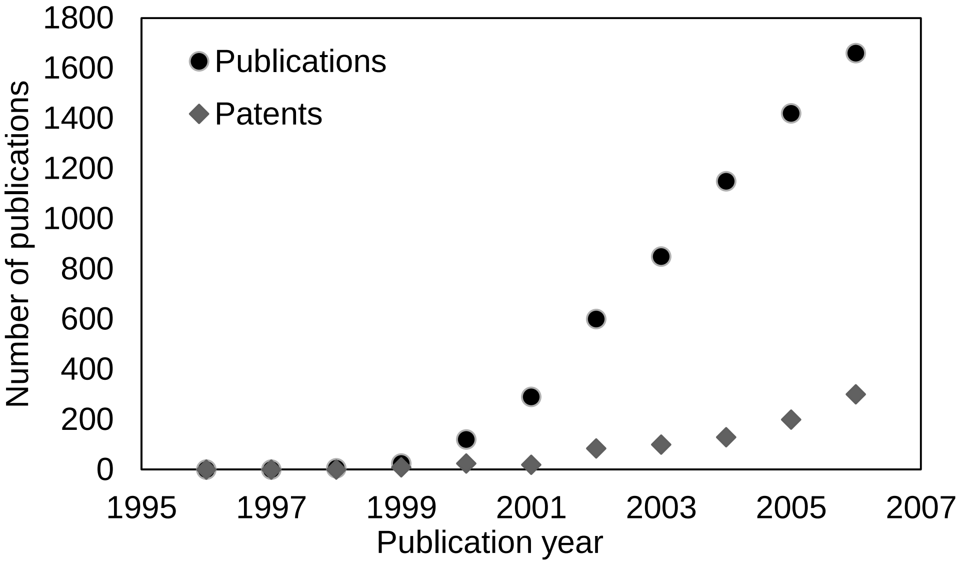


Figure 2-6: The growing interest in ionic liquids, represented by the number of publications in which they appear, between 1996 and 2006 (Deetlef, adopted from Plechkova & Seddon (2008)).

Altough ILs have attracted increasing attention, not many industrial application have been found. In 2013 only two industrial applications existed (the Diphasol™ process and the BASIL™ process). The lack of industrial applications for ILs are mainly due to their difficult and costly synthesis and their high sensitivity to impurities. (Durand, Lecomte & Villeneuve, 2013). Yet the significant potential that ILs show on a laboratory scale is motivating research into the commercialisation of ILs and the results are indicating that the large-scale production of ILs is not necessarily expensive and could become a commercial reality (Chen *et al*, 2014).

2.5 Cellulose dissolution using ILs

It is thought that both the cation and the anion of the ILs are involved in the dissolution of cellulose (Pinkert *et al,* 2009) and when selecting an IL for cellulose dissolution, both ions should be considered. Most ILs with the ability to dissolve cellulose have large, asymmetric anions (Liebert & Heinze, 2008) preventing the formation of a closely packed ionic network (Yang *et al,* 2004), resulting in higher ion mobility. It is expected that ILs have stronger cellulose dissolution power than other solvent systems, such as LiCl/DMAc, due to the higher mobility of the IL ions allowing them to interact with hydroxyl groups of the cellulose (El Seoud *et al,* 2007).

ILs with chloride, acetate or formate as anions and nitrogen containing cations are seen as the most promising for cellulose dissolution (Liebert & Heinze, 2008; Pinkert *et al,* 2009). Most ILs capable of dissolving cellulose have cations with methylimidazolium and methylpyridinium cores and allyl-, ethyl-, or butyl side chains (Pinkert *et al,* 2009). The solubility of cellulose in 1-alkyl-3-methylimidazolium type ILs are directly related to the length of the alkyl chain, with an odd-even effect for short chain lengths (Erdmenger *et al*, 2007). This means that 1-alkyl-3-methylimidazolium ILs with short even numbered alkyl chains dissolve cellulose better than those with short odd number alkyl chains.

ILs with acetate as a counter-ion can dissolve cellulose even better than those with chloride as a counter ion (Liebert & Heinze, 2008). It appears that interest is moving from ILs with chloride anions towards those with acetate anions, in particular 1-Ethyl-3-methylimidazolium acetate (EmimAc) (Brandt *et al*, 2013). When combining Bmim- or Emim- cations with an acetate ion rather than a chloride ion, IL solutions with higher cellulose concentrations were achieved (Kosan, Michels & Meister*,* 2008). Cellulose treated with acidified BmimCl showed 66 % conversion of cellulose to glucose, but no hydrolysis of cellulose took place when treated with acidified EmimAc under the same conditions (Binder & Raines, 2010). Also, high concentrations of cellulose (> 20 %) could be prepared in EmimAc without hydrolysis causing chain degradation (Hermanutz *et al*, 2008). Since degradation of cellulose chains are undesired during ACC production, the lower tendency of EmimAc to hydrolyse cellulose is a desirable property. When compared to BmimCl, EmimAc is a promising IL, because it is considered to be non-toxic, non-corrosive and biodegradable (Liebert & Heinze, 2008).

2.6 Dissolution mechanism

Cellulose dissolved in BmimCl have a disordered polymer structure, proving that the hydrogen bond network is disrupted by the presence of BmimCl (Moulthrop *et al,* 2005). This disruption can, at least partially, be contributed to a one-to-one stoichiometric hydrogen bonding of the cellulose hydroxyl protons and the chloride anions (Remsing *et al,* 2006). The mechanism through which cellulose is dissolved has often been described as solely the breaking of interchain hydrogen bonding in cellulose. But for cellulose chains in water, water-cellulose hydrogen bonds exist of the same strength as cellulose-cellulose hydrogen bonds (Lindman, Medronho & Theliander, 2015). Yet dissolution of cellulose in water does not occur. This inability of water to dissolve cellulose indicates that other interactions than hydrogen bonding alone determine the solubility of cellulose in a solvent (Lindman, Karlström & Stigsson, 2010).

Solvents very different in nature are able to dissolve cellulose and the role of amphiphilic solvents are becoming clear (Lindman *et al,* 2015). Successful cellulose solvents, N-methylorpholine-N-oxide and ILs, both show amphiphilic characteristics (Medronho & Lindman, 2014). The general interaction mechanism during dissolution of cellulose is still obscure and needs further research (Lindman *et al,* 2015).

The linear cellulose polymer chains are linked by hydrogen bonds to form flat sheets (Brandt *et al,* 2013). Van der Waals interactions are probably the main interaction between the sheets of native cellulose (cellulose I_β) (Nishiyama *et al,* 2003). It is thought that the cation of a cellulose-dissolving IL interacts with the top and bottom surfaces of the cellulose sheets, replacing the stacking interactions between the sheets and that the anion separates the cellulose chains from each other within the sheet (Brandt *et al*, 2013). When native cellulose is dissolved and regenerated, the crystal symmetry of the cellulose changes (often transforming cellulose I to cellulose II) and hydrogen bonds form between the sheets (Figure 2-7) (Dinand *et al*, 2002).

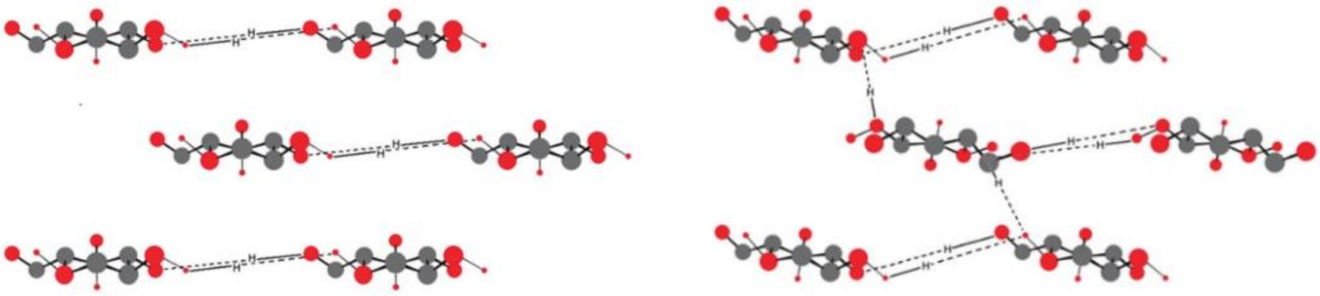

Cellulose I
Cellulose II

Figure 2-7: The different interaction between the sheets of cellulose I and cellulose II (adapted from Brandt *et al*, (2013).

2.7 Choice of cellulose starting material

Lignin and hemicellulose are also soluble in certain ILs (Brandt *et al*, 2013) and when selecting a cellulose starting material, high cellulose purity is important to prevent contamination of the IL solvent with decomposed lignin and hemicellulose fractions. The high viscosity of cellulose solution in IL makes processing of the solution more difficult and it is worth considering that the solutions become increasingly viscous as the length of the dissolved cellulose chains increases (Moulthrop *et al,* 2005).

The one-step ACC production route (using LiCl/DMAc or BmimCl as solvent) has been investigated using various cellulose sources. These sources include microcrystalline cellulose (MCC) (Gindl & Keckes, 2005), microfibrillated cellulose (MFC) (Duchemin *et al*, 2009a), filter paper (Nishino & Arimoto, 2007; Duchemin *et al*, 2009a), LDR-Lyocell, HDR-Lyocell and Byocell fibre (Soykeabkaew *et al,* 2009). Commercially available dissolving wood pulp has not been investigated. The term dissolving pulp refers to a high purity pulp with more than 95 % cellulose (Biermann, 1996: 72), which is used in the existing viscose and Lyocell processes. Dissolving pulp can be produced by the alkali sulphate (kraft) process if an acid prehydrolysis step is added to the process (Biermann, 1996: 73) or by acid-sulphite pulping.

2.8 Parameters

The structure of cellulose, especially the degree of orientation and crystallinity of the cellulose chains, determines the resistance to dissolution of the cellulose (Huber *et al,* 2012). The main process parameters controlling the rate and extent of the dissolution are temperature, time and the cellulose-to-solvent ratio (Duchemin *et al*, 2009a). The selection of these parameters depends on the starting material (Huber *et al,* 2012) and the degree of dissolution that is desired. For the production of ACCs with BmimCl, published studies investigated ranges of dissolution times to determine the optimal conditions for the starting material (Table 2-1).

Duchemin *et al* (2009a) mentions that temperatures below 80 °C were too low to promote dissolution and temperatures above 100 °C led to fast dissolution of MFC.

Table 2-1: Different dissolution parameter ranges investigated for the production of ACCs using BmimCl.

Starting material	Temperature	Time	Concentration
MFC sheet	80 °C[1]	20, 40, 80 and 160 min[1]	~ 7.5 %[1]
Canola straw MFC sheet	85 °C[2]	Five time increments between 5 min and 8 h[2]	Unknown[2]

1) (Duchemin *et al*, 2009a); 2) (Yousefi *et al,* 2011)

Solutions containing up to 25 % cellulose could be prepared by microwave heating using chloride containing ILs, but solutions with 5 % to 10 % were easier to prepare (Swatloski *et al,* 2002). Apart from the economic, environmental and health advantages that processing with high cellulose concentration and reduced solvent concentrations may hold, high cellulose concentrations (in a LiCl/DMAc solvent system) also had the advantage of minimising shrinkage of the cellulose material during the precipitation and drying stage (Duchemin, Newman & Staiger, 2007).

Sufficient surface dissolution of microfibres occur after 30 min in BmimCl at 85 °C to ensure bonding of the microfibres upon regeneration and complete dismantling of the microfibres occur after 120 min in BmimCl at 85 °C. The dissolution ability of IL is very water sensitive and water content exceeding 1 % causes IL to be incapable of dissolving cellulose (Swatloski *et al,* 2002). For this reason it is essential that BmimCl be dried before use, since it is highly hydrophilic with an ultimate water-sorption capacity of 20 % (Cao *et al*, 2012).

Cellulose is regenerated from the solution in an IL by the addition of a polar coagulant (Pinkert et al, 2009) (commonly water, alcohol or acetone, which disrupts the ability of the IL to dissolve cellulose). The IL in the regenerated matrix is displaced with the coagulant and the coagulant is subsequently removed from the matrix by evaporative drying (Duchemin *et al*, 2009a; Yousefi *et al,* 2011; Huber *et al*, 2012) . The regeneration step is an important contributor to the structure and properties of the produced ACC (Duchemin, Newman & Staiger, 2009b; Chen & Liu, 2014). Duchemin *et al* (2009b) investigated the effect that precipitation rate had when ACCs were produced using LiCl/DMAc. They found that a slower rate of cellulose precipitation lead to ACCs with a 10 % to 14 % higher Crystallinity Index (CrI) and consequently better mechanical properties. The increased crystallinity was probably due to the slower precipitation route, allowing more time for the cellulose chains to orientate themselves into a more stable, lower energy configuration (Huber *et al,* 2012).

Upon regeneration, contact with the coagulant (especially when using water) leads to swelling of the cellulose. Warping of the cellulose material can occur if a diffusion gradient of coagulant from the surface to the interior of the material forms, leading to differential shrinkage, delamination and void formation in the material (Huber *et al,* 2012). Differential shrinkage also becomes a problem when the regenerated and undissolved phases of the ACC swell by different amounts, resulting in void formation on the interface of the two phases and mechanical weakening of the material (Duchemin *et al*, 2009b).

The regeneration method by precipitation is similar to the regeneration method used when cellulose is dissolved using NMMO. Yet when deionised water was used as a coagulant, fibres regenerated from NMMO showed a higher degree of crystallinity and higher strength, whereas cellulose regenerated from ILs showed a lower degree of crystallinity than the starting material (Pinkert *et al,* 2009). Chen and Liu (2014) determined that the tensile strength of regenerated cellulose films prepared from wheat straw was higher when the coagulation temperature was low and decreased with increasing temperature. Elongation at break of these films showed the opposite response to increasing temperature with higher elongations achieved at higher coagulation temperatures.

Apart from the parameters that will affect the produced cellulose product, parameters for the recovery of IL after use should also be considered. BmimCl (Pinkert *et al,* 2009) is not acutely toxic, but the toxicity of 1-alkyl-3-methylimidazolium cation ILs increase with increasing alkyl chain length (Swatloski *et al,* 2004; Ranke *et al,* 2004). Furthermore, ILs containing imidazolium salts have poor biodegradability (Romero *et al,* 2008). When considering the high cost of IL, lack of IL biodegradability and possible toxicity, the importance of efficient recovery and reuse of IL is apparent. For the production of ACCs with BmimCl, the removal of BmimCl from the produced ACC was achieved by rinsing stages. Limited information on the rinsing methods for IL recovery exists in published literature (Table 2-2).

Table 2-2: Rinsing methods for recovering BmimCl after ACC production

Number of stages	Rinsing solvent	Water/cellulose mass ratio per stage	Duration of stage	ACC film thickness (mm)
2	Water	Unknown	~24 h	0.1 to 0.2
10	Methanol	Unknown	Total of 12 h, for 10 rinsing stages	Unknown

1) (Duchemin *et al*, 2009a); 2) (Yousefi *et al,* 2011)

The ACC containing BmimCl was placed in a container with rinsing solvent and after a desired time, the solvent was replaced with fresh solvent. Each replacement of the solvent started a next stage in the rinsing process.

2.9 Problems with IL and IL recovery

Vapour pressure of ILs are negligible at near ambient conditions, reducing pollution of the atmosphere and improving the recyclability of ILs. This property has led to ILs being described as green solvents, but this description should take into consideration that ILs are not necessarily non-toxic or biodegradable. (Plechkova & Seddon, 2008; Durand *et al*, 2013)

For ILs to be competitive as a cellulose solvent for the production of fibres the following requirements were identified (Hermanutz *et al*, 2008):

- The ILs should have a low melting temperature, but a high decomposition temperature,
- No cellulose decomposition should occur,
- The cellulose solution (dope) should be stable and storable,
- The cellulose solution should be easy to process and easy to regenerate,
- The recovery of the IL should be uncomplicated,
- The process should be non-toxic and no volatiles should be produced,
- The process should be cost effective.

Many investigations on the toxicity, stability and recyclability of ILs have been done and some methods for efficient recovery, product isolation and reuse of ILs on an industrial scale have been investigated. These methods include extraction of the IL with a benign solvent, pervaporation or distillation and the use of gaseous carbon dioxide to simplify the separation of IL and water (Park & Kazlauskas, 2003).

ILs are often described as being thermally stable, but long term exposure to elevated temperatures will result in thermal degradation (Pinkert *et al,* 2009; Brandt *et al*, 2013). Thermal decomposition (mass loss) for BmimCl starts at about 290 °C when analysed thermogravimetrically, but before mass loss becomes apparent, degradation of the IL to imidazoles and other by-products is already underway (Meine, Benedito, & Rinaldi, 2010). BmimCl shows degradation to imidazoles when kept at 140 °C for one day, but shows no degradation even after ten days' exposure to a temperature of 120 °C (Meine *et al,* 2010). To improve the likelihood of reusing ILs, it is preferable to perform cellulose treatments with IL at the lowest possible temperature to limit long term thermal degradation.

ILs, especially imidazolium salts are seen as being chemically inert, but they do have a potential reactivity and reaction with cellulose cannot be completely ruled out (Liebert & Heinze, 2008). BmimCl acted as a non-derivatising solvent for the cellulose (did not form covalent bonds with the cellulose) at 90 °C, but was a derivatising solvent at 120 °C (Iguchi et al. 2013). Furthermore, the ability of IL to dissolve cellulose appears to be very sensitive to the presence of impurities and water (Brandt *et al*, 2013). Work done by Le, Rudaz & Butova (2014) demonstrated the reduced ability of an IL to dissolve cellulose in the presence of water. Studies have been done on the reusability of ILs for the treatment of lignocellulose materials and it appears that a clean-up step after a few reuses will be necessary to remove contaminants (Brandt *et al*, 2013), motivating research into IL purification.

Contrary to the wide belief that ILs could not evaporate under any conditions, it is possible to distil ILs and this could prove to be a valuable purification method for the recovery of used ILs (Earle *et al* quoted in Plechkova & Seddon, (2008)). The distillation of ionic liquids require appropriate conditions of high temperature and low pressure (Earle *et al* quoted in Plechkova & Seddon, (2008)) and IL can still be described as having the environmentally friendly property of a negligible vapour pressure close to ambient conditions where they will most likely be used.

2.10 XRD analysis

Cellulose I forms a nicely ordered structure, consisting of hydrogen bonded layers, in contrast to the three-dimensional, hydrogen-bonded, very likely disordered network of cellulose II (Kroon-Batenburg & Kroon, 1997). Different models for the crystalline structures of cellulose I and cellulose II exists, but the model describing cellulose I structure as parallel chain orientation and cellulose II as antiparallel appears to be most likely (Dinand *et al*, 2002). Other allomorphs of cellulose have also been observed, with cellulose II, cellulose III and cellulose IV being the most common (Huber *et al,* 2012). The cellulose phases present in ACCs have mainly been characterised using wide-angle X-ray diffraction (WAXS) (Huber *et al*, 2012) and the peak positions for cellulose I and cellulose II are well known (Table 2-3).

Table 2-3: XRD peak positions for cellulose I and cellulose II using Cu Kα radiation source.

