# Production and Optimisation of All Cellulose Composites using Native and Regenerated Cellulose Fibres.



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Submitted in accordance with the requirements for the degree of Doctor of Philosophy December 2024 I confirm that the work submitted is my own, except where work which has formed part of jointly authored publications has been included. My contribution and the other authors to this work has been explicitly indicated on the next page. I confirm that appropriate credit has been given within the thesis where reference has been made to the work of others.

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## **Author's Publications**

# Paper 1: Use of interleaved films to enhance the properties of all-cellulose composites.

Ashley Victoria, Michael E Ries, Peter J Hine Composites Part A: Applied Science and Manufacturing 2022 Pages 107062 ISSN: 1359-835X DOI: https://doi.org/10.1016/j.compositesa.2022.107062

#### Author Contributions:

Ashley Victoria: Conceptualization, Methodology, Investigation, Formal Analysis, Validation, Data curation, Writing- Original draft preparation, Writing- Reviewing and Editing.

Peter Hine: Supervision, Conceptualization, Writing- Reviewing and Editing.

Michael E. Ries: Supervision, Conceptualization, Writing- Reviewing and Editing.

Paper 2: Design of experiments in the optimization of all-cellulose composites. *Ashley Victoria, Peter J Hine, Keeran Ward, Michael E Ries* Cellulose 2023 Vol. 30 Issue 17 Pages 11013-11039 ISSN: 1572-882X DOI: 10.1007/s10570-023-05535-8

#### Author Contributions:

Ashley Victoria: Conceptualization, Methodology, Investigation, Formal Analysis, Validation, Data curation, Writing- Original draft preparation, Writing- Reviewing and Editing.

Peter Hine: Supervision, Conceptualization, Writing- Reviewing and Editing.

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Michael E. Ries: Supervision, Conceptualization, Writing- Reviewing and Editing.

# Paper 3: Design of experiments investigation into the production of all cellulose composites using regenerated cellulosic textiles.

Ashley Victoria, Peter J Hine, Keeran Ward, Michael E Ries Composites Part A: Applied Science and Manufacturing 2024 Pages 108510 ISSN: 1359-835X DOI: https://doi.org/10.1016/j.compositesa.2024.108510

## Author Contributions:

Ashley Victoria: Conceptualization, Methodology, Investigation, Formal Analysis, Validation, Data curation, Writing- Original draft preparation, Writing- Reviewing and Editing.

Peter Hine: Supervision, Conceptualization, Writing- Reviewing and Editing.

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Michael E. Ries: Supervision, Conceptualization, Writing- Reviewing and Editing.

# Acknowledgements

I would like to thank my academic supervisors Dr Peter Hine and Dr Keeran Ward, as well as Professor Michael Ries for the incredible support they have provided to me throughout my journey so far. It is with their encouragement that I continue to find inspiration and enthusiasm with my PhD project and develop myself to be the best I can be.

I would like to give special thanks to Dr Daniel Baker for being a fantastic help to me during my PhD, providing his expertise and insight through lab inductions and equipment training. Without this individual, the laboratory spaces would probably cease to exist. I would also like to thank Dr Faye Esat for her help in generating the XRD data for analysis.

I would like to thank the Biopolymer Dream Team, a truly unique and fantastic group of individuals whose support has helped me through the good, the bad and the stressful parts of my PhD journey.

This research was supported through a studentship supported by the Engineering and Physical Sciences Research Council (EPSRC) Centre for Doctoral Training in Molecules to Product (EP/SO22473/1), for which I am greatly thankful.

Finally, I would like to thank the two Mikes in my life. My father Mike, who has supported me through every mad decision I've made throughout my life. He's an absolute legend and without doubt in my mind, the best father a girl could have. And my partner Mike, thank you for not letting me give up and thank you for being part of my story. I fly. This thesis is dedicated to my late mother, a truly beautiful human who encouraged me to believe that I could achieve anything. She inspired me to chase my dreams and live a life free of regrets.

#### Abstract

All-cellulose composites (ACCs) are gaining interest as renewable material alternatives to traditional fossil fuel derived composites. In contrast to traditional composite materials, whereby the matrix and reinforcing components are formed from different materials, ACCs feature matrix and reinforcing components comprising entirely of the renewable biopolymer, cellulose. The ACCs studied and discussed throughout this thesis were produced via a partial dissolution method, using alternating textile layers of either cotton or regenerated cellulose fibres and an interleaved cellulosic film immersed in solvent solution, and heating them under an applied pressure. The solvent used was a mixture of the ionic liquid 1-Ethyl-3-methylimidazolium acetate ([C2MIM][OAc]) combined with a co-solvent dimethyl sulfoxide (DMSO).