Primary Peaks (2θ)	Secondary Peaks (2θ)	Reference
	Cellulose I	
22.6°	14.8° and 16.8°	(Ago, Endo & Hirotsu, 2004)
21.8° to 22.7°	14.3° and 16.8° for Iα	(Thygesen *et al,* 2005)
	Cellulose II	
19.8° and 22.0°	12.1°	(Ago *et al*, 2004)

Different cellulose phases have been observed for regenerated cellulose in published literature. The regenerated phase after IL dissolution has been found to be dependent on the type of cellulose substrate, the dissolution conditions and regeneration conditions (Wahlström & Suurnäkki, 2015). Regenerated cellulose, dissolved with ILs, reportedly precipitates as either amorphous cellulose, cellulose II, a mixture of amorphous cellulose and cellulose II or a mixture of amorphous cellulose and cellulose I (Wahlström & Suurnäkki, 2015). Furthermore, a paracrystalline phase forms when MCC is dissolved with LiCl/DMAc (Duchemin *et al*, 2007). This paracrystallite forms when cellulose I is ordered into crystallites with a width of under 2 nm resulting in all the cellulose chains being exposed on the surfaces of the crystallite. Duchemin *et al* (2007) proposed a mechanism in which the solvent peels layers from the original cellulose I crystallites, the layers retain some ordering of the cellulose I crystal structure and upon removal of the solvent, the peeled layers regenerate into a paracrystalline matrix.

A parameter termed the crystallinity index (CrI) has been used to compare the crystallinity of different cellulose samples by describing the relative amount of crystalline to amorphous cellulose. Different methods for evaluating crystallinity and calculating CrI exist. Park *et al* (2010) reviewed the different methods used for determining CrI in cellulose. They mention that solid-state ^{13}C nuclear magnetic resonance (NMR), Fourier transform infrared (FTIR) spectroscopy and X-ray diffraction (XRD) can be used to analyse cellulose crystallinity. Furthermore they compared three methods for determining CrI from an XRD intensity profiles. They concluded that the commonly used, convenient XRD peak height method (Segal method) (Equation 1; Figure 2-8) gives excessively high CrI values. Even though the peak height method was used in 75 % to 80 % of the articles they studied; they suggested that peak deconvolution or the subtraction of an amorphous standard rather be used.

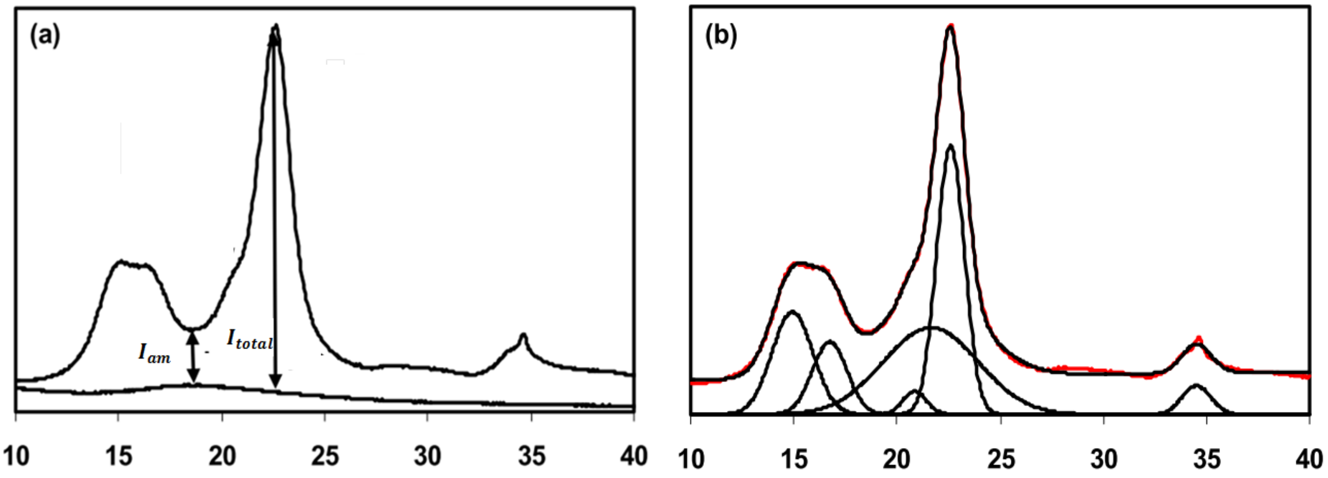


Figure 2-8: Measurements used in the peak height method (a) and peak deconvolution (b) for the determination of CrI (adapted from (Park *et al,* 2010)).

$$CrI = \frac{I_{total} - I_{am}}{I_{total}} \cdot 100 \qquad (1)$$

where I_{total} = The intensity of the primary peak after subtraction of the background signal

I_{am} = The intensity at the minimum between the primary and secondary peaks, after subtraction of the background signal

Possible reasons for the unrealistic high results of the peak height method, are that the cellulose crystallites are so small that peak overlap occurs in the region of 18° for cellulose I_β, giving too high values for I_{am} and that overestimation of I_{total} occurs due to preferred orientation of the crystallites (Thygesen *et al,* 2005).

The XRD intensity profile can be separated into the amorphous and crystalline contributions by deconvolution of the spectra into peaks (Figure 2-8). Four or five peak positions can be assumed for the deconvolution and Gaussian (Equation 2), Lorentzian or Voigt functions can be used to describe the peaks (Park *et al,* 2010). The amorphous contribution to the XRD intensity profile of cellulose can also be determined by preparing an amorphous standard and the difference in area under the intensity profiles of the cellulose sample and the amorphous cellulose standard is assumed to be due to crystalline regions.

$$f(x) = a \cdot \exp[-\frac{(x-b)^2}{2c^2}] \qquad (2)$$

where a = The maximum value of $f(x)$

b = The maximum value of x

c = The peak half width

2.11 Future processing

Cellulose materials will likely form an important part of future biodegradable and sustainable materials. The main obstacle that remains is developing cost effective, safe and environmentally benign processing methods. The one- and two-step methods for producing ACCs are classified as wet-processing methods. Thermal processing of pure cellulose has not been achieved, because the T_g of cellulose is above its decomposition temperature (Wu *et al,* 2014). The T_g of starch was lowered by the addition of plasticiser to produce thermoplastic starch (Bendaoud & Chalamet, 2013). Similarly, to enable thermal processing, cellulose was plasticised with BmimCl and processing by two roll mill, plate vulcanising machine and injection machine have been attempted (Wu *et al,* 2014). If the current interest in cellulose processing methods continues to grow, cellulose materials have a promising future.

3 MATERIALS AND METHODS

A method for the dissolution and regeneration of cellulose, using and ionic liquid, to produce an all-cellulose composite film was developed. This method makes use of a cellulose sheet as starting material and film casting or film pulling was not used. General considerations for the developed of this method and the materials used are discussed in Section 3.1.

3.1 Developing methods for ACC production

3.1.1 Materials

1-Butyl-3-methylimidazolium chloride (BmimCl) (>95 %, BASF) was selected for use, because it was the most used IL for ACC production and has many desirable properties. Dissolving pulp (>91 % α-cellulose) supplied by Sappi Ltd, produced by a sulphite pulping process, was used as cellulose source. Dissolving pulp was used as cellulose source, because it is the feedstock for the existing cellulose dissolution and regeneration industry.

Sheets of the dissolving pulp were formed using a Blattbildner “Rapid Köthen” System (Paper Testing Instruments GmbH) handsheet maker. This machine diluted, agitated, stilled and drained the pulp through a screen to form a sheet which was dried at 95 °C between two press plates under a vacuum of approximately - 80 kPa. The formed hand sheets contained 2 g dry α-cellulose, had a thickness of approximately 0.16 mm and a dry α-cellulose mass-to-area ratio of 41.5 g/m^2.

Circles, with a diameter of 90 mm, were cut from the formed hand sheets. This diameter was similar to the glass petri dish diameter in which dissolution of the sheets was performed. Before use, the 90 mm diameter circle sheets were randomised to remove the effect of possible variation between the different hand sheets.

3.1.2 The development of a synthesis process

The one step method was selected for the production of ACC, because of its intrinsic simplicity. From published literature on the one step method (Duchemin *et al*, 2009a;

Yousefi *et al*, 2011) five steps for the dissolution and regeneration of cellulose using IL were identified (Figure 3-1):

1) Drying of the starting cellulose material, the IL and the glassware to avoid any negative effect of water on the dissolution of cellulose.
2) Dissolution of the cellulose in the IL at the desired dissolution temperature.
3) Regeneration of the cellulose by the addition of a coagulant.
4) Removal and recovery of the IL from the cellulose matrix by displacement thereof with a coagulant (rinsing).
5) Removal of the coagulant from the cellulose matrix by evaporation (drying). This drying step is performed under pressure to prevent warping of the final product.

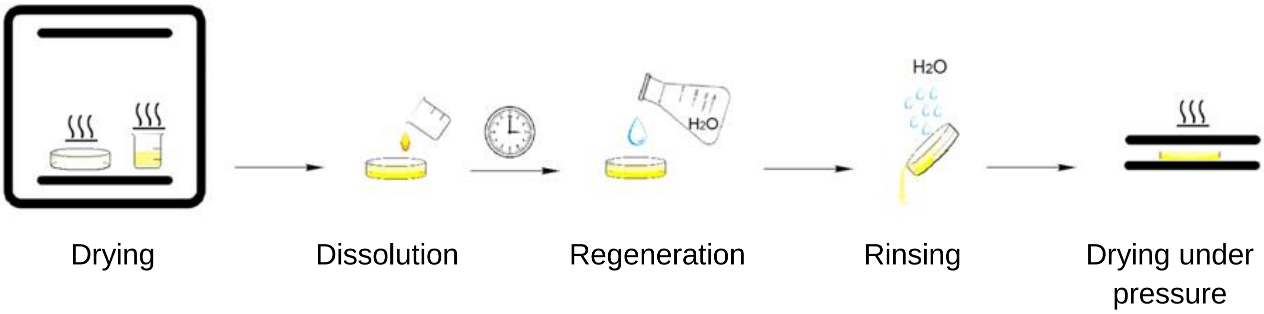


Figure 3-1: The five steps required for the dissolution and regeneration of cellulose using IL.

Based on the five steps for the dissolution and regeneration of cellulose, the following detailed experimental method was developed:

The 90 mm diameter cellulose sheets, the BmimCl and the glassware were first oven-dried overnight at 105 °C to avoid any negative effect of water on the dissolution of cellulose. The dried sheets were weighed and the required weight of BmimCl was calculated for each sample using the selected cellulose-to-solvent ratio. The BmimCl was added to, and spread over the bottom of petri dishes. The dried sheets were placed on top of the BmimCl and the petri dishes containing the sheets and BmimCl were transferred to a fan oven set to the desired dissolution temperature.

After the selected dissolution time, each sample was removed from the oven and placed in the headspace, above water level, of a laboratory water bath set to 80 °C. The samples were allowed to regenerate in this condition for 60 min. The samples were placed in the high humidity environment to allow gradual exposure to moisture, stopping the dissolution process and resulting in precipitation of cellulose from solution to a solid cellulose sheet.

The regenerated sheets were rinsed to displace the BmimCl by submersing the sheets in the desired amount of coagulant. Demineralised water was selected as coagulant and will onwards be referred to as rinsing water. The rinsing water was sequentially replaced with fresh rinsing water and each replacement started a next stage of rinsing. The volume of rinsing water for each rinsing stage was determined using a ratio of 2.4 ml rinsing water per gram of BmimCl originally added to the sample.

After rinsing, the rinsing water remaining in the cellulose structure was removed by pressing and drying the sheets at 95 °C between two press plates under a vacuum of approximately - 80 kPa.

The rinsing water was collected after each rinsing stage and the collected liquid was vacuum filtered to remove small pieces of regenerated cellulose fractions that were visibly present in the rinsing water. It was assumed that only rinsing water and BmimCl was present in the liquid after filtration. The filtration supernatant for each treatment was added to a separate glass beaker of which the dry weight was predetermined. The beakers containing the liquid were placed in a fan oven at 105 °C for at least 24 h (constant mass reached) after which they were weighed. It was assumed that only BmimCl remained in each beaker after evaporation of the rinsing water for 24 h. The weight percentage recovery of BmimCl was calculated on the basis of BmimCl originally used for each sample.

3.1.3 Selecting dissolution condition

The cellulose-to solvent ratio or BmimCl concentration, dissolution temperature and dissolution time all contribute to the extent of cellulose dissolution. They can collectively be expressed as the dissolution conditions. From literature (refer to Section 2.8) the limits for independent dissolution variables were selected (Table 3-1).

In additions to the upper and lower limit a third intermediate value was selected for each independent variable. These values were 14 g/g BmimCl/cellulose concentration, 90 °C dissolution temperature and 1.25 h dissolution time.

Table 3-1: The limits selected for independent dissolution variables.

Variable	Lower limit	Upper limit	Comments
BmimCl concentration (g/g)	9 g/g	19 g/g	This relates to a 5 % to 10 % cellulose solution
Dissolution temperature (°C)	80 °C	100 °C	
Dissolution time (h)	0.5 h	2 h	

3.2 Analysis methods

3.2.1 Visual analysis

Selected samples were inspected for visual differences including whether undissolved fibres could be observed, changes in transparency and film fractures or holes.

3.2.2 Tensile testing

Samples were conditioned at 50 % ± 2 % relative humidity and 25 °C ±1 °C for at least 24 h prior to tensile testing. The stress−strain curves of the specimens were determined using a tensile tester (Hansfield H5K-S) at 25 °C ±1 °C. The clamp distance was 10 mm and the specimens had a width of 10 mm. The load cell and extension rate were 500 N and 5 mm/min, respectively.

3.2.3 SEM

The surfaces of selected samples were carbon coated and imaged using a FE-SEM (Sigma Zeiss).

3.2.4 XRD analysis

X-ray diffraction (XRD) spectra of the film samples were created with a diffractometer (PANalytical X'Pert PRO) equipped with a Co K_α source (λ = 0.179 nm). The XRD scan was performed for 2θ values from 5° to 90° at increments of 0.08°.

The CrI was determined from the XRD spectra by the Peak height method (Segal method) and by peak deconvolution. These methods are explained in Section 2.10.

For the peak deconvolution method, five Gausian peaks were fitted to the XRD spectra. The curve fitting was performed by using Microsoft Excel Solver to simultaneously fit the curves. Figure 3-2 shows the result of peak deconvolution of the XRD spectra of the dissolving pulp starting material. This method for peak fitting was possible, because initial values for the peak positions and heights could be closely approximated.

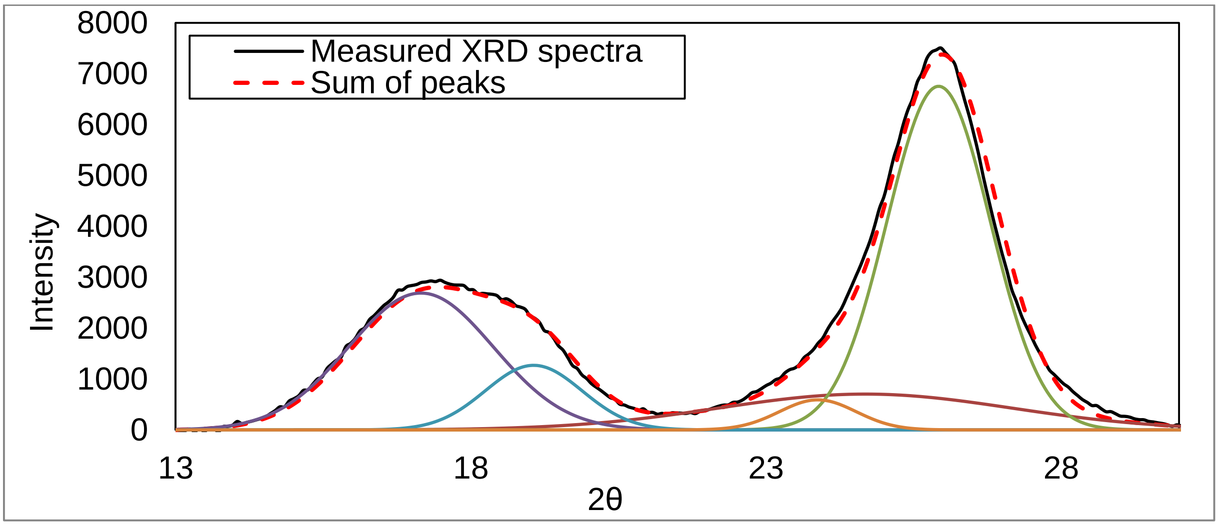


Figure 3-2: Peak deconvolution of the XRD spectra of the cellulose starting material.

The primary and secondary peaks for cellulose as given in Section 2.10 were determined using Cu K$_\alpha$ sources (λ = 0.154 nm). By applying Bragg's Law, the peak positions for Co radiation could be determined from the known peak positions (Table 3-2).

Table 3-2: The 2θ peak positions for cellulose for a Co K$_\alpha$ radiation source calculated from the known peak positions for cellulose when Cu K$_\alpha$ is used.

Radiation source	Cellulose I		Cellulose II		Amorphous cellulose
	Primary peak	Secondary peak	Primary peak	Secondary peak	
Cu K$_\alpha$	22.6°	14.8° & 16.8°	19.8° & 22.0°	12.1°	21.5°
Co K$_\alpha$	26.3°	17.2° &19.6°	23.1° & 25.6°	14.1°	25°

3.2.5 Statistical analysis

Three replicates of all the treatments investigated were performed. Where applicable, post-hoc analysis using Tuckey HSD test in conjunction with ANOVA (tested using $\alpha = 0.05$) was performed to determine whether a statistical significant difference between the measured values for the treatments exists.

4 INVESTIGATION A: THE RECOVERY OF IL USING RINSING STAGES

Although the recovery of IL is often described as a determining factor to ensure cost efficiency and an environmentally benign process, published literature on the process of recovering IL is very limited. Three experiments were performed to quantify 1-butyl-3-methylimidazolium chloride recovery with respect to the temperature of the coagulant, the extent to which cellulose was dissolved and the duration and amount of rinsing stages. The conditions for dissolution were selected from the experimental range defined in Section 3.1.3.

4.1 Rinsing water temperature

4.1.1 Experimental method

The removal of BmimCl from the precipitated cellulose material is achieved by transfer of the BmimCl from the cellulose to the rinsing water. If the rinsing is performed at a higher temperature it is likely that the diffusion rate will increase and that recovery of BmimCl from the cellulose will be improved.

To determine the effect of rinsing water temperature on BmimCl recovery, cellulose samples were dissolved and regenerated using the method as explained in Section 3.1.2. The samples were dissolved using 14 g/g as BmimCl concentration at 90 °C for 1.25 h. After regeneration, rinsing water at approximately 80 °C and 25 °C was used, respectively, for rinsing the samples. Rinsing was performed using stages as discussed in Section 3.1.2. When rinsing water at 80 °C was used, the samples were placed in the headspace of the water bath, above the water level, for the duration of the rinsing. This was done to ensure that the sample remained heated during rinsing, without evaporation of the rinsing water. When rinsing water at 25 °C was used, the samples were left outside the water bath at ambient temperature and conditions for the duration of rinsing.

The volume of rinsing water that was added per stage was constant for all the stages and calculated according to the ratio in Section 3.1.2. Four rinsing stages for both 80 °C and 25 °C rinsing water were performed. The rinsing stages were of 10 min, 15 min, 20 min and 90 min duration, respectively.

The percentage mass recovery of BmimCl for each stage was determined as discussed in Section 3.1.2. The cumulative mass recovery was expressed relative to the cumulative rinsing time.

Three replicates for both 25 °C and at 80 °C rinsing water were performed. Significant variance between the BmimCl recovery values for the different treatments were analysed as discussed in Section 3.2.5. An exponential curve (Equation 3) was fitted to data using least squares regression by the variation of two parameters using Microsoft Excel Solver.

$$R = a\left(1 - e^{(-b \cdot t)}\right) \tag{3}$$

where R = Cumulative mass percentage recovery BmimCl

t = Cumulative rinsing time

a, b = Parameters

4.1.2 Results and discussion

The transfer of BmimCl to the rinsing water during the first rinsing stage occurred much faster than expected. In other published work relating to the dissolution of cellulose with BmimCl (Duchemin et al. 2009a; Yousefi et al. 2011) the total rinsing times for the removal of BmimCl were 12h and 48h, respectively. A higher rinsing water temperature was found to accelerate and improve BmimCl recovery (Figure 4-1). The BmimCl recovery for the first rinsing stage statistically differed significantly for the two different rinsing water temperatures. Approximately 30 % better BmimCl recovery was obtained for the first rinsing stage when water at 80 °C was used compared to rinsing water at 25 °C. There was no statistical significant difference in the BmimCl recovery for the different temperatures from the second to the fourth rinsing stage or between the final cumulative recovery values. The cumulative recovery values when rinsing water at 80 °C was used appears to be higher than when rinsing water at 25 °C was used. Whether this recovery is truly higher for rinsing water at 80 °C is unclear due to the lack of significant difference between the measured values.

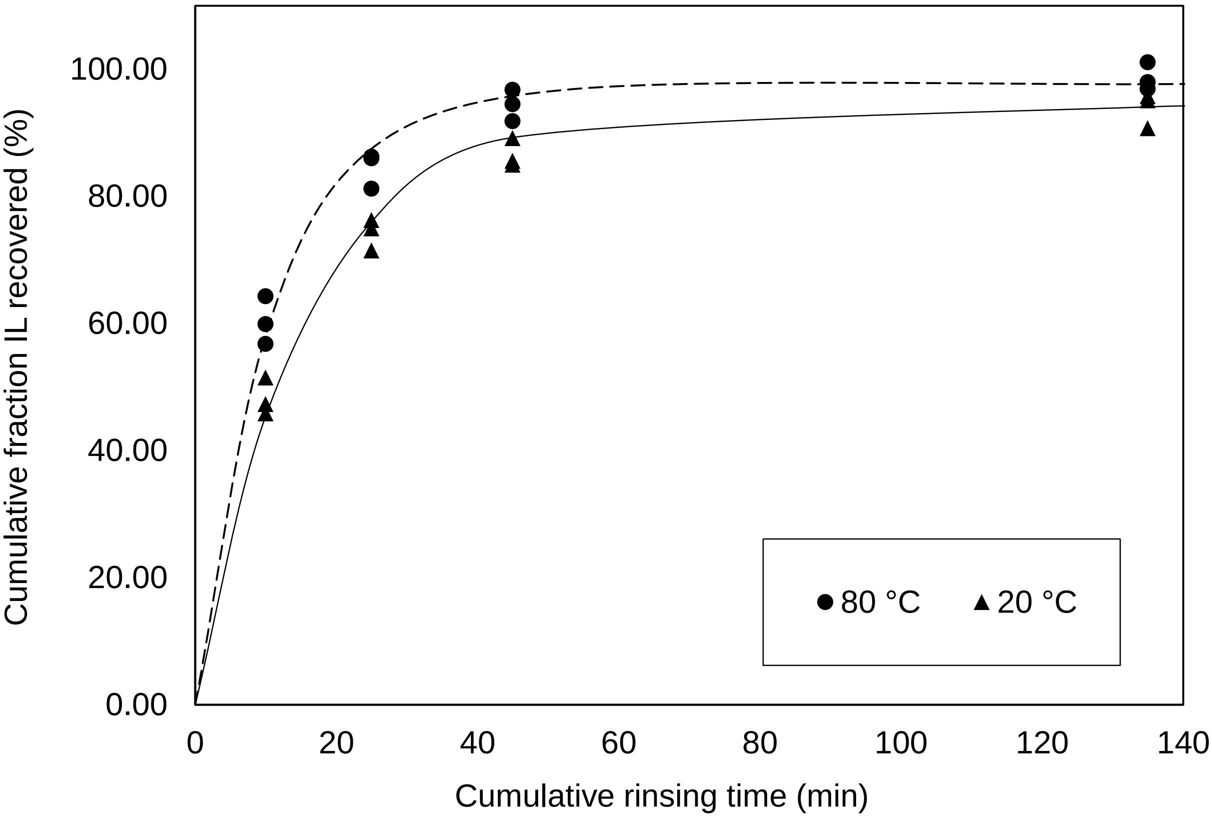


Figure 4-1: The cumulative mass percentage BmimCl recovery for the cumulative rinsing time.

When BmimCl recovery is considered from a process perspective, it is desirable to recover the maximum BmimCl in the shortest time using the minimum amount of water. The observed accelerated BmimCl recovery motivated the use rinsing water at 80 °C for the following experiments.

4.2 Different degrees of cellulose dissolution

The morphology of cellulose changes as it undergoes dissolution and regeneration. It was expected that the diffusion of BmimCl from the cellulose structure might be different for different cellulose morphologies.

4.2.1 Experimental method

To evaluate BmimCl recovery for different morphologies due to different degrees of dissolution, a constant rinsing method was applied to samples that was dissolved using different dissolution conditions. Three dissolution treatments were selected from the dissolution condition ranges defined in Section 3.1.3 (

Table 4-1).

Degree of dissolution	BmimCl/cellulose concentration (g/g)	Dissolution temperature (°C)	Dissolution time (h)
High	19	100	2.00
Intermediate	14	90	1.25
Low	9	80	0.50

Table 4-1: Dissolution conditions selected to achieve different degrees of dissolution.

Degree of dissolution	BmimCl/cellulose concentration (g/g)	Dissolution temperature (°C)	Dissolution time (h)
High	19	100	2.00
Intermediate	14	90	1.25
Low	9	80	0.50

Dissolution and regeneration of the samples were performed as described in Section 3.1.2. After regeneration, samples were rinsed using five sequential rinsing stages of 10 min, 15 min, 20 min, 20 min and 12 h duration, respectively. The temperature of the rinsing water was 80 °C based on the (from the results of Section 4.1). The percentage mass recovery of BmimCl for each stage was determined as discussed in Section 3.1.2.

Three replicates for each of the three dissolution conditions were performed and an exponential curve (Equation 3) was fitted to the data using least squares regression by the variation of two parameters using Microsoft Excel Solver. Significant variance between the BmimCl recovery values for the different treatments were analysed as discussed in Section 3.2.5

4.2.2 Results and discussion

Different degrees of cellulose dissolution affected the efficiency with which BmimCl could be recovered. A higher degree of cellulose dissolution slowed the recovery of

BmimCl down (Figure 4-2). This slower recovery was probably due to a denser matrix structure than the samples that were less dissolved.

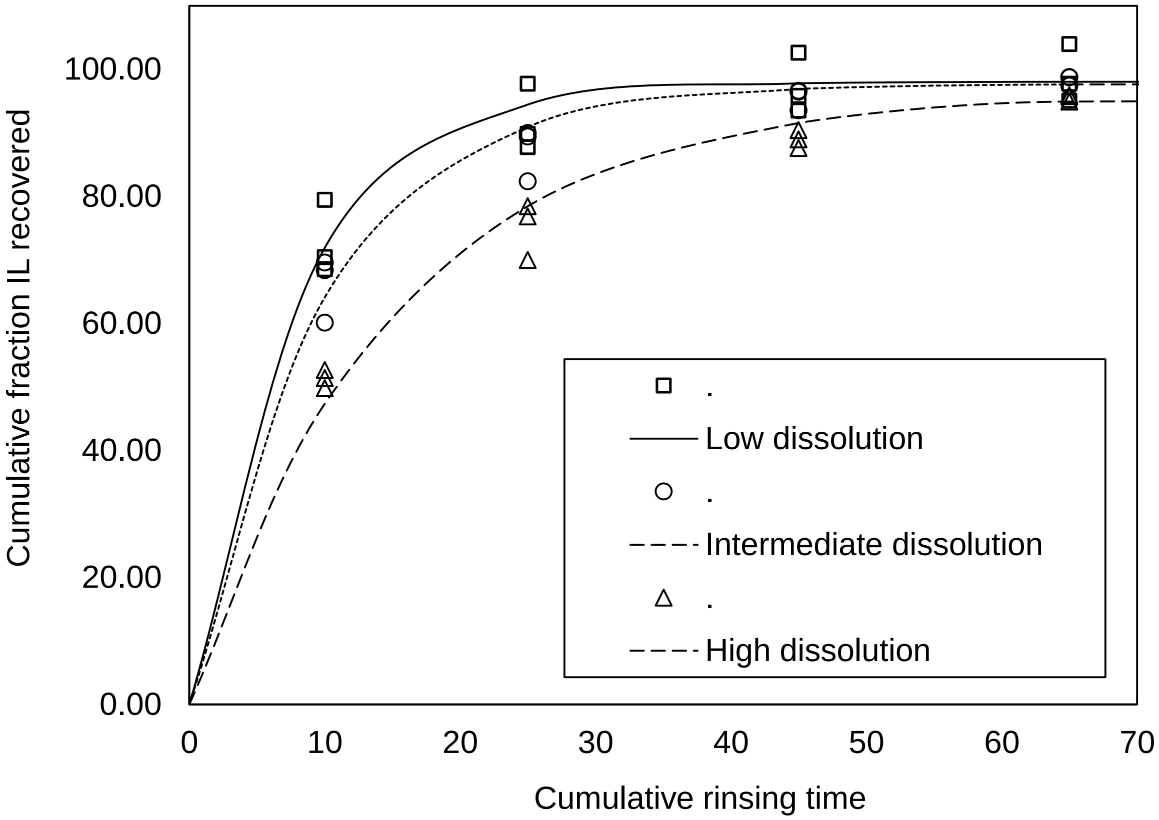


Figure 4-2: BmimCl recovery for different cellulose dissolution conditions. The cumulative values of the first four rinsing stages are shown.

The recovery during the first rinsing stage was statistically significantly less for the samples prepared at the high dissolution condition relative to the other two treatments. Greater BmimCl recovery in following rinsing stages for the highly dissolved samples were observed. This improved recovery in later stages was probably due to the higher amount of BmimCl still available for removal after the first rinsing stage. A difference in the cumulative BmimCl recovery could be observed between the highly dissolved samples compared to the other two treatments after three rinsing stages, but not after four or five rinsing stages. The total recovery after four rinsing stages was 97.60 % (+/- 2.66 %) statistically independent of the degree of dissolution. Thus, if sufficient rinsing is performed on samples, the difference in their degree of dissolution should not affect the total percentage recovery of BmimCl.

4.3 Determining rinsing stage durations

4.3.1 Experimental method

Published literature on the production of ACCs report long total rinsing times for the recovery of BmimCl. Yousefi *et al* (2011) used a total rinsing time of twelve hours and Duchemin *et al* (2009a) rinsed their samples for approximately forty-eight hours. If a concentration equilibrium forms during a rinsing stage, further diffusion of BmimCl to the rinsing water will not occur even if long rinsing durations are allowed. Concentration profiles of BmimCl in the rinsing water over time for each rinsing stage were generated to determine if a concentration equilibrium was achieved. The concentration profiles were used to determine an appropriate duration for each rinsing stage.

Each rinsing stage was investigated separately for concentration equilibriums. Three replicates for every rinsing stage investigated were performed. Samples for rinsing were dissolved and regenerated as explained in Section 3.1.2. Dissolution conditions were selected as 14g/g BmimCl concentration at 90 °C for 1.25 hours.

Samples of the rinsing liquid were drawn at selected time increments as rinsing progressed. It was suspected that the concentration profile of the first rinse would show a fast increase in BmimCl concentration and a sample was drawn every minute. For the stages following the first stage, samples were drawn every second minute.

BmimCl concentrations of the samples were determined by drying the liquid samples in small containers of which the dry weights were predetermined. The samples were dried at 105 °C for at least 12 h (constant mass reached).

Three replicates for each of the three dissolution conditions were performed. Whether a significant increase in BmimCl recovery was taking place was analysed as discussed in Section 3.2.5. An exponential curve (Equation 3) was fitted to the data using least squares regression by the variation of two parameters using Microsoft Excel Solver.

From the generated BmimCl concentration profiles, suitable rinsing stage times could be selected. The aim was to select a rinsing stage time in which the BmimCl concentration will reach or come close to equilibrium. The concentration profile for the first stage was evaluated and stage duration for the first rinsing stage was selected. This duration for the first rinsing stage was then used for the preparation of samples to evaluate the second rinsing stage concentration profile with. The selected duration for the second rinsing stage, along with that of the first rinsing stage was then used to prepare samples to evaluate the concentration profile for the third rinsing stage. Again, the selected durations of rinsing stages one, two and three were used to prepare samples for the concentration profile evaluation of rinsing stage four.

4.3.2 Results and discussion

The BmimCl concentration profile of the first rinsing stage (Figure 4-3) showed a quick increase in BmimCl within the first and second minute. After the second minute of rinsing, the increase in BmimCl started to slow down. The increase in BmimCl concentration between 5 min and 12 min for the first rinsing stage was statistically insignificant.

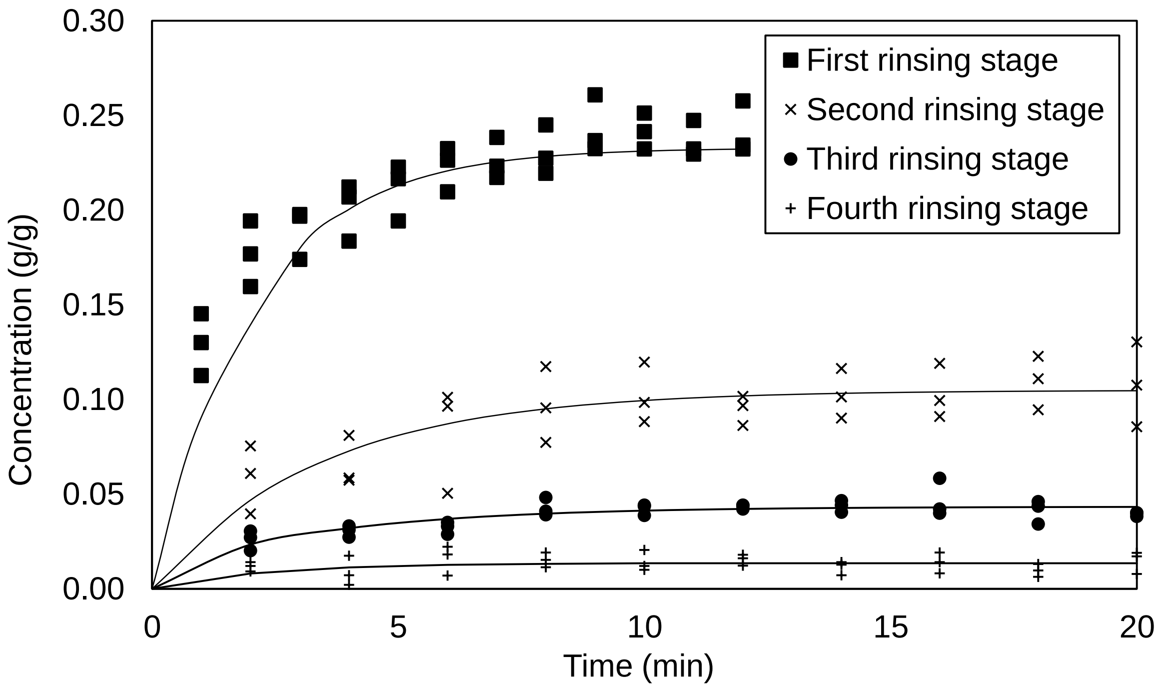


Figure 4-3: The BmimCl concentration profile over time for the duration of the first rinsing stage.

The diffusion of BmimCl to the rinsing water during the first rinsing stage occurred faster than expected, considering the total rinsing times of 12 h and 48 h that was used in other published works (Duchemin *et al*, 2009a; Yousefi *et al,* 2011). For practical reasons, 10 min was selected as sufficient time for the first rinsing stage. A BmimCl concentration of 0.242 g/g (+/- 0.008 g/g) was reached within 10 minutes (Figure 4-3). This concentration represented more than 65 % recovery that could be achieved by a single rinsing stage, using only 2.4 ml rinsing water for each gram of BmimCl used.

No statistically significant increase in concentration occurred between 2 min and 20 min for the second rinsing stage and between 6 min to 20 min for the third rinsing stage (Figure 4-3). For practical reasons 10 minutes was selected as adequate time for each of the two following rinsing stages. In ten minutes an average BmimCl concentrations of 0.102 g/g (+/- 0.017 g/g) for the second stage and 0.042 g/g (+/- 0.003 g/g) for the third stage were achieved.

The exponential trend that could be fitted to the BmimCl concentration profile of the first, second and third rinsing stage, could not be observed for the fourth rinsing stage (Figure 4-3). Because 0.1 ml samples were drawn for the determination of each concentration value, the BmimCl mass measurements per value were under 0.0025 g. The balance used to weigh the samples reported up to four decimals of a gram. It is likely that the error in the third and fourth decimal of the balance was too big to determine the small BmimCl concentration accurately enough. It was however apparent that the concentration values for the fourth stage were below 0.025 g/g. Consistent with the previous stages, it was decided that the fourth stage should be of 10 min duration too.

Four rinsing stages of 10 min each should provide sufficient BmimCl recovery from the treated cellulose films. It is possible that even shorter rinsing times than these selected might provide sufficient recovery. This rinsing method was used in all the following experiments.

4.4 Conclusions

An increase in rinsing water temperature from 25 °C to 80 °C lead to approximately 30 % better recovery of BmimCl during the first rinsing stage. For rinsing stages following the first rinsing stage, no improvement in BmimCl recovery was observed when warm rinsing water was used. It was unclear whether rinsing water with a higher temperature improved the overall recovery after four rinsing stages.

The removal of BmimCl from the regenerated cellulose matrix was slower if the matrix was highly dissolved when compared to removal of BmimCl from less dissolved samples. Although this slower recovery rate was observed during the first rinsing stage, the BmimCl recovery of the highly dissolved sample was higher than those of the lesser dissolved samples in later stages. The total recovery after four rinsing stages was 97.60 % (+/- 2.66 %) independent of the degree of dissolution that the cellulose samples underwent.

By determining the concentration profile for the duration of each rinsing stage, it was found that diffusion occurred faster than expected and that the recovery of BmimCl could be achieved in a shorter time than the rinsing times used in published literature. More than 65 % of the BmimCl used could be recovered during the first stage of rinsing in 10 min when only 2.4 ml rinsing water per gram of BmimCl was used. Four rinsing stages of 10 min duration each should provide sufficient BmimCl recovery values.

5 INVESTIGATION B: DISSOLUTION CONDITIONS

5.1 Experimental method

The three dissolution condition variables, as defined in Section 3.1.3, were investigated in one complete factorial experiment to establish the effect of different dissolution conditions on the finished product. Three values for each of the independent dissolution conditions were used as selected in Section 3.1.3.

Twenty-seven dissolution conditions were investigated in total. The sequence in which the treatments were performed was not randomised with respect to dissolution temperature. First all treatments that required a dissolution temperature of 80 °C were performed, thereafter treatments requiring 90 °C were performed and then treatments requiring 100 °C were performed. This was done to limit the amount of times that the oven had to be set to a different temperature and to reduce possible variation for each of the selected temperatures. For each dissolution temperature the sequence of treatments was randomised with respect to the 1-Butyl-3-methylimidazolium chloride concentration and dissolution time.

Dissolution and regeneration of the samples were performed as described in Section 3.1.2 and the rinsing method for BmimCl recover was determined from the results of Investigation A, Section 4.3. BmimCl recovery for each treatment was quantified by analysing the liquid recovered after rinsing as described in Section 3.1.2.

Three replicates of each of the treatments were performed and the samples were analysed (Section 3.2) by comparing their visual appearance, including images from SEM, their tensile strengths and their crystallinity as determined from XRD.