Firstly, for the ACCs based on the cotton textile layers, the addition of the interleaved film was found to contribute to a significant improvement in interlayer bonding when compared to processing without the film, as quantified by peel strength measurements. With an optimised [C2MIM][OAc] and DMSO ratio of 80/20, Young's modulus was improved from 2.2 +/- 0.2 GPa to 4.2 +/- 0.2 GPa and peel strength reached as high as 917 +/- 73 N/m. The increased interlayer adhesion was additionally found to improve uniformity between longitudinal and transverse mechanical properties. Optimization of the processing variables for producing ACCs was carried out using statistical design of experiments (DoE). A full factorial design (2<sup>3</sup>) was applied to explore the effects of dissolution temperature, pressure, and time on ACC mechanical properties, which were then optimised using Response Surface Methodology (RSM). A relationship between Young's modulus and processing

conditions was revealed and used to identity optimum process condition to maximise this property. Temperature and time settings of 101 °C and 97 minutes respectively, were identified, from which a Young's modulus of 3.3 GPa was predicted to yield. In-lab validation samples were found to exhibit a very similar Young's modulus of  $3.4 \pm 0.2$  GPa, confirming the adequacy of the predictive model. The optimized samples had an average tensile strength and peel strength of  $72 \pm 2$  MPa and  $811 \pm 160$  N/m respectively, as well as a favourable density resulting from excellent consolidation within the material microstructure.

ACCs were then produced using a regenerated cellulose fibre-based textile, Tencel, and DoE was again applied to investigate the effect of process conditions of temperature, time, and [C2MIM][OAc] concentration, as well as the benefits of the interleaf film. A full factorial screening design was expanded to a central composite face-centred (CCF) design which captured the process using the film more strongly. It was found that the film remained in between the textile layers, rather than penetrating through the fibre assembly, as observed in previous work on cottonbased ACCs, offering insights into the structural differences between Tencel and cotton. Multi-response optimization led to a prediction for Young's modulus and strain-to-failure to be obtained. An optimized processing temperature of 30 °C with 70 % IL / 30 % DMSO was identified to yield a Young's modulus and strain-tofailure of 5.3 GPa and 3.5 % respectively. In-lab samples were made and found to exhibit a Young's modulus and strain-to-failure of  $4.9 \pm 0.2$  GPa, and  $3.3 \pm 0.3$  % respectively.

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# List of Abbreviations

ACC	All cellulose composite
ANOVA	Analysis of variance
[C2MIM[OAc]	1-Ethyl-3-methylimidazolium Acetate
CCD	Central composite design
CCC	Central composite circumscribed design
CCI	Central composite inscribed design
CCF	Central composite face-centred design
CLT	Classical lamination theory
COV	Coefficient of variance
СР	Centre point
CSA	Cross-sectional area
[DBNH]OAc	1,5-diazabicyclo[4.3.0]non-5-enium acetate
DMAc	N,N-dimethylacetamide
DMSO	Dimethyl sulfoxide
DSD	Definitive screening design
DoE	Design of experiments
DF	Degrees of freedom
FRCs	Fibre reinforced composites
HBA	Hydrogen bond acceptor
HDPE	High-density polyethylene
IL	Ionic liquid
LiCl	Lithium chloride
LCA	Life cycle analysis
MCC	Microcrystalline cellulose
MMCFs	Man-made cellulosic fibres

NMMO	N-Methylmorpholine N-oxide
ML	Machine learning
MS	Mean square
NFRCs	Natural fibre reinforced composites
OFAT	One-factor-at-a-time
PLA	Polylactic acid
PET	Polyethylene terephthalate
PP	Polypropylene
$\mathbb{R}^2$	Coefficient of determination
RTILs	Room temperature ionic liquids
RSM	Response surface methodology
RTM	Resin transfer moulding
S/C	Solvent to cellulose
SIP	Solvent infusion processing
SS	Sum of squares
TEA	Techno-economic analysis
VARTM	Vacuum assisted resin transfer moulding
XRD	X-Ray Diffraction