5.2 Results and discussion

5.2.1 Visual analysis

Undissolved fibres was observed for very few of the selected dissolution conditions. Only samples treated at 80 °C using any dissolution time and 9 g/g BmimCl or 0.5 h using 14 g/g BmimCl showed some visible remnants of the original fibres.

The transparency of the films improved as dissolution proceeded at these low dissolution conditions. Figure 5-1 shows this improvement in transparency. For the two films on the left (Figure 5-1a & 5-1b), fibrous structures could be observed, but the film on the right (c) had a completely uniform, highly transparent appearance. This change is also shown, on a different background, between the least and most transparent films produced (Figure 5-1d)

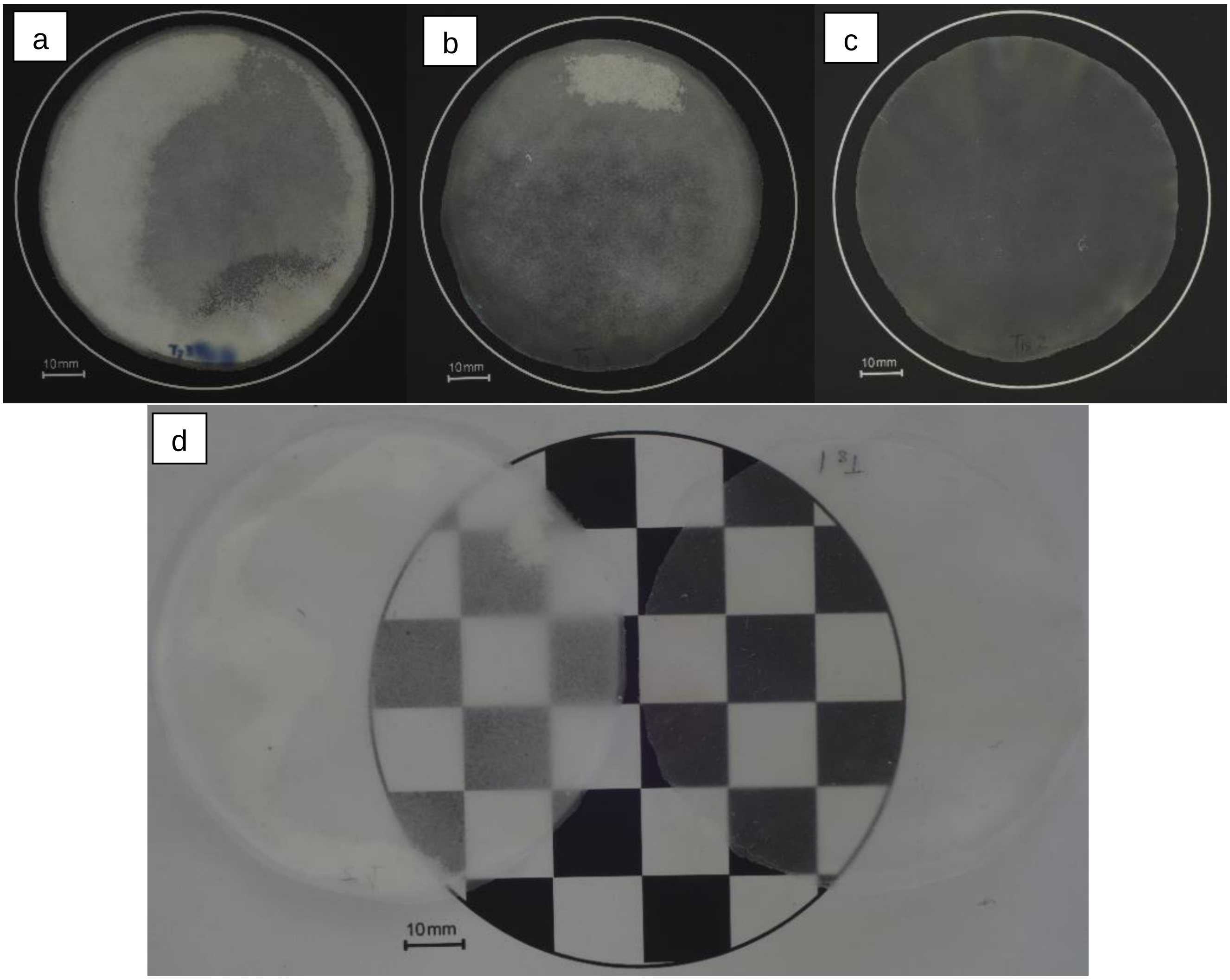


Figure 5-1: The improvement in transparency as the cellulose fibres are dissolved.

Defects, visible as opaque areas, could be observed in most of the films. These defects reduced the transparency of the films produced at high dissolution conditions. These defects and holes were present for all samples treated at 100 °C, using 14 g/g and 19 g/g BmimCl, all samples treated at 80 °C or 90 °C using 19 g/g BmimCl and samples treated at 90 °C for 2 h using 14 g/g BmimCl. It is possible that at high dissolution, the polymer chains are reduced to oligomers which interfere with polymer chain orientation and result in defects within the film structure.

Defects resembling flow patterns could also be observed in most samples that were prepared using 19 g/g BmimCl and some that were prepared using 14 g/g BmimCl (Figure 5-2). It is possible that flow channels could have formed when considering the large volume of BmimCl that needed to escape from the cellulose matrix. These theoretical channels would then leave voids in the cellulose structure after removal of the BmimCl, leading to a weakened structure.

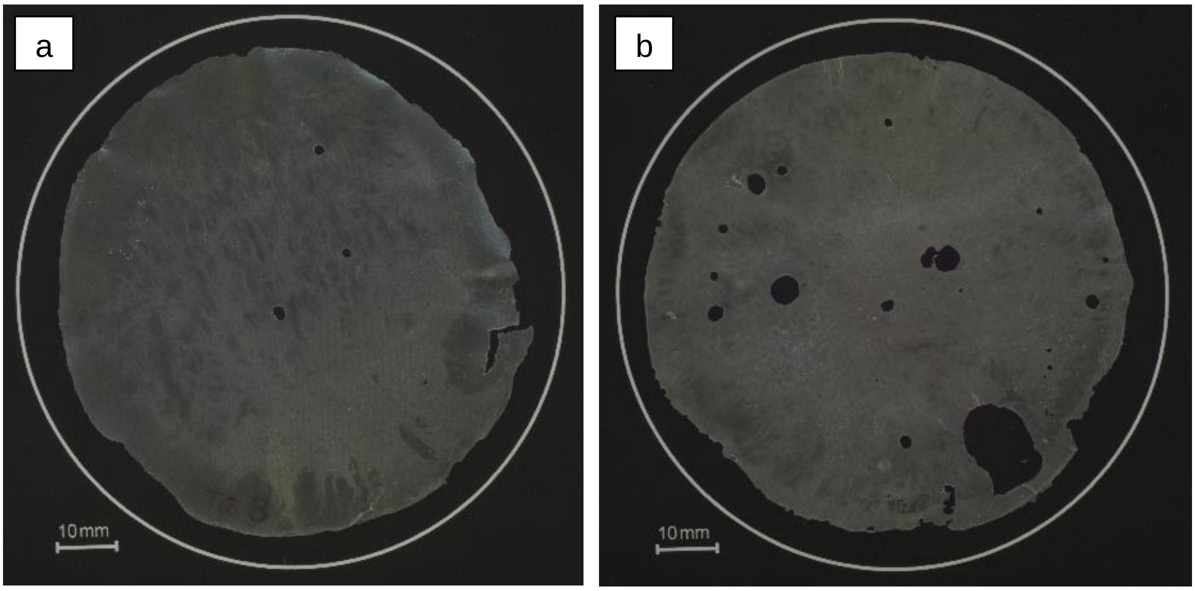


Figure 5-2: Reduced transparency and hole formation resulting from too high dissolution conditions.

Some of the samples had a film fracture through the middle after drying which was thought to be due to shrinking within the sample (Figure 5-3a). Shrinking of the films occurred during the regeneration and rinsing step and to a large extend during drying. In Figures 5-1, 5-2 & 5-3 the white outlined circle shows the original size of the 90 mm diameter film that was used as starting material. No measures for preventing shrinking during regeneration and rinsing was put in place, but the samples were dried in a press to prevent further shrinkage during drying. Inhibiting the shrinking process during drying, might have resulted in excessive internal stress and the fracture of the film under these stresses.

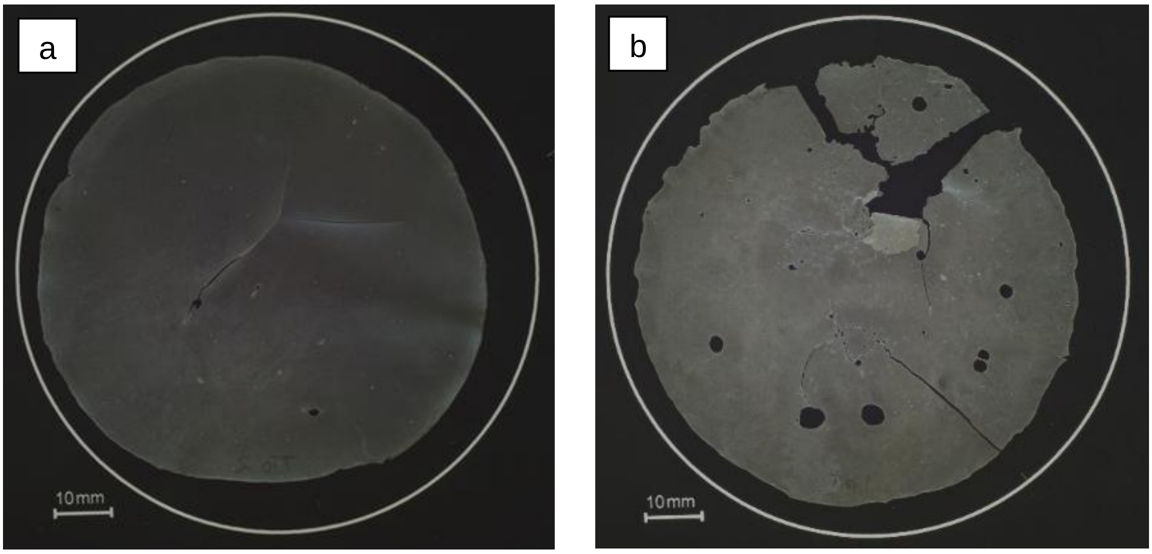


Figure 5-3: (a) Film fracture that formed for some of the films during drying and (b) the complete mechanical failure due to high dissolution conditions

All dissolution conditions at 100 °C using 19 g/g BmimCl and those at 90 °C for 2 h using 19 g/g BmimCl resulted in complete embrittlement of the material (Figure 5-3b). During rinsing material disintegrated from the films treated at these high dissolution conditions and had to be removed by filtration.

From the visual analysis it was apparent that when 19 g/g BmimCl was used 0.5 h was a too long dissolution time, independent of the temperature. When dissolution was performed using 14 g/g, excessive dissolution was observed for 0.5 h dissolution time at 100 °C and 2 h dissolution time 90 °C.

5.2.2 Tensile testing

The untreated dissolving pulp sheet showed very weak tensile properties (Figure 5-4). The sulphite pulping used to produce the high cellulose purity pulp likely resulted in weak fibres and weak fibre bonding properties of the pulp. Some of the tensile dissolution treatments resulted produced materials with tensile strengths more than 30 times stronger than that of the untreated cellulose sheet. Some degree of clamp slip was observed for most of the tested samples.

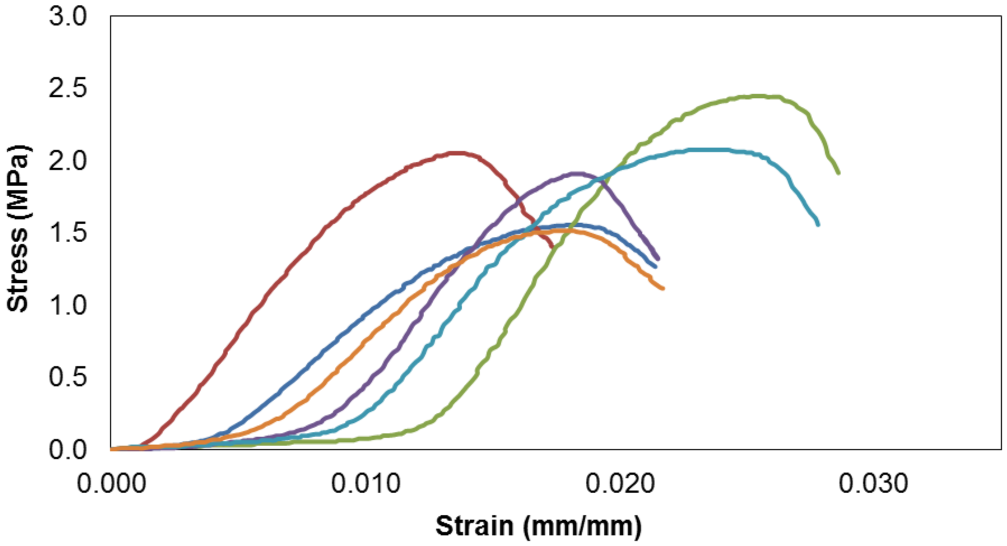


Figure 5-4: Tensile behaviour of the dissolving pulp film used as starting material.

The ultimate tensile strengths for each one of the three parameters investigated was plotted independent of the other two parameters in Figure 5-5. The BmimCl concentration had a significant effect on the ultimate tensile strength of the films (Figure 5-5). An increase in the BmimCl concentration used had a weakening effect on the tensile properties of the film. The weakening of the film at higher BmimCl concentrations was probably due to a higher degree of differential shrinkage and subsequent delamination through the width of the film Duchemin et al (2009b).

For samples treated with 9 g/g and 19 g/g BmimCl, at very low or very high dissolution conditions, the reaction temperature, the reaction time and the interaction between these had a significant effect on the ultimate tensile strength. It appears that an optimal tensile strength is achieved as the dissolution process progresses. The partially dissolved films at very low dissolution resulted in weaker tensile strengths and the films prepared at very high dissolution conditions started to disintegrate and lose mechanical integrity. No significant difference for different dissolution times and temperatures for samples that were prepared with 14 g/g BmimCl was observed. All of the samples dissolved using intermediate dissolution conditions probably underwent complete dissolution, without the onset of degradation, resulting in the similarity of the end products.

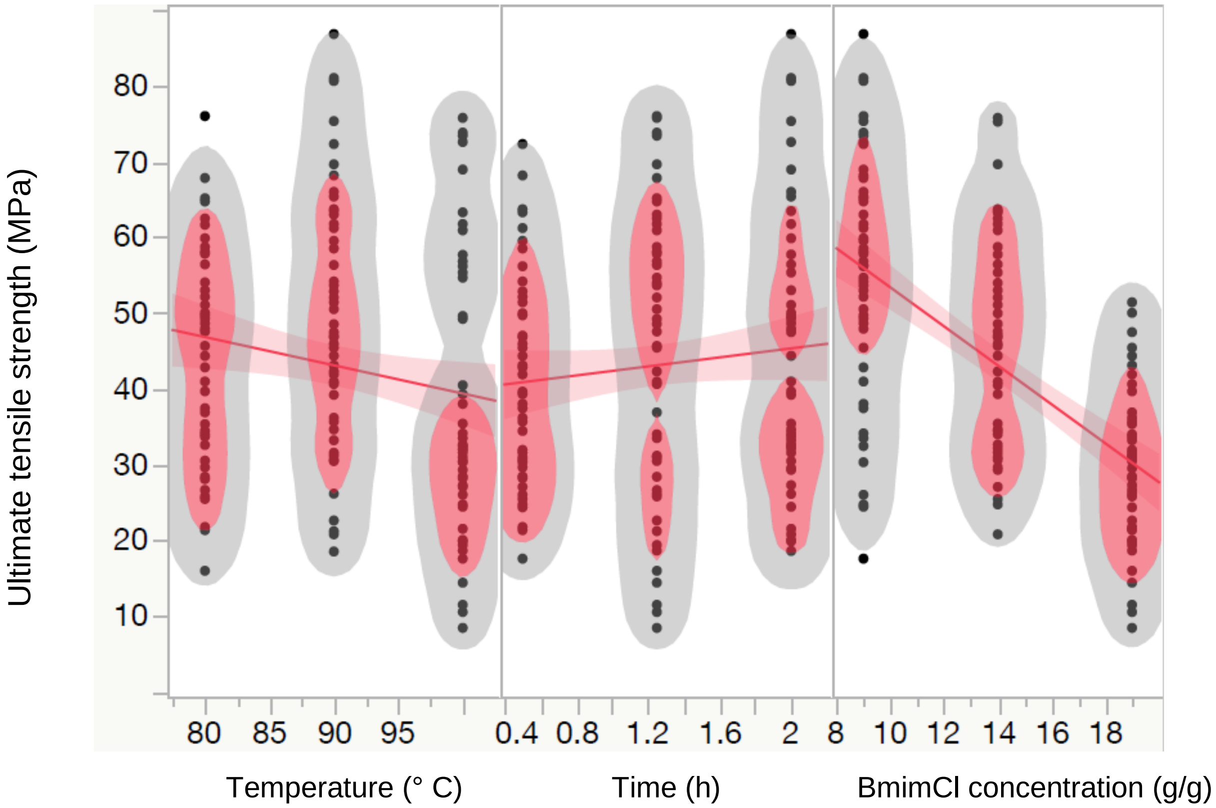


Figure 5-5: Ultimate tensile strength as affected by the three different dissolution parameters.

The tensile strength of the produced films were lower than some of those reported for ACCs produced with BmimCl (Duchemin *et al*, 2009a; Yousefi *et al,* 2011) or LiCl/DMAc (Nishino & Arimoto, 2007). The range of tensile strengths was comparable films produced using BmimCl to combine cellulose and rice husk (Zhao et al , 2009), films produced by dissolving filter paper using BmimCl (Duchemin *et al*, 2009a) and films produced.by dissolving MCC in LiCl/DMAc (Duchemin et al, 2009b).

A large amount of variance in the tensile properties for all the treatments was observed (Figures 5-6, 5-7 & 5-8). The preparation method appears to have resulted in non-uniform films. This variation was probably induced by the BmimCl being dispersed uneven in or removal uneven from the cellulose film, the observed defects or internal stresses resulting from the drying process. As mentioned before, if a diffusion gradient of coagulant from the surface to the interior of the material form during regeneration, delamination and void formation in the material can occur (Huber *et al,* 2012)

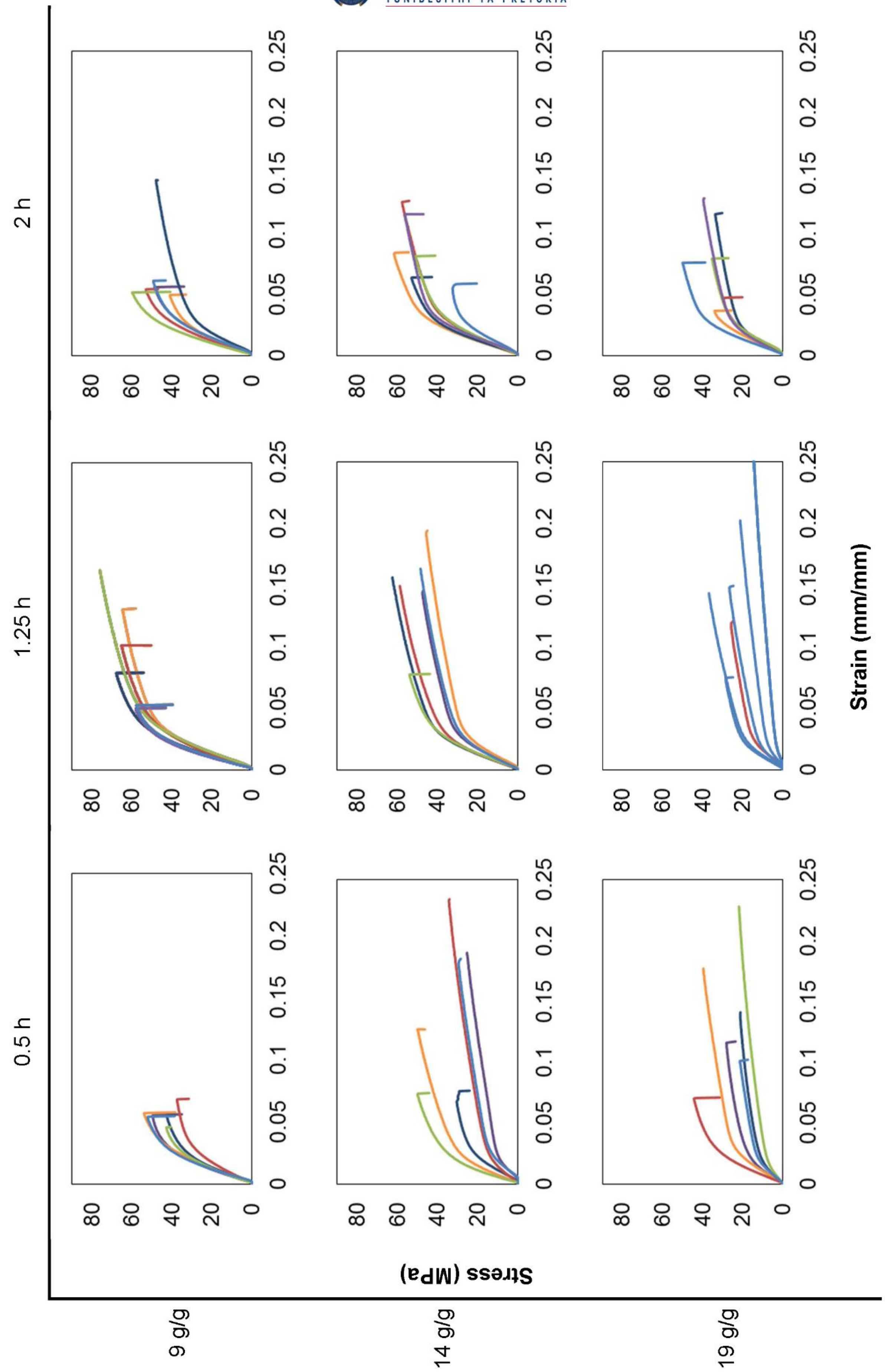


Figure 5-6: Tensile results for the samples that were dissolved at 80 °C. Each row represents the concentration of BmimCl that was used and each column represents the dissolution time of the treatments.

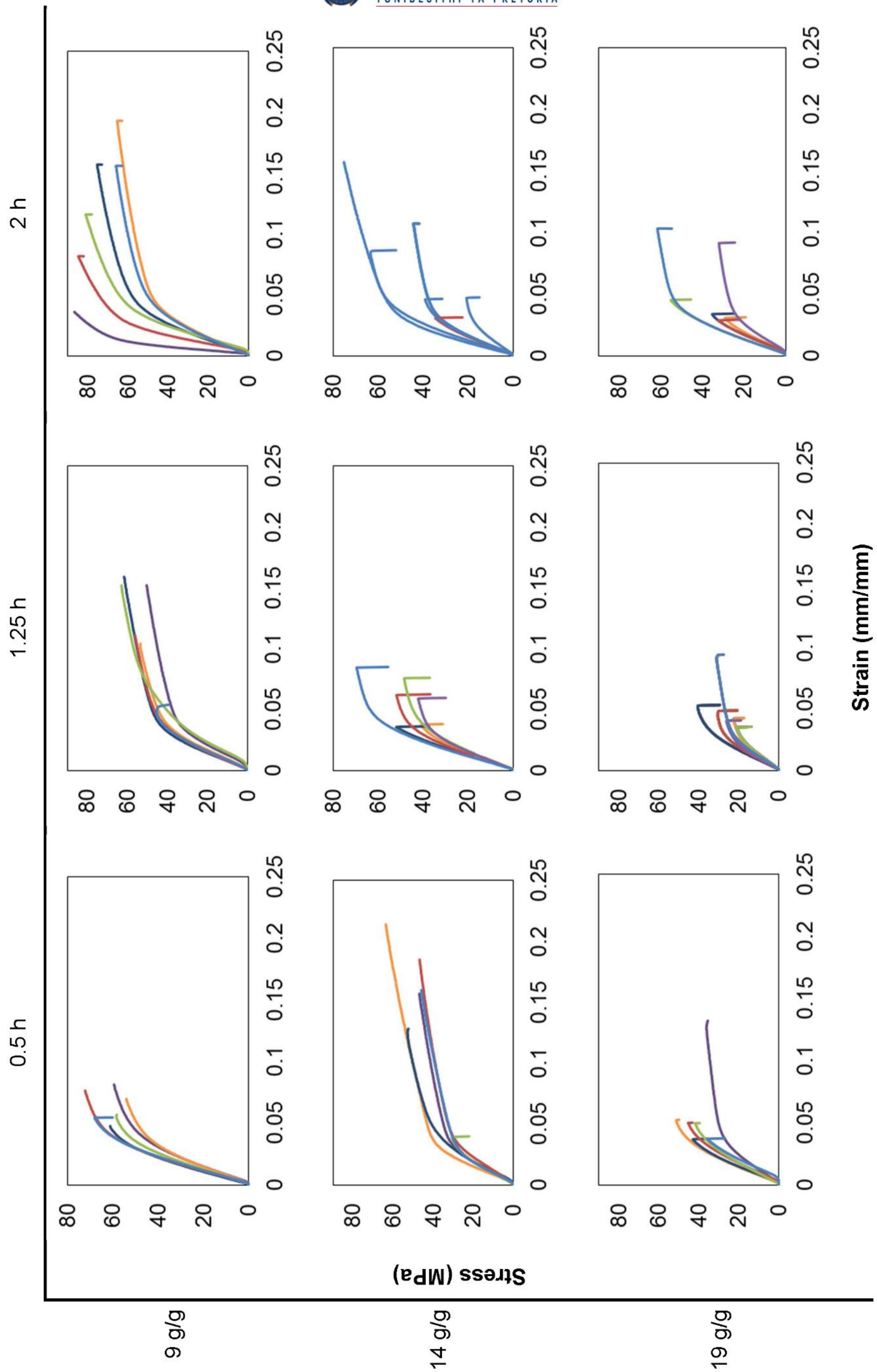


Figure 5-7: Tensile results for the samples that were dissolved at 90 °C. Each row represents the concentration of BmimCl that was used and each column represents the dissolution time of the treatments.

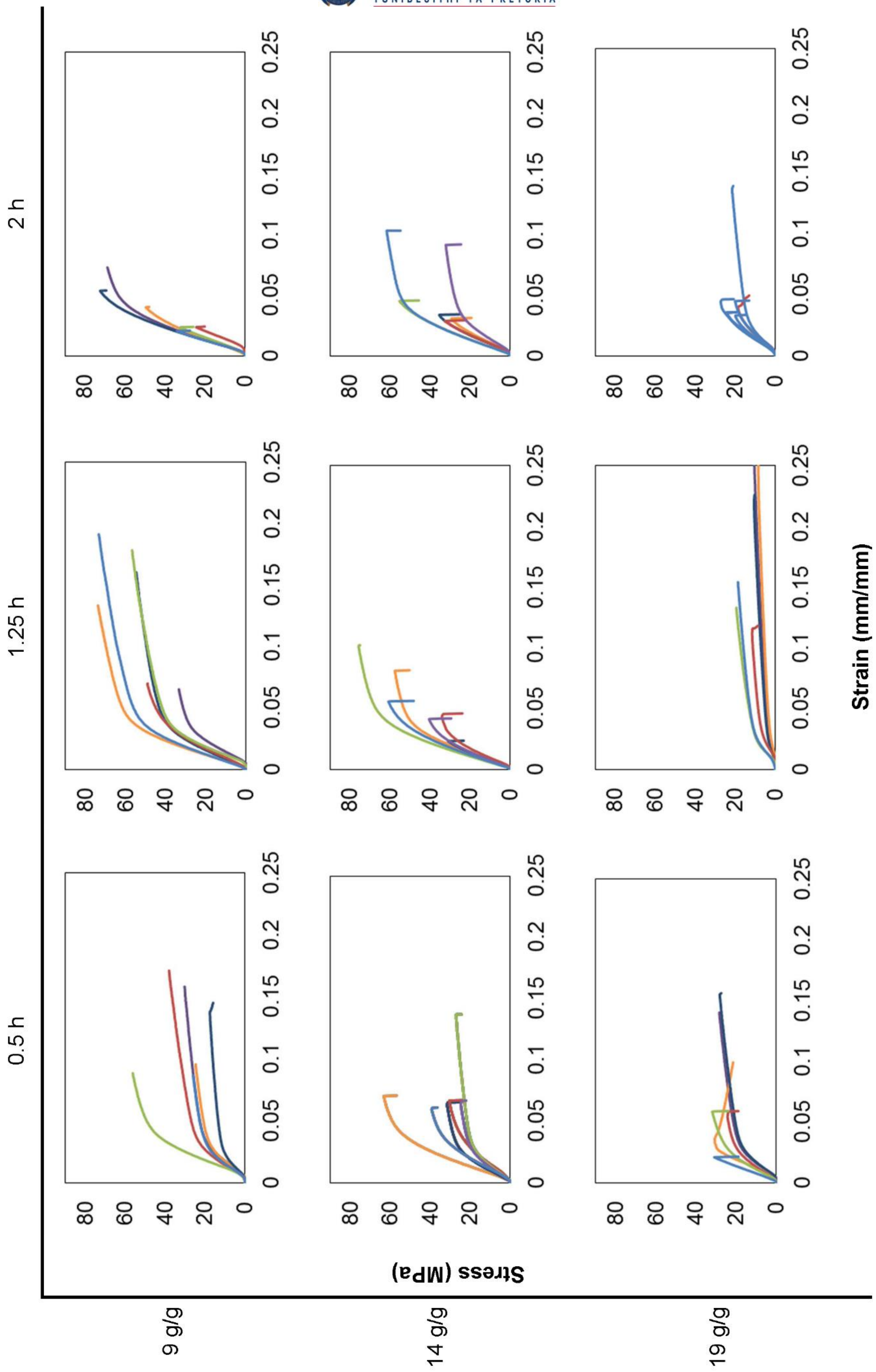


Figure 5-8: Tensile results for the samples that were dissolved at 100 °C. Each row represents the concentration of BmimCl that was used and each column represents the dissolution time of the treatments

5.2.3 BmimCl recovery

A total average BmimCl recovery of 95.8 % (+/- 1.5 %) was achieved when all the dissolution treatments are considered. The percentage BmimCl recovery for different dissolution conditions did not vary significantly. This observation is consistent with the results of Section 4.2. When considering that the percentage recovery is expressed on the basis of BmimCl originally used, it is apparent that more BmimCl was lost when a higher BmimCl concentration was used (Figure 5-9). The mass of BmimCl lost for each gram of cellulose treated was significantly more when 19 g/g BmimCl was used in comparison to when 9 g/g or 14 g/g was used.

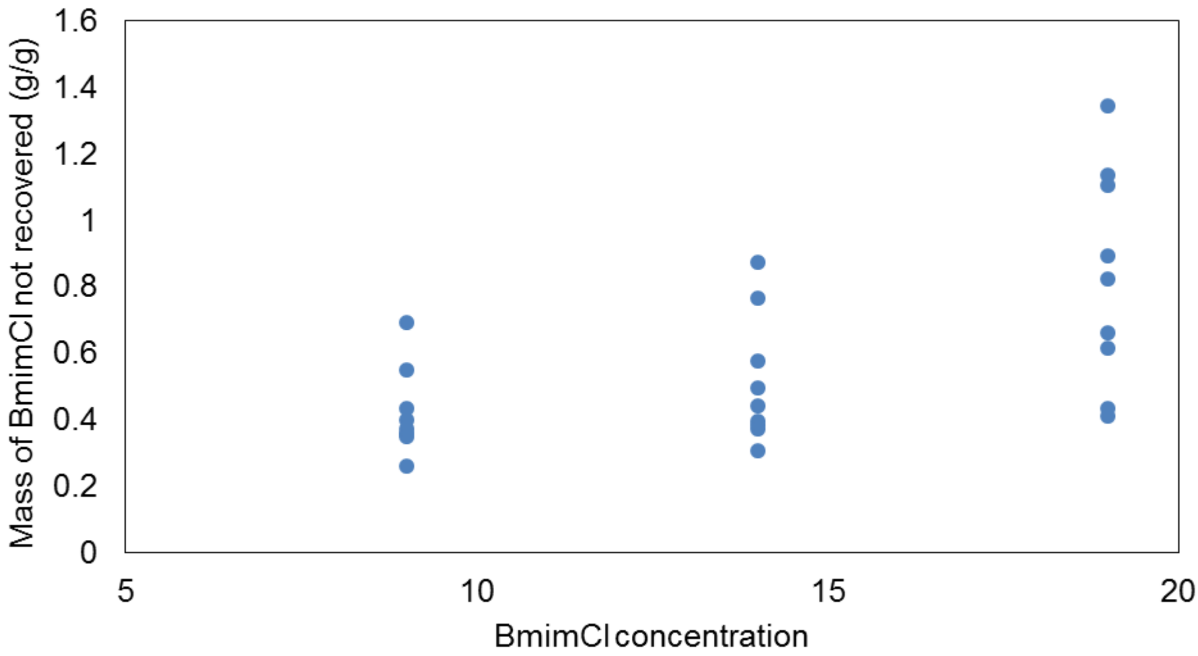


Figure 5-9: The mass of BmimCl that was not recovered for dissolution treatments using different BmimCl concentrations. The mass lost is expressed as gram of BmimCl not recovered per gram of cellulose treated.

5.2.4 SEM

The SEM images in Figure 5-10 shows the fibres of the dissolving pulp and how bonding of the fibres and disintegration to microfibrils occurred as dissolution progressed. The two phase nature of the partially dissolved materials was apparent, with remnants of the native fibre structure being bonded in by a matrix of regenerated cellulose.

After dissolution of the fibres for 1.25 h at 80 °C using 14 g/g BmimCl, no fibrous structures could be observed with SEM. The tensile testing surface showed a blunt fracture for the sample treated under these conditions (Figure 5-11a). Spherical agglomerates could be observed on the surface of many of the samples (Figure 5-11b). These spherical shape resembled those of the amorphous cellulose particles observed by Ioelovich (2013) shown in Figure 2-4. It was suspected that complete dissolution had occurred in 1.25 h at 80 °C using 14 g/g BmimCl, because of this similarity in structure to amorphous cellulose and the absence of fibrous structures.

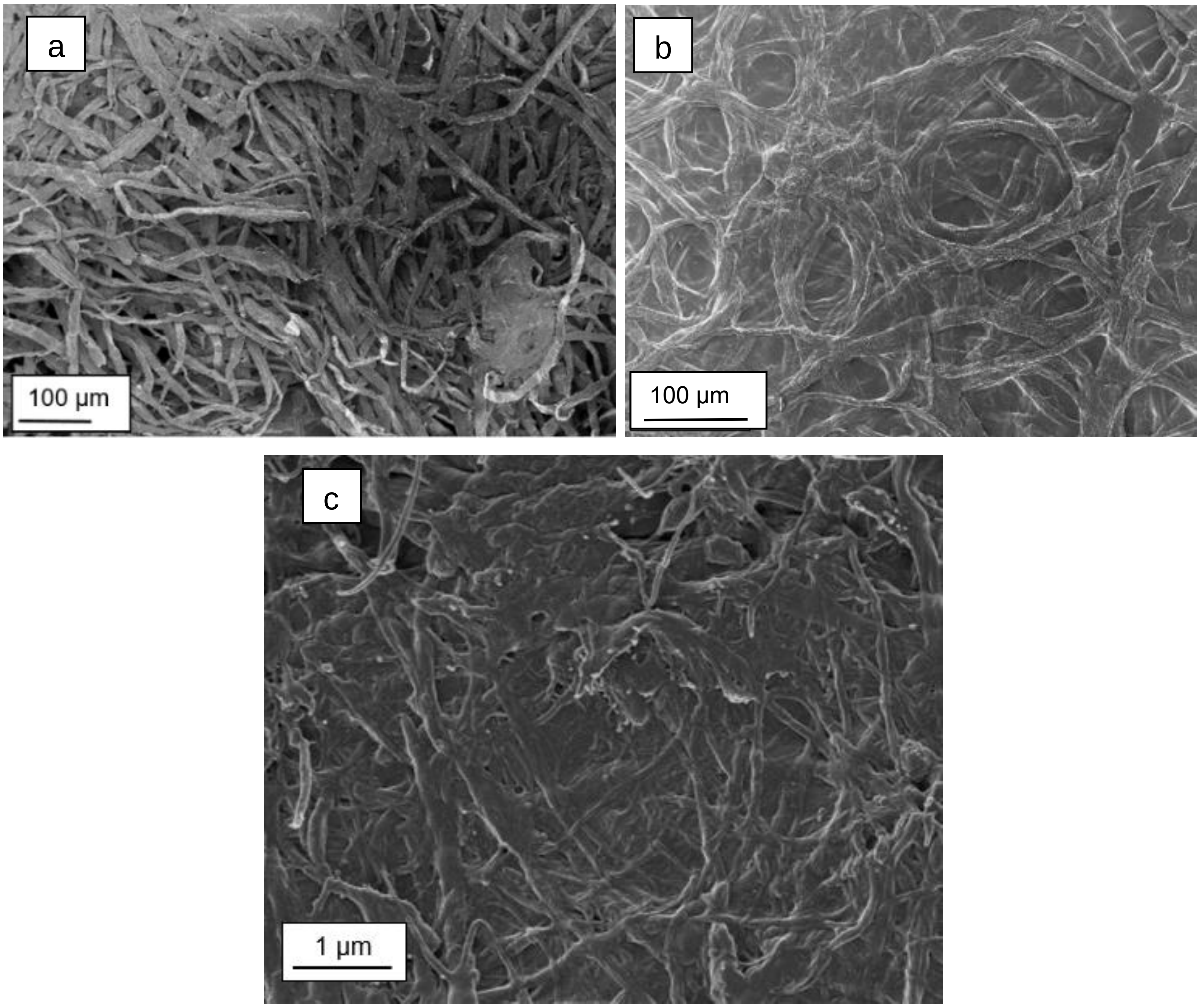


Figure 5-10: SEM images of (a) the fibres present in the starting material, (b) these fibres bonded by dissolved and regenerated fibre fractions and (c) the microfibrils bonded by regenerated cellulose.