# Chapter 1. Introduction and Literature Review

## **1.1 Introduction**

All cellulose composites (ACCs) have attracted significant attention within the research community in recent years as sustainable alternatives to petroleum-derived materials [1-6]. Unlike traditional composites that comprise different material components, both matrix and reinforcing components of ACCs are made entirely of cellulose, a naturally occurring biopolymer with intrinsically good mechanical properties [7, 8]. This one-component system negates the need for prior separation when considering end-of-life processing [3, 5, 9]. In addition to possessing excellent mechanical properties [7, 10] and thermal stability [5], cellulose is renewable and biodegradable [1, 5, 11], making it a favourable choice of polymer with regard to sustainable materials development. The use of renewable or waste biomass is of particular importance when addressing climate change and resource scarcity [3, 12-14] and there is an eagerness to develop sustainable materials that can better support a circular system.

The motivation of this thesis lies in advancing the development of sustainable materials through resource-efficient methodologies and paving the way for the use of recycled textiles in the production of truly circular composite materials. This is achieved by addressing the challenges in developing ACCs to optimise their mechanical performance and exploring the use of different cellulose sources. The work initially begins with the use of native cellulose (cotton), and then shifts into the use of regenerated cellulose (Tencel) to demonstrate the potential for waste-derived regenerated fibres to be used in ACCs.

### **1.2 Cellulose**

Cellulose is a biopolymer composed of carbon, hydrogen, and oxygen atoms. It is the primary component in the walls of plants cells and also produced by living organisms such as fungi, bacteria and algae [15-17]. The structure of cellulose is shown in Figure 1-1, along with the conventional numbering of the carbon atoms in the ring. The repeat unit aligns with the nomenclature conventions of the International Union of Pure and Applied Chemistry and the International Union of Biochemistry and Molecular Biology [18].



Figure 1-1. Cellulose structure. Credit: French AD (2017) Glucose, not cellobiose, is the repeating unit of cellulose and why that is important. Cellulose 24:4605-4609:4605 [19]

The polysaccharide structure comprises a linear unbranched chain of the  $\beta$ -glucose units, linked together by  $\beta(1-4)$  glycosidic covalent bonds [19-21]. In other words, the carbons at positions 1 and 4 are involved in the links between units [15]. This

chain consists of many hydroxyl groups available to form hydrogen bonds (Hbonds).

At the molecular level (< 1 nm), hydroxyl groups on the chains form intrachain Hbonds with hydroxyl groups on the same chain, making the chain strong and rigid [22, 23]. At the intermolecular level (~ 1 nm), interchain H-bonds are formed between the hydroxyl groups of neighbouring chains. Cellulose I is the name given to the crystal structure of native cellulose [20] in which the interchain hydrogen bonding between chains described above is such that the chains are aligned parallel to each other [21, 24, 25] as shown in Figure 1-2.



Figure 1-2. Intrachain O(3)-H···O(5) and O(2)-H···O(6), and interchain O(6)-H···O(3) and hydrogen bonding network present in native cellulose I. The red numbers refer to the carbon atoms position, and the respective oxygen atoms involved in the bonding.

From here, flat sheets are formed that stack into a crystalline arrangement to form microfibrils (~ 5 nm), held together by intersheet H-bonds and van der Waals

bonding [12, 26, 27]. Larger structures (~10-100 nm) can then form from bundles of microfibrils which are highly orientated. The structure of cellulose at different length scales is illustrated in Figure 1-3.





Whilst cellulose I occurs naturally and cannot be produced, it can undergo processing from which additional crystalline forms (allomorphs) emerge. The most technically significant allomorph is Cellulose II, generated via chemical treatment of cellulose I such as mercerisation or solvent dissolution and regeneration (elaborated on in section 1.2.2). One notable difference in structure between cellulose I and cellulose II is seen at the intermolecular level where the cellulose chains form Hbonds with each other to form sheets. X-ray studies on cellulose II have indicated that the chains are aligned anti-parallel to each other, contrary to the parallel packing that exists in cellulose I [25]. It has been suggested that precipitation from solutions of disordered chains accounts for this anti-parallel arrangement, however, chemical treatment undergone by cellulose I (for example, mercerisation) involves swelling rather than any change in molecular orientation [15, 25]. As such, it is not fully understood how the treatment of cellulose I (with its parallel alignment) gives rise to the anti-parallel structure in cellulose II. Additionally, strong intermolecular bonds are present between cellulose II sheets which are not present in cellulose I [27]. Instead, a combination of weak dispersion forces and weak CH-O hydrogen bonds link the sheets together [27, 28]. Cellulose II is a more thermodynamically stable allomorph than cellulose, and as such the conversion back to cellulose I is not possible [15]. Figure 1-4 outlines the hydrogen bonding present in cellulose II.