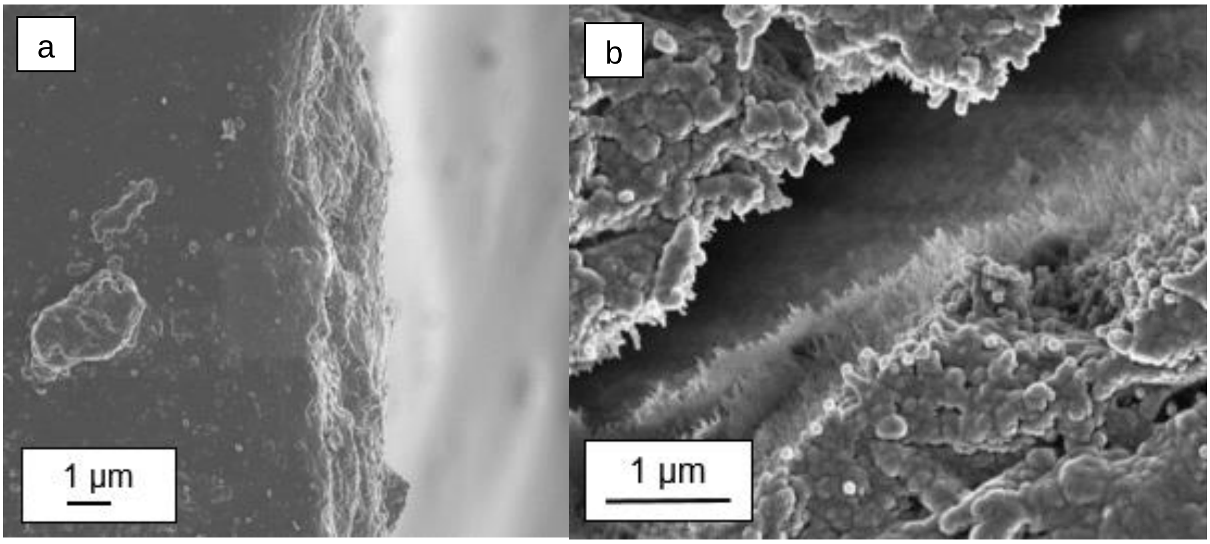


Figure 5-11: (a) The fracture surface after tensile testing of a sample, (b) the surface texture of a sample that was dried without pressing.

5.2.5 XRD analysis

The XRD spectra showed a decrease in crystallinity as dissolution of the cellulose progressed (Figures 5-12, 5-13 & 5-14). The peaks of the three lowest dissolution conditions at 80 °C (9 g/g and 0.5 h, 9 g/g and 1.25 h and 14 g/g and 0.5 h) strongly resembled that of cellulose I. This motivated that the main contributor to the crystallinity of these samples were cellulose I crystals that were not disintegrated during dissolution. Because of the remnant crystals from the native cellulose structure present, these three dissolution treatments could correctly be classified as all-cellulose composites.

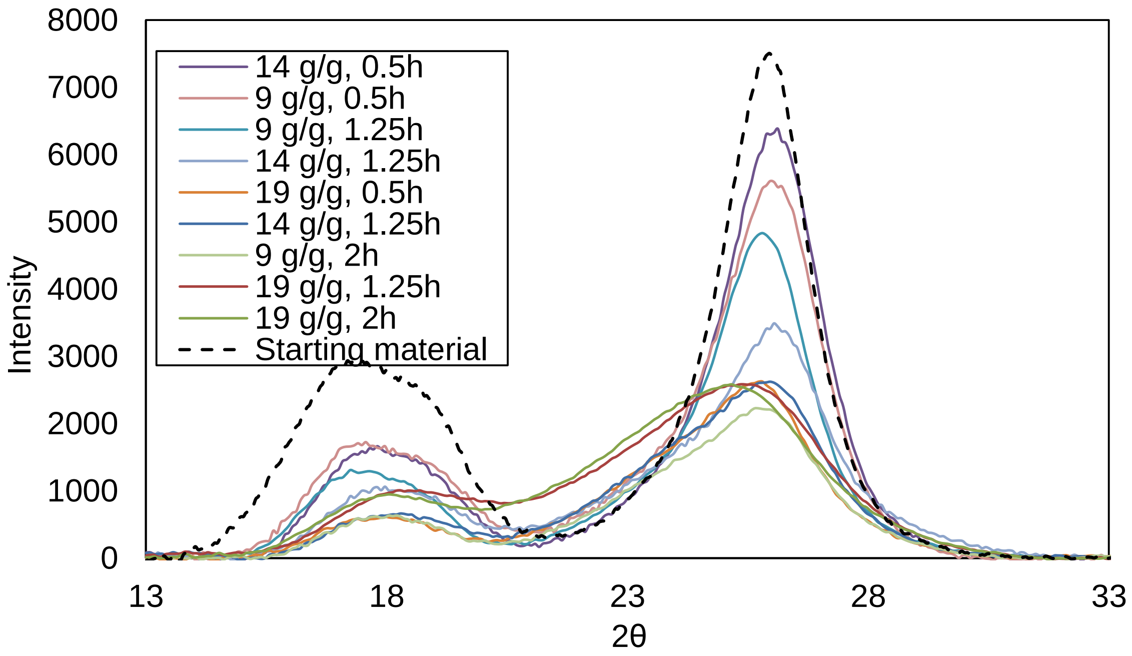


Figure 5-12:XRD spectra of samples dissolved at 80 °C.

Remnant cellulose I crystals could probably also have been present for higher dissolution conditions at 80 °C. The continued decrease in peak intensity as dissolution conditions increases shows a steady reduction in cellulose I crystallinity.

The regenerated cellulose also had a degree of crystallinity and it was expected that cellulose II would be observed for the regenerated phase. The XRD spectra of treated samples showed a move of the primary peak from 26.3° to 25°, which was originally interpreted as a move from the primary peak of cellulose I to that of cellulose II. But the absence of the prominent secondary peak, characteristic of cellulose II, at 14.1° motivated that the structure of the regenerated crystals was not cellulose II.

For all of the samples treated at 90 °C a significant reduction in crystallinity was observed (Figure 5-13) compared to the starting material. The move towards 25° was again observed, but the lowest dissolution condition (9 g/g and 0.5 h) appeared to have some remnants of cellulose I with a primary peak positon close to 26.3°.

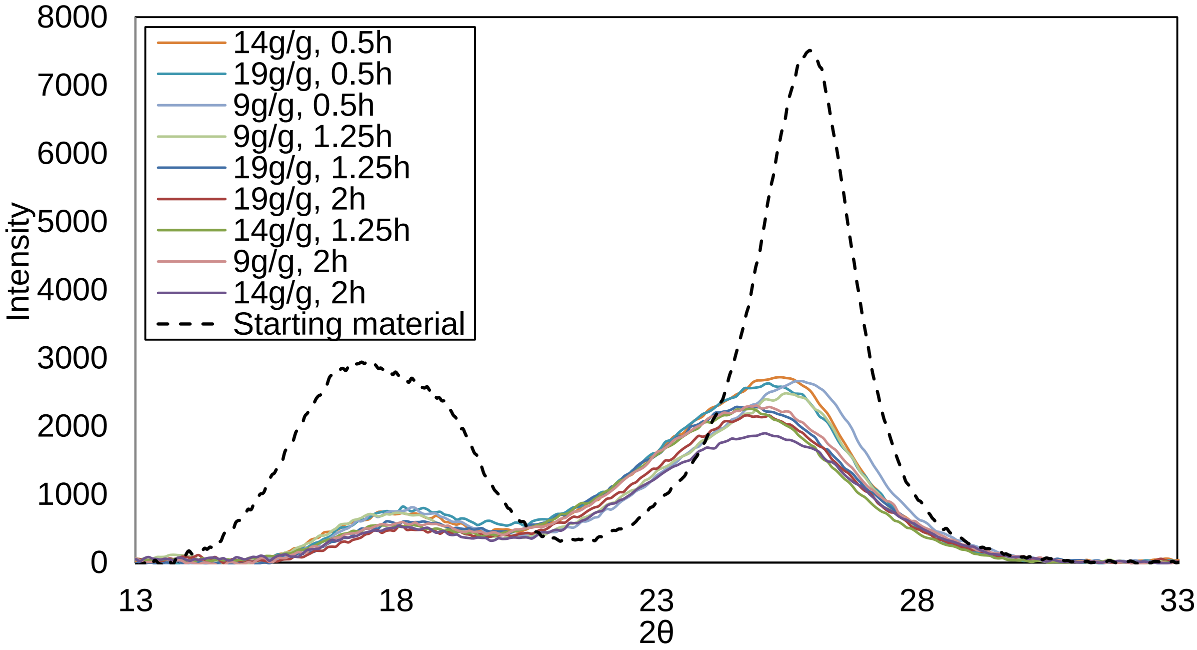


Figure 5-13: XRD spectra of samples dissolved at 90 °C.

The reduced crystallinity and move of the primary peak to 25° were also observed for samples treated at 100 °C (Figure 5-14). Many of the samples dissolved at 90 °C and most of the samples dissolved at 100 °C had similar tensile properties and XRD spectra. This similarity gave rise to the idea that complete cellulose dissolution occurs for dissolution conditions above 90 °C and 0.5 h for all BmimCl concentrations. The observed crystallinity is purely from the recrystallisation of the cellulose after complete dissolution. As previously motivated, the crystal structure of the regenerated cellulose was not that of cellulose II, but more likely a paracrystallite.

Results from an independent study contradicted the observation of the current study that crystallinity reduces with increasing dissolution. They observed that samples that were dissolved with BmimCl was more amorphous when shorter dissolution times and lower temperatures (90 °C) were used, compared to higher crystallinity at higher dissolution temperatures (120 °C) (Iguchi *et al*, 2013).

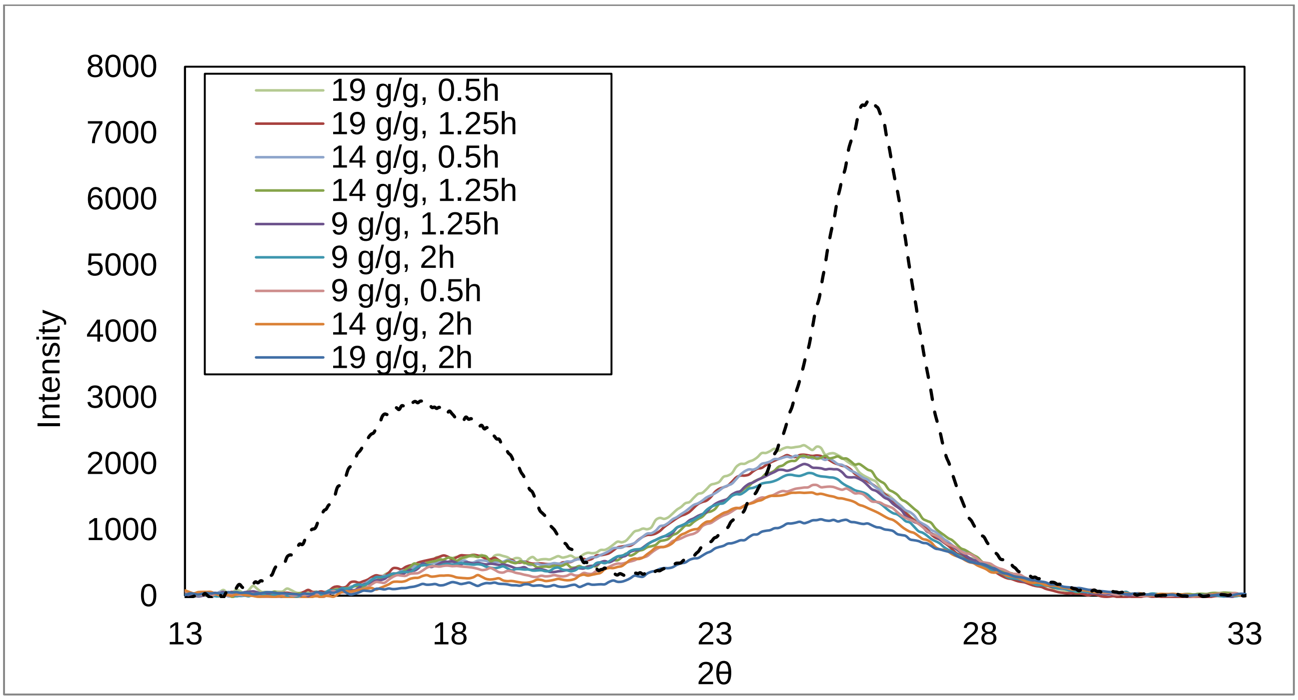


Figure 5-14: XRD spectra of samples dissolved at 100 °C.

The XRD spectra of these samples dissolved above 90 °C and 0.5 h showed strong amorphous characteristics, but the peak intensities were too high to have been purely amorphous. This increased XRD intensity suggesting that a paracrystallite phase, as described by Duchemin *et al* (2007) could be forming in the regenerated crystalline phase

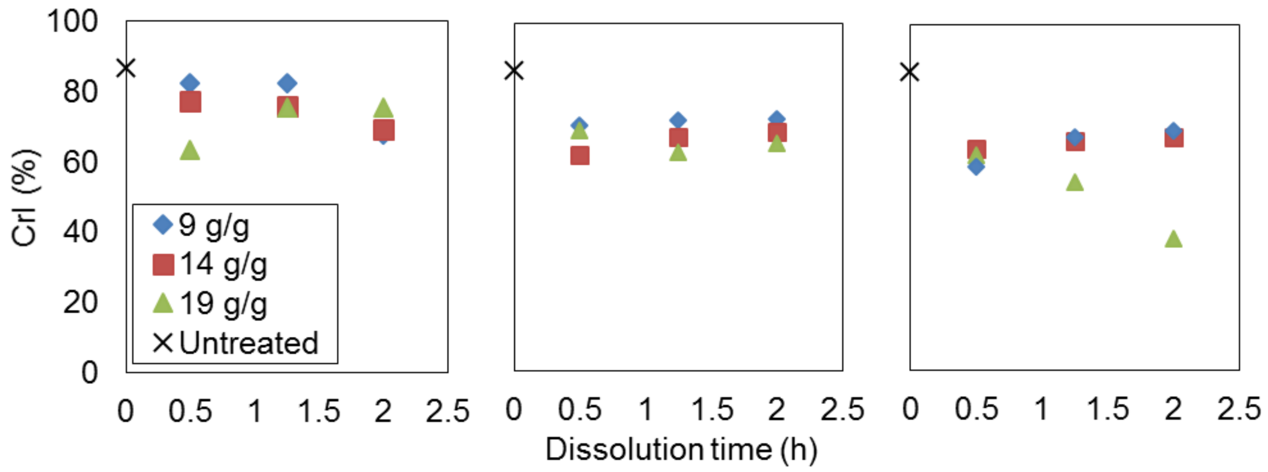
The lack of cellulose I peaks, motivates that complete dissolution could almost be achieved in 0.5 h if dissolution was performed at 90 °C and complete dissolution could be obtained in under 0.5 h at 100 °C. The samples produced by these conditions cannot be described as all-cellulose composites, because complete and not partial dissolution had occurred. Complete dissolution of the dissolving pulp was achieved in much shorter dissolution times than what was expected. It is recommended that dissolution times under 0.5 h be investigated if partial dissolution of dissolving pulp with BmimCl is desired.

The peak height method (Segal method) resulted in higher CrI values than those calculated by peak deconvolution for all but one of the samples (Table 5-1). The CrI for the treatment with the highest dissolution was determined to be 89 % when determined with the peak height method compared to 38 % when using peak deconvolution. Visual comparison of the XRD spectra of the starting material to that of the sample that underwent the highest dissolution, showed that the dissolution resulted in a significant reduction in crystallinity (Figure 5-14). It was apparent that a CrI of 89 % for the most dissolved sample was too high. This observation that the peak height method produces too high CrI values was consistent with the findings of Park et al (2010).

Table 5-1: CrI for selected samples to compare the results from the Peak height method to that of the Peak deconvolution method for CrI determination.

	Dissolution conditions						
Temperature (°C)	0	80	80	90	90	100	100
BmimCl concentration g/g	0	9	19	9	19	9	19
Time (hours)	0	0.5	2.0	0.5	2.0	0.5	2.0
	CrI (%)						
Peak height method	97	94	72	86	86	61	89
Peak deconvolution method	87	82	76	71	66	59	38

The reduction in crystallinity as the dissolution reaction progresses can be seen from the CrI, calculated using peak deconvolution (Figure 5-15). The starting material had a CrI of 86.6 % and the next three highest CrIs agrees with the three dissolution conditions for which remnants of the original fibre structures could be observed (Refer to Visual analysis). Nearly all the treatments performed at 90 °C and 100 °C had CrIs between 60 % and 72 %.



(a) (b) (c)

Figure 5-15: Cristallinity index (CrI) of samples dissolved at 80 °C (a), 90 °C (b) and 100 °C (c), relative to the dissolution time used.

This similarity in CrI supports the idea that complete dissolution occurred for most, if not all, of these samples and that the observed crystals formed in the regenerated phase. Two of the treatments at 100 °C, especially the highest dissolution condition (19 g/g & 2 h), had lower CrI. It is possible that these dissolution conditions were too high and started to degrade the cellulose polymer. For the highest dissolution condition, poor tensile properties was observed (Figure 5-8), the material was notably brittle and had many holes and a low transparency (Figure 5-3b).

5.3 Conclusions

The dissolution conditions that were selected for investigation were too high for the production of ACCs. Only a few of the lower conditions resulted in some of the native fibre structure remaining undissolved. The absence of fibrous structures on SEM, the observation of spherical particles similar to amorphous cellulose, the similarity in tensile strengths and the low crystallinity before removal of BmimCl motivated that complete dissolution occurred for the majority of dissolution conditions investigated. Because complete dissolution occurred, these samples cannot be described as ACCs

The few samples that could be classified as ACCs because of the apparent presence of remnant native fibre structures had weaker properties than the samples that underwent complete dissolution. Partial dissolution of dissolving wood pulp could thus result in the production of ACCs, but the undissolved fractions of the fibres did not offer any strengthening properties.

From visual analysis it was apparent that some of the dissolution conditions investigated were too high, probably resulting in disintegration of the cellulose polymer chains leading to weak, brittle films with holes. This excessive dissolution was observed for all the dissolution temperatures and times when 19 g/g BmimCl was used as well as for all dissoluion times at 100 °C when 14 g/g BmimCl was used and for 2 h at 90 °C when 14 g/g BmimCl was used.

The use of 19 g/g BmimCl had a statistically significant weakening effect on the produced films when compared to 9 g/g or 14 g/g BmimCl. This result agrees with the findings of the visual analysis of the films.

Most of the sheets showed a large amount of variation which was suspected to be due to uneven dispersion and removal of the BmimCl through the film, the defects discussed or internal stresses resulting from the drying process.

6 INVESTIGATION C: THE EFFECT OF RINSING AND REGENERATION CONDITIONS

In this investigation the processing steps to regenerate and rinse the BmimCl from the cellulose matrix were considered. In Investigation A the effect of temperature on the recovery of BmimCl during rinsing was investigated. Investigation C focuses on the effects of rinsing temperature and duration on the properties of the produced cellulose matrix. The effect of BmimCl remaining in the cellulose matrix on the film was also investigated, since this is a function of the rinsing conditions.

6.1 The effect of regeneration temperature and duration

Most studies involving the dissolution of cellulose with BmimCl and regeneration by the addition of water as coagulant appeared to have used water at ambient temperature (Zhao *et al*, 2009; Duchemin *et al*, 2009a; Yousefi *et al,* 2011). The aim of this experiment was to determine the effect of temperature during the regeneration and rinsing stages on the produced cellulose film.

6.1.1 Experimental design

Samples were dissolved as described in Section 3.1.2 using 9 g/g 1-Butyl-3-methylimidazolium chloride concentration at 90 °C for 0.5 h. The regeneration time and temperature were independent variables for this experiment. The amount of stages and duration of each stage was selected from the results of Investigation A, Section 4.3.4.

Regeneration and rinsing at 25 °C and 80 °C

After dissolution, the samples were regenerated at ambient temperature and rinsed using rinsing water at 25 °C. Four treatments at ambient temperature were performed allowing 0 min, 60 min, 120 min and 180 min for regeneration, respectively.

The same four regeneration times was also investigated for regeneration at 80 °C. After dissolution, the samples were regenerated in the headspace of a laboratory water bath at 80 °C and rinsed using water at 80 °C.

Analysis

Tensile testing and XRD analysis was performed as described in Section 3.2.

6.1.2 Results and discussion

Visual analysis

Films regenerated and rinsed at 25 °C were more transparent than films regenerated and rinsed at 80 °C (Figure 6-1). Samples that were not allowed regeneration time and underwent rinsing directly after dissolution were less transparent. These samples also shrunk more and were stiffer to the touch than when regeneration was allowed. These differences between the samples that were allowed time to regenerate and those that were immediately rinsed was more apparent for regeneration and rinsing at 80 °C.

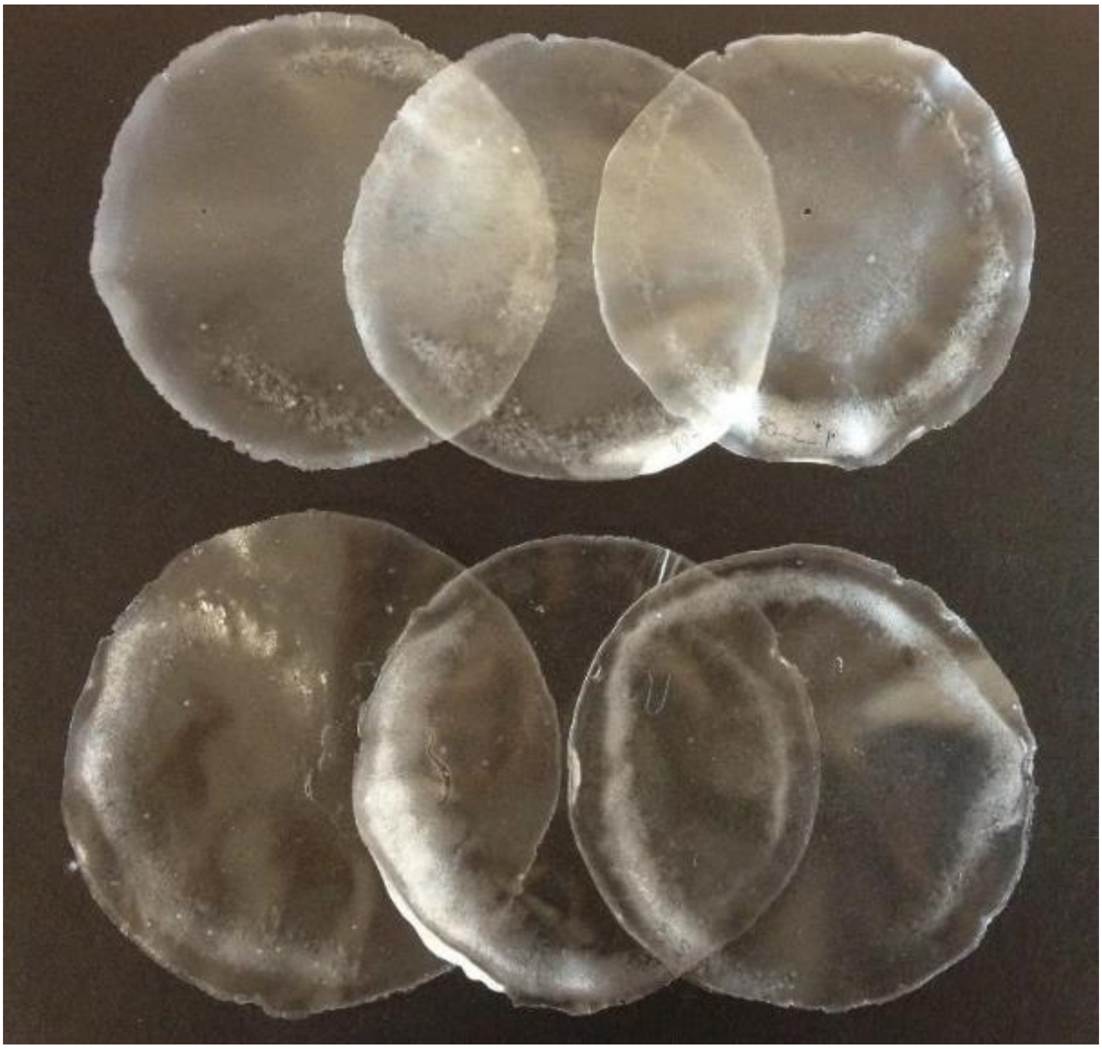


Figure 6-1: Improved transparency of the films when regeneration and rinsing is performed at 25 °C (bottom) compared to regeneration and rinsing at 80 °C (top).

Tensile testing

Regeneration and rinsing at 25 °C had a plasticising effect on the final product when compared to regeneration and rinsing at 80 °C (Figure 6-2). Although the time that was allowed for regeneration appeared to affect the ultimate tensile strength of the material, the correlation was unclear and further investigation is needed. It appears that improved tensile strengths were obtained when regeneration was allowed for 120 min when regenerating and rinsing at 25 °C and 60 min when regenerating and rinsing at 80 °C, respectively.

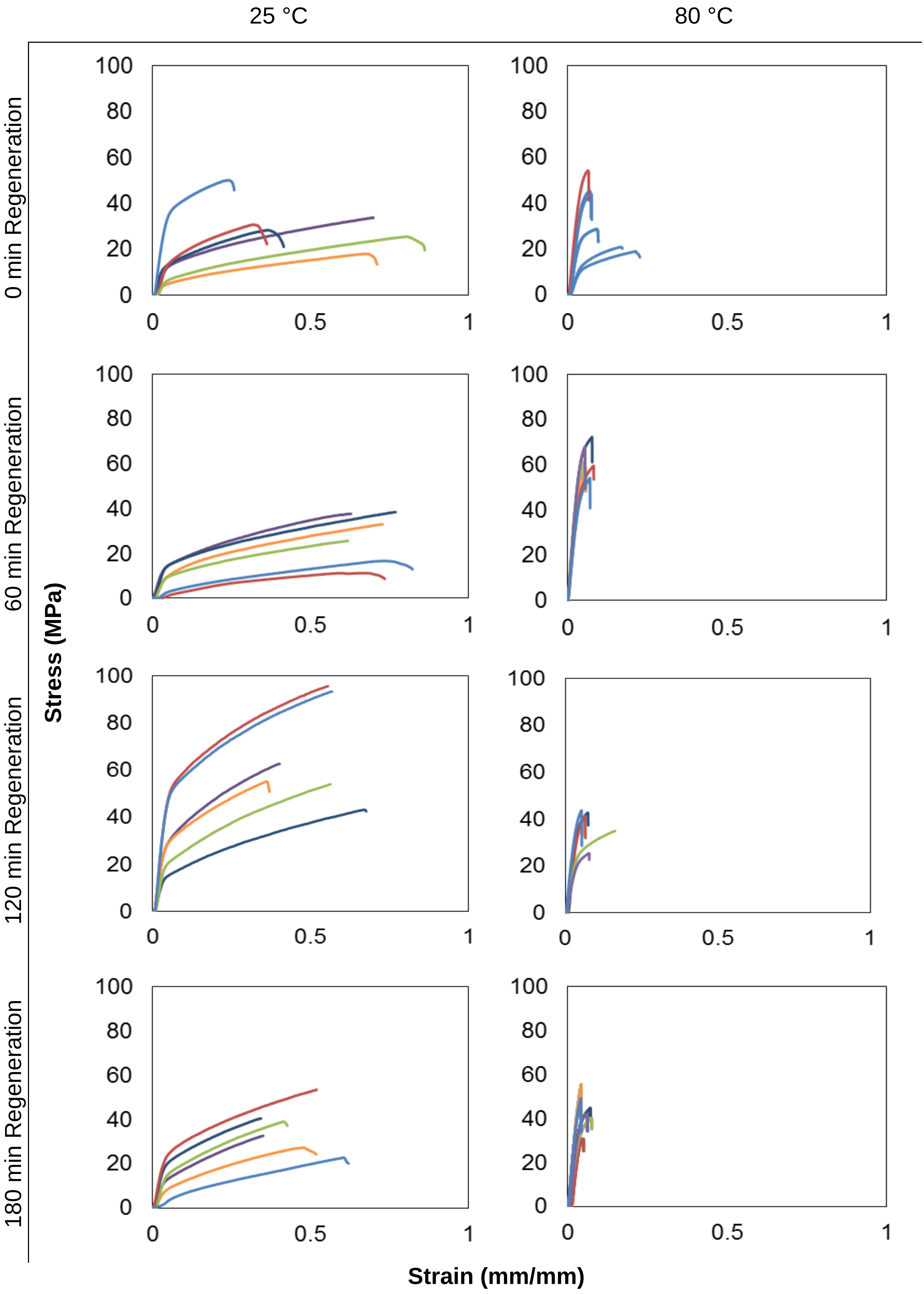
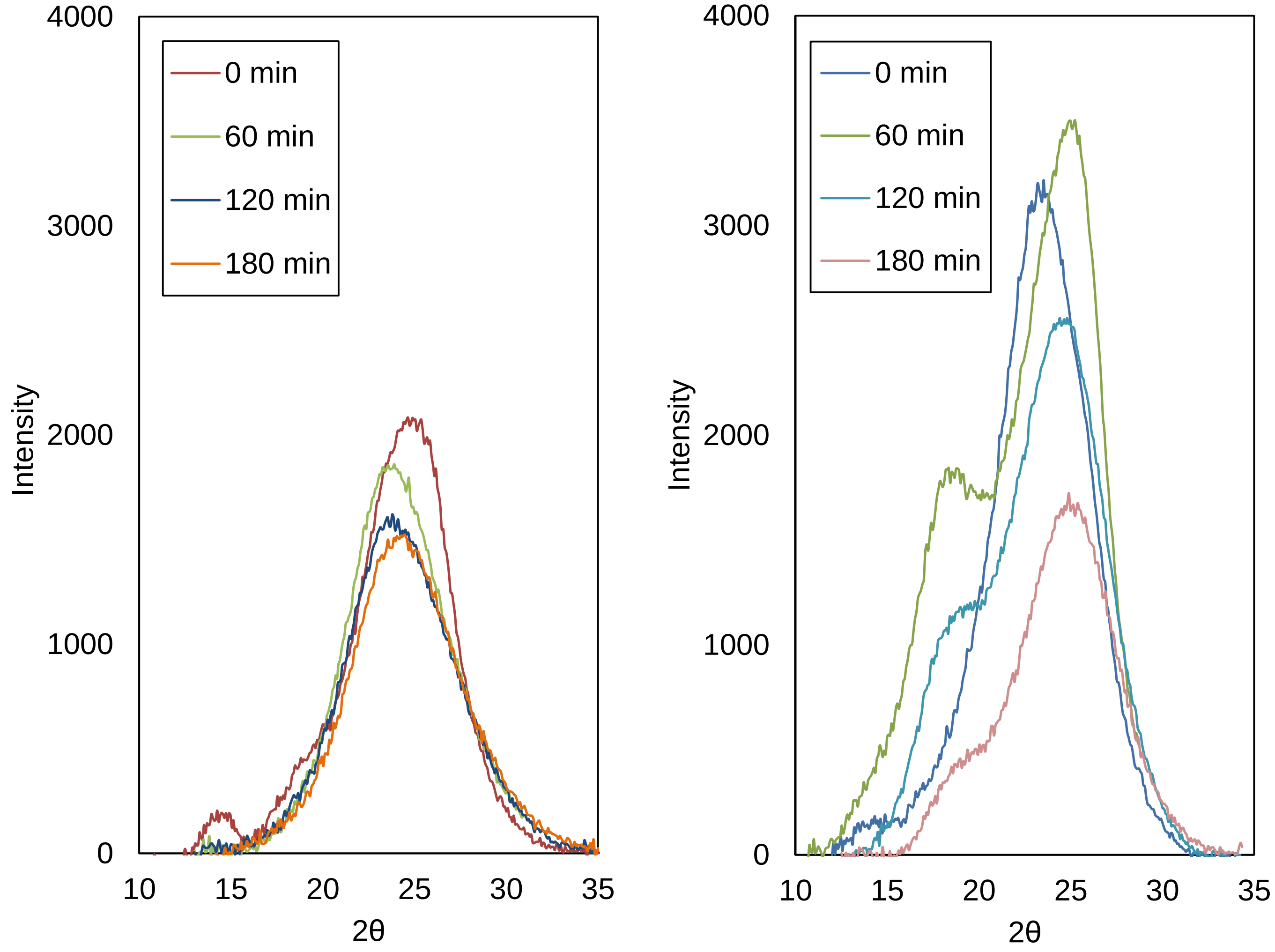


Figure 6-2: How tensile properties are affected by the regeneration conditions of cellulose from solution.

Duchemin et al (2009b) observed that slower regeneration (precipitation) conditions of cellulose from a LiCl/DMAc solution resulted in tensile strength improving by more than double compared to when fast regeneration was performed. In their study fast regeneration was achieved by immediate exposure to water after dissolution compared to the almost 100 h allowed before exposure to water for the slow regeneration route. The improvement in tensile strength with longer regeneration time might be more apparent in the study by Duchemin et al (2009b) due to the significantly longer regeneration time investigated compared to the current study. Or regeneration after dissolution with LiCl/DMAc might show different behaviour when compared to dissolution with BmimCl since the results in Figure 6-2 did not show constant improvement of the tensile strengths as longer regeneration was allowed.

XRD analysis

Regeneration and rinsing at 80 °C lead to increased crystallinity compared to 25 °C. The plasticising effect observed when regeneration and rinsing was performed at 25 °C instead of 80 °C (Figure 6-2) can be explained by the reduced crystallinity of the samples regenerated and rinsed at 25 °C. The lower temperature must have inhibited the formation of crystals, maybe due to less energy being available for the cellulose chains to orientate themselves into crystals, resulting in a more plastic material. The crystalline structures also appear to differ (Figure 6-3) for the two different temperatures. A peak at 18° appears for the higher regeneration and rinsing temperature which is absent for most of the samples regenerated and rinsed at 25 °C. A longer regeneration rate resulted in reduced crystallinity. This is in contrast to the findings of Duchemin *et al* (2009b) who observed a 10 % to 14 % higher CrI for slower precipitation rates when ACCs were prepared using LiCl/DMAc. This contrast is probably due to the different interactions of the different solvents with the cellulose chains, in the same way that improved crystallinity resulted from NMMO-dissolution of cellulose, compared to the reduced crystallinity of cellulose after dissolution using ILs (Pinkert *et al,* 2009).



(a) (b)

Figure 6-3: The effect of regeneration temperature and time and rinsing water temperature on the crystallinity of regenerated cellulose. (a) Regeneration performed at 25 °C and (b) regeneration performed at 80 °C.

It appears that the direct addition of rinsing water after dissolution, thus not allowing time for regeneration, leads to the formation of cellulose II. The primary peak for cellulose II is a doublet at 23.1° and 25.6° and the secondary peak lies at 14.1°. The characteristic secondary peak was observed for the samples for which no regeneration time after dissolution was allowed. The peak at 14.1° is more prominent when rinsing water at 25 °C rather than 80 °C was used.

The conclusion that the crystal type of the regenerated cellulose, after dissolution with BmimCl, is affected by the regeneration conditions is consistent with literature. Studies in which regeneration was performed by exposure to coagulant directly after dissolution (Sun *et al*, 2015; Zhao *et al*, 2009) resulted in the formation of Cellulose II crystals. If the dissolved cellulose was allowed time to cool down before being exposed to the coagulant, a paracrystallite phase was observed (Duchemin *et al*, 2009a)

BmimCl recovery

Regeneration and rinsing of the cellulose film at a higher temperature result in higher BmimCl recovery (Table 6-1). This higher ability of heated rinsing water to recover BmiCl was expected from the results of Investigation A

Table 6-1: The BmimCl recovery for different regeneration and rinsing conditions.

Regeneration time (min)	Regeneration temperature (°C)	BmimCl recovery (%)
0	25	93.55
60		83.38
120		96.61
180		94.39
0	80	96.79
60		92.94
120		98.99
180		94.97

Again, when regeneration and rinsing is performed at 25 °C, reduced crystallinity is observed, explaining the plasticising effect observed.

6.1.3 Conclusions

Regeneration and rinsing at different temperatures had a visible effect on the produced cellulose films. Films regenerated and rinsed at 25 °C instead of 80 °C were more transparency and were less stiff to the touch. Tensile testing proved that regeneration and rinsing at 25 °C did indeed have a plasticising effect on the produced films when compared to regeneration and rinsing at 80 °C. 1-Butyl-3-methylimidazolium chloride recovery was lower if rinsing water at 25 °C was used when compared to 80 °C. It was concluded that the plasticising was mainly due to reduced crystal formation in the regenerated phase when regeneration and rinsing was performed at 25 °C.

The regenerated phase did not only have a lower crystallinity when regenerated and rinsed at 25 °C, but the cellulose crystal structures also differed for the two different temperatures. Cellulose II was observed if no time was allowed for regeneration and rinsing was directly started after dissolution. This was especially true when rinsing water at 25 °C was used.

The time allowed for regeneration affected the tensile properties and the crystallinity of the produced samples. The general effect of increased regeneration time was a reduction in crystallinity.

6.2 The effect of remnant BmimCl

Results from Investiagation A and Invesitgation B made it apparent that BmimCl recovery values above 95% is easily achieved. The aim of this experiment was to determine what fraction of the weight of the produced cellulose film was BmimCl and what the effect of the remnant BmimCl would be on the film properties.

6.2.1 Experimental design

From Investigation A and B it was apparent that all 1-butyl-3-methylimidazolium chloride is not removed from the formed cellulose films. To analyse the effect that remaining BmimCl has on the mechanical properties of regenerated cellulose, the rinsing stages as determined in Investigation A (Section 4.3), were only performed partially to allow some BmimCl to remain in the cellulose matrix.

Samples were prepared using two different dissolution conditions. The first set of samples was prepared using 9 g/g BmimCl concentration at 90 °C for 1.25 hours. The second set of samples was prepared using 9 g/g BmimCl concentration at 90 °C for 0.5 h. Regeneration for all the samples were performed as described in Section 3.1.2. For both sets of dissolution conditions, rinsing was stopped after three rinsing stages or two rinsing stages. For both the dissolution conditions, three replicates of both rinsing treatments were performed.

After the partial rinsing the samples were dried as described in Section 3.1.2. For all the previous experiments it was assumed that mostly rinsing water would remain in the cellulose structure after rinsing and that drying at an elevated temperature and reduced pressure would remove the rinsing water by evaporation. If BmimCl was not completely rinsed from the cellulose structure, it would not be removed by evaporation, because of the negligible vapour pressure of BmimCl. The pressure that was applied during drying would likely press some of the BmimCl and rinsing water from the cellulose structure.

To quantify the amount of BmimCl that was pressed from the sample during drying, the each sample was dried between two absorption paper sheets. The dry weights of the absorption sheets before and after drying of the samples were determined and the mass gain was attributed to absorption of BmimCl. Drying of the absorption sheets was performed at 105 °C for at least twelve hours.

Analysis

Tensile testing and XRD analysis were performed as described in Section 3.2. The results were compared to the tensile testing and XRD analysis results of samples that were rinsed using four stages (complete rinsing). Only XRD was performed on the samples that were evaluated for the long term effect of BmimCl on the cellulose films.

The long-term effect of BmimCl presence on cellulose.

To evaluate the long term effect of BmimCl on the cellulose films, the same prepared samples containing BmimCl was allowed to age for three months and compared to the unaged samples.