Figure 1-4. Intrachain O(3)-H···O(5) and interchain O(6)-H···O(2) bonding in Cellulose II. The red numbers refer to the carbon atoms position, and the respective oxygen atoms involved in the bonding.

In addition to the crystalline forms of cellulose I and cellulose II, cellulose

comprises amorphous (non-crystalline) regions [15, 20]. These amorphous regions

exist alongside the crystalline regions and are such that the glucose chains are not arranged as they are in cellulose I and cellulose II, rather, they are disordered.

# **1.2.1** Cellulose fibres and structure

Cellulose-based fibres can be broadly categorised as native (natural), and man-made. Native fibres such as cotton, flax, jute and hemp originate from the various cellulose-producing parts of certain plant species [17]. Whilst predominantly cellulosic, these fibres are not comprised of 100 % cellulose, instead they form from a mixture of cellulose along with hemicelluloses, lignin, and components such as pectin, proteins and waxes [17]. The percentage content of these components varies among different fibres, some of which are removed prior to being spun into a yarn that can then be woven into a textile. Bast fibres such as flax, hemp and ramie are found at the plant stem, and seed fibres such as cotton are produced on the seeds of various plants [29]. Structurally, these native fibres are essentially elongated cells from the various parts of the plant, for example the majority of plants fibres are elongated cells of sclerenchyma, a plant tissue found in the non-growing parts of the plant such as the plant stems that provides structural support to the plant [30].

Plant cells typically have a primary wall (P), and a thicker secondary cell wall (S) consisting of three sub-layers (S1, S2 and S3) [17] as shown in Figure 1-5 which depicts a cotton fibre. An outer layer of waxes, pectins and fats surrounds the P and S layers, and the centre of the cell is known as the lumen. The cellulose fibrils in the walls are embedded in lignin and hemicelluloses.



Figure 1-5: Structure of a plant cell exemplified by cotton fibres. The primary cell wall (P) consists of less aligned fibrils, the secondary walls comprise layers S1 and S2, with helically orientated fibrils. The fibrils in S2 are orientated more in the direction of the overall fibre direction.

The majority of fibrillar material is contained in the secondary wall and thus, it is the most important wall for determining the fibre mechanical and physical properties [31]. Here, the fibrils are arranged helically and the angle with respect to the overall fibre direction differs between the sub-layers, and this is specific to the fibre type [17, 31, 32]. Cotton for example, is a single, unicellular extension of the epidermis cells that grow on the surface of a cotton seed [17, 30, 33]. This elongated cell is considered one of the simplest and largest of all plant cells [31]. The fibrils present in cotton fibres become more aligned towards the inner layers of the cell wall, with the primary wall consisting of less aligned fibrils [31].

#### **1.2.2** Man-made cellulosic fibres (MMCFs)

As mentioned briefly in Section 1.2, native cellulose (cellulose I) can be chemically treated to form cellulose II through treatment with concentrated alkaline solution, or a solvent dissolution process [34], the latter of which is utilized in the production of man-made cellulosic fibres (MMCFs) such as viscose rayon and lyocell. Viscose rayon is the most widely known MMCF, produced via the Viscose process. In the Viscose process, wood pulp derived cellulose is steeped in sodium hydroxide to form a slurry of alkali cellulose. The slurry is pressed to drain out the excess sodium hydroxide and stored to allow the oxygen in the air to oxidise it. The alkali cellulose is then derivatised using carbon disulphide to form a cellulose xanthate which can then be dissolved into a solution from which the viscose fibres are spun [35]. Here, the cellulose is chemically modified prior to dissolution, to a form that can be dissolved in a specific solvent. Over the years alternate routes to producing MMCFs have been developed including the lyocell process where fibres are produced via direct dissolution of wood pulp in N-Methylmorpholine N-oxide (NMMO), eliminating the need for derivatisation as required by the Viscose process [36]. The name 'lyocell' is now generically given to fibres produced via this route as well as the process itself [37] and, furthermore, has been defined by the Federal Trade Commission as a cellulose fibre that is precipitated from an organic solution in which no substitution of the hydroxyl groups takes place and no chemical intermediates are formed [38]. Tencel is a trade name for lyocell fibres originally produced by UK based manufacturer Courtaulds. In 2000, the company's Tencel division was sold to Lenzing AG who maintained the trade name Tencel for their lyocell fibres [38]. Since commercialisation in 1990, lyocell fibres have gained popularity as an alternative MMCF, with a growth rate predicted to exceed that of viscose in the near future [39].

'Regenerated cellulose' is the term given to fibres produced via derivatisation, that is, where cellulose is dissolved in a solvent, chemically modified, and subsequently precipitated out into a form that can be spun into a continuous filament to produce a fibre [40]. However, it is not uncommon to see the term 'regenerated' applied to fibres produced via direct dissolution, where no chemical modification has taken place. Regenerated fibres are made up of multiple filaments, bundled together to form a fibre that is then woven into textile form. The filament cross section is largely circular and smooth [38, 41, 42], allowing them to pack together closely. This contrasts with that in a native yarn such as cotton, which is made up of many bundles of irregular shaped cotton fibres [41, 43].

## **1.2.3** Cellulosic textiles

Both natural and man-made cellulosic fibres feature extensively in the textiles industry. The most well-known native fibre used in textiles is cotton, which accounted for nearly a quarter of the total fibre production in 2022 [44]. In the context of MMCFs, global production has more than doubled over the last 20 years from 3 million tonnes to 7.2 million tonnes, accounting for 6 % of total global fibre consumption [44].

Native fibres are bundled together and mechanically spun to produce yarns which are used to form textiles. The term 'yarn', however, is not typically used when referring to MMCFs at the same scale. Once spun into continuous filaments, they are instead referred to as 'fibres'. These native yarns and man-made fibres are then woven into a textile structure.

## **1.2.4** Cellulose in the materials industry

In addition to the textiles industry, cellulose has applications in the materials industry, for example, flax, hemp, and wood fibres have been used in combination with synthetic, fossil derived polymers to form bio-composite materials. These are a development from traditional composite materials where the reinforcing component (such as carbon or glass, for example) is replaced with a natural fibre.

To truly harness the potential of biopolymer such as cellulose, exploring ways to develop bio-composites that are independent of fossil-derived components [45] is an area worth exploring. Section 1.3 explores composite materials from both a traditional (non-biobased) point of view as well as developments into biobased and single-polymer composite materials.

## **1.3 Composite materials**

Composite materials contain two or more different component materials, and by combining components that have different properties it is possible to create something with improved, or enhanced properties [46]. In general terms a composite consists of a continuous phase known as the matrix, which surrounds a dispersed phase known as the reinforcement. Composite materials can provide enhanced performance above that of plastics alone [47], and do so by combining a base polymer with a reinforcing component such as a fibre or another polymer. There are different methods that can be used to form composites, and the method applied typically relates to the kind of reinforcement used. This can include reinforcement in the form of particles or fibres or creating structural reinforcement from layers of different materials [48, 49].

Polymers reinforced using fibres are known as fibre-reinforced composites (FRCs), where a fibre is added to create material that has increased strength, or capability to withstand increased loads. In FRCs, the matrix component is the polymer, and the reinforcement is the fibre. A polymer may exhibit a desirable strength and low density, but due to its low modulus may lack the strength or stiffness needed for a particular application. In this case, the addition of fibres such as glass or carbon would produce a composite material with enhanced properties [50]. One of the first fibres used to create FRCs was glass, which when added to a polymer would create a lightweight material with high strength [51]. Carbon fibres are used frequently in composites to provide stiff yet lightweight alternatives to metals [52]. There are many other synthetic fibres used in composite materials, for example aramid fibres, polyethylene, and different variations of glass fibres. The use of natural fibre reinforcements such as cellulosic fibres will be discussed later in the chapter.

# **1.3.1** Composite manufacture

In traditional fibre reinforced composites, there are many different fabrication technologies that can be applied to achieve structure and thickness in composite materials. One way involves using a pre-preg, which is a sheet made by impregnating an arrangement of fibres with resin. The pre-preg is then consolidated and cured using pressure and heat [53]. A variation of this involves the use of fibres arranged in a sheet or woven structure known as a dry pre-form, which is then enclosed within an impermeable membrane under vacuum [53]. Resin is then injected into the enclosure which impregnates the pre-form, and this is known as vacuum assisted resin transfer moulding (VARTM). A common construction in composite forming is known as a laminate, produced by stacking multiple layers together. The layers comprise unidirectionally orientated fibre reinforcement that are then stacked according to the requirements of the material. These layers are referred to as plies or laminae, and these are an example of multi-layered composites