6.2.2 Results and discussion

Tensile testing

The presence of BmimCl had a plasticising effect on the cellulose material (Figure 6-4). This plasticisation due to remnant BmimCl might be the cause of the high elongation values observed for the tensile test in Investigation B (Figures 5-6, 5-7 & 5-8). The observation that remnant BmimCl can plasticise the cellulose film resulted in the thought that remnant BmimCl might be the cause for the plasticing effect seen in section 6.1.2. The samples regenerated and rinsed at 25 °C contained higher amounts of remnant BmimCl and was more plastic than samples regenerated and rinsed at 80 °C. But when the extent of plasticising relative to the amount of BmimCl remaining in the cellulose matrix is considered for 25 °C and compared to the plasticising effect of BmimCl (Figure 6-4,Table 6-2) it becomes apparent that too little BmimCl remains to justify the plasticising effect solely on remnant BmimCl.

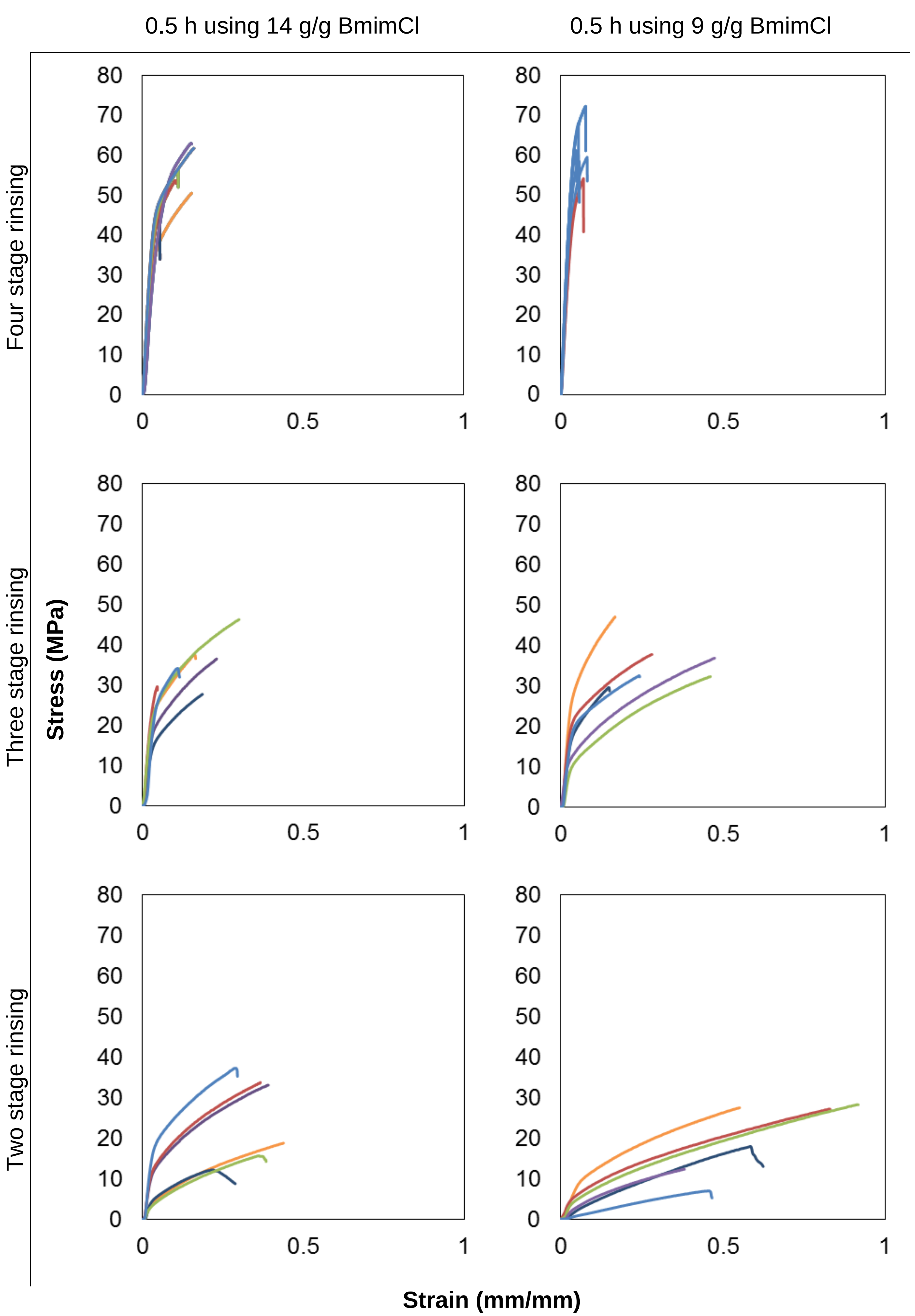


Figure 6-4: How tensile properties are affected by the presence of BmimCl.

BmimCl recovery

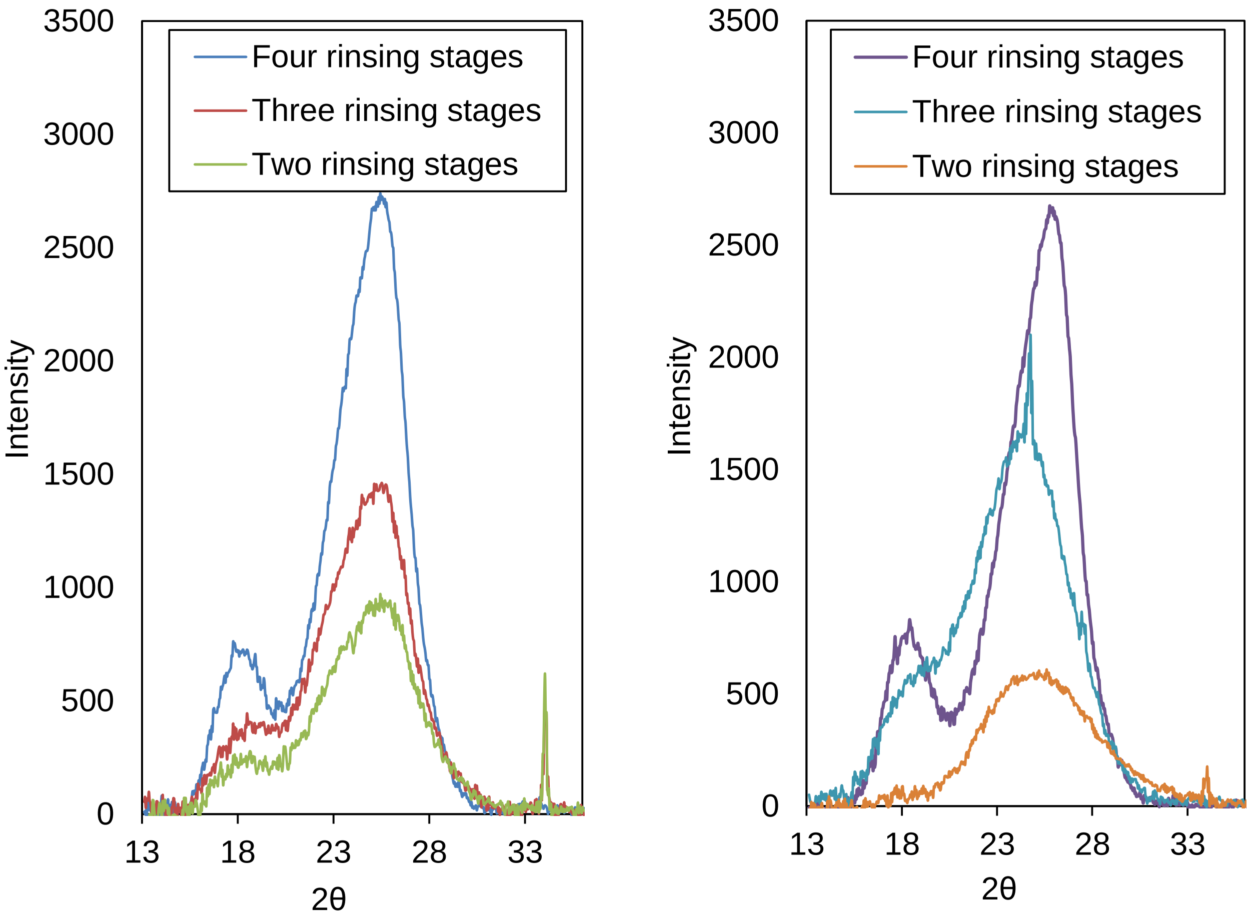
As expected, the percentage recovery of BmimCl decreased as less rinsing stages were performed (Table 6-2). The BmimCl remaining in the cellulose structure contributed significantly to the weight of the produced film. Even when close to 96 % of the BmimCl was recovered from the film, the BmimCl remaining in the cellulose structure contributed 18 % to the weight of the final film. This meant that even when a satisfactory percentage recovery of BmimCl was obtained, the produced film still contained a large amount of BmimCl.

Table 6-2: The BmimCl recovery and the percentage of the produced film which is BmimCl if the rinsing method is partially performed.

Amount of rinsing stages	BmimCl recovery (%)	BmimCl in finished product (%)
Four	96	18
Three	93	23
Two	82	55

XRD analysis

It was originally thought that crystals formation in the regenerated phase would occur as soon as the dissolution process was stopped and cellulose precipitated to form a solid structure. The increase in crystallinity as more BmimCl was removed from the solid regenerated cellulose structure (Fig 6-2) shows that crystallite formation does not happen upon precipitation of the cellulose to a solid, but rather in the solid phase, as BmimCl is removed. The plasticising effect that BmimCl has on cellulose could be attributed to the disruption of crystallite formation in the regenerated phase by the presence of BmimCl.



(a)

(b)

Figure 6-5: The effect of BmimCl on the crystallinity of samples prepared by dissolution at 90 °C for 0.5 h using 14 g/g BmimCl (a) and 9 g/g BmimCl (b) respectively.

The effect of BmimCl presence on cellulose after aging of the material

The crystallinity of samples increased as they aged (Figure 6-6). It appears that the crystal formation that was initially inhibited by the presence of BmimCl slowly occurs if sufficient time is allowed. The total crystallinity for BmimCl containing samples was still less than the crystallinity of samples containing less BmimCl.

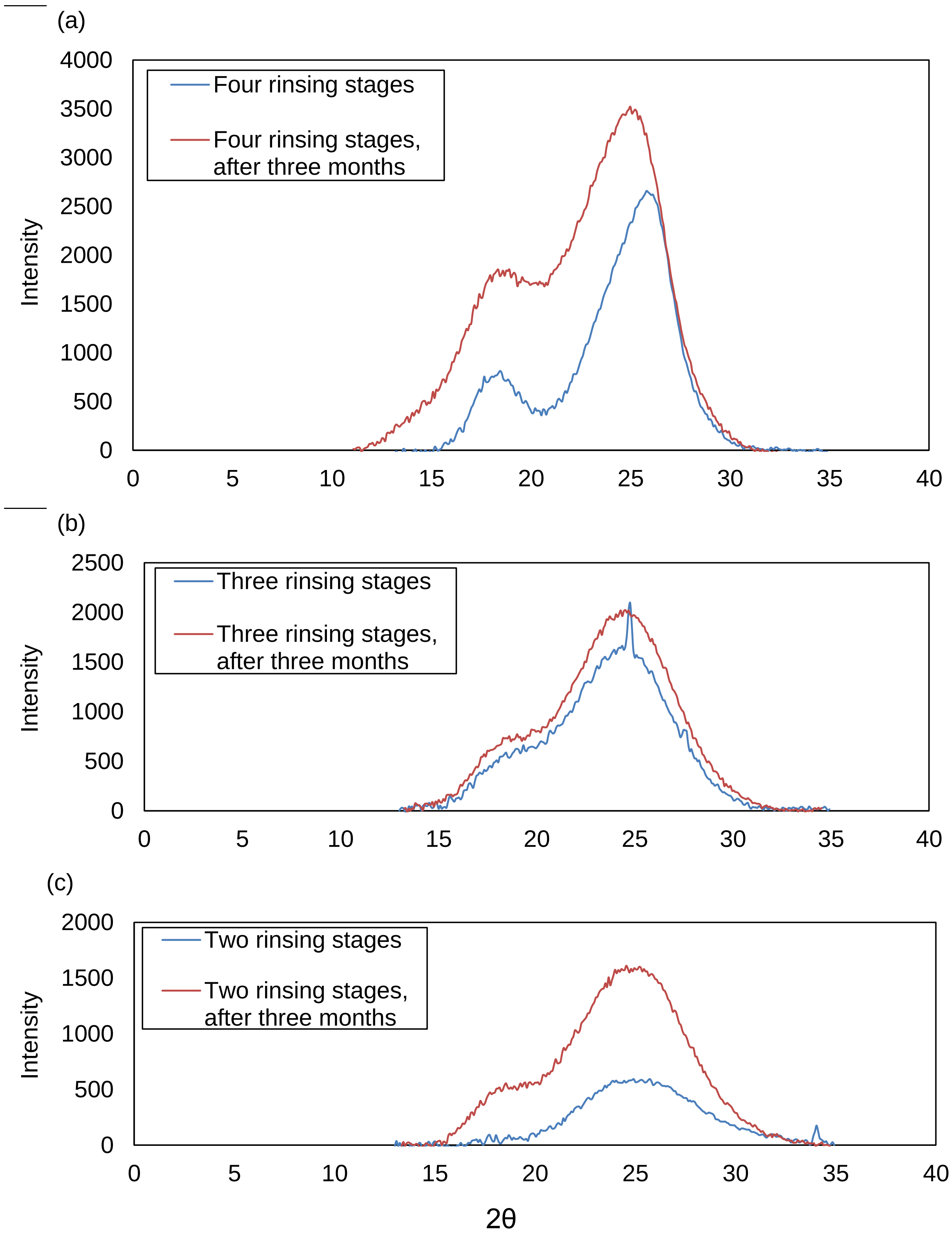


Figure 6-6: The effect of aging the material for three months on the crystallinity.

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6.2.3 Conclusions

The presence of BmimCl was found to have a plasticising effect on the cellulose film produced. If BmimCl was not properly removed from the film, it inhibited the formation of crystals, probably resulting in the plasticising effect.

It also became apparent that the crystals that form in the regenerated phase did not form during the regeneration step, when the cellulose chains precipitate from solution to a solid. The crystals formed in the solid phase only after the removal of BmimCl from the solid cellulose structure.

The crystal formation in the solid phase continued as the cellulose films were allowed to age. The long term effect of BmimCl was to reduce this crystal formation in the regenerated phase over time, but an increase in crystallinity was still observed independent of the presence of BmimCl in the celluose

When almost 96 % BmimCl recovery was achieved for the 9 g/g BmimCl originally added, 18 % of the weight of the finished film was BmimCl. This was a significant amount of BmimCl still remaining in the film indication that the percentage recovery alone could not serve as a measure for BmimCl recovery.

7 DISCUSSION OF RESULTS FROM ALL INVESTIGATIONS

Although partial dissolution for the production of an all-cellulose composite was attempted, complete dissolution was observed for nearly all the dissolution conditions tested. The low crystallinity observed for samples that were only rinsed using two stages motivates that complete disintegration of cellulose I crystals from the native structure had occurred after 0.5 h at 90 °C using 9 g/g BmimCl. Therefore most of the crystallinity observed in Investigation B (Figures 5-13 & 5-14) for samples dissolved at and above dissolution conditions of 90 °C for 0.5 h using 9 g/g, is due to crystal formation after dissolution and not due to remnant crystals from the native structure. The same is probably true for some of the higher dissolution conditions at 80 °C (Figure 5-12). Most of the samples prepared using different dissolution conditions did not have significantly different mechanical properties, which would be explained if all of these samples underwent complete dissolution.

For the few low dissolution conditions where partial dissolution did occur, it is clear that the undissolved fibre fractions did not offer reinforcing of the regenerated matrix since the completely dissolved samples had better mechanical properties. This suggested that dissolving wood pulp is unsuitable for the production of ACCs. Samples that were dissolved at high dissolution conditions underwent a complete loss of mechanical integrity, probably due to the disintegration of the cellulose polymers.

Complete dissolution of dissolving pulp occurs much faster than anticipated form the dissolution conditions for other cellulose sources tested used in other published literature. This fast dissolution is advantageous if BmimCl is considered for the replacement of current industrial cellulose dissolution processes, which is aimed at the complete dissolution of cellulose.

Ionic liquid (IL) recovery will be an essential part to enable industrialisation for cellulose dissolution. The BmimCl recovery process could be performed in a much shorter time than anticipated, using rinsing stages. The recovery process was accelerated when the rinsing water at 80°C is used rather than rinsing water at 25 °C and the samples had undergone less dissolution. Although good percentage recoveries were achieved, it is apparent that this cannot be the only consideration- even at recoveries higher than 96%, 18% of the finished cellulose film will still be BmimCl. The recovered BmimCl showed darkening after use, motivating that the studies into the purification of the BmimCl recovered is an essential part to make the process industrially feasible.

Plasticisation of the cellulose films were observed as a result from two different process considerations. If BmimCl was not removed from the cellulose film, the presence of the BmimCl in the finished product would result in a more plastic material. But when regeneration and rinsing of the films were performed at 25 °C instead of 80 °C, an even more significant plasticising effect was observed, without needing BmimCl to remain in the product. In both instances, the plasticisation effect was accompanied by reduced crystallinity of the final product.

Shrinkage of the product was one of the main obstacles during the development of the synthesis process. During dissolution some shrinkage was observed, but the majority of shrinkage occurred during regeneration, rinsing and drying. Samples underwent more shrinkage when:

- No time for regeneration was allowed and rinsing was immediately started,
- Rinsing was performed at 80 °C instead of 25 °C,
- Drying was not performed under pressure.

The observed shrinkage suggests that the amount of deformation in the samples was related to the rate of crystallisation after dissolution. The cellulose crystal type was also dependant on whether regeneration time was allowed or whether rinsing was immediately started. Differential shrinkage during the regeneration, rinsing and drying steps most probably resulted in large amounts of variation throughout the films.

These observations would support that of Duchemin *et al*, (2009b): that the cellulose precipitation conditions should be one of the main considerations for the dissolution and regeneration of cellulose.

8 RECOMMENDATIONS

It is recommended that a stronger cellulose fibre type, such as cotton, be added to the starting material. The stronger fibres can be introduced during the sheet forming process. These stronger fibres might dissolve slower and form a more rigorous support structure in the final product.

Shorter dissolution times should be investigated, because most of the dissolution conditions investigated in complete dissolution of the cellulose or even degradation of the cellulose. Considering the negative effect that high BmimCl concentration had, solutions with lower BmimCl concentrations should also be investigated. Microwave heating can be considered for this purpose because the cellulose concentration in solution when using BmimCl can be increased from 10 % to 25 % when microwave heating is used instead of convective or radiative heating (Swatloski *et al,* 2002).

Factors contributing to the non-uniform nature of the sheets should be investigated. These possibly include uneven BmimCl dispersion throughout the film, flow when the cellulose is in dissolution and uneven removal of BmimCl from the finished structure. The process used to dry the sheets should also be assessed to determine if variation in the sheets result from stresses within the material during drying.

There is inconsistency in the crystal structure reported for cellulose regenerated from dissolved with ILs. Amorphous cellulose, cellulose II, a mixture of amorphous cellulose and cellulose II or a mixture of amorphous cellulose and cellulose I have been reported (Wahlström & Suurnäkki, 2015). From the observed formation of cellulose II and reduced crystallinity of regenerated cellulose in the presence of BmimCl, a hypothesis is formulated for further investigation:

- The different types of cellulose crystals observed in published studies are due to different regeneration conditions.
- Amorphous cellulose is observed in these studies due to the incomplete removal of the ILs, which inhibits crystal formation in the regenerated phase.

The last step in the synthesis process, the drying step to remove the rinsing water from the cellulose matrix was performed under reduced pressure and at 105°C for all the investigations. It is possible that the relatively high drying heat might have resulted in weakened films. As mentioned, shrinkage occurs during the drying step and some of the films cracked during the drying process. It is recommended that the dying step be investigated using reduced pressure and temperatures lower than 105°C.

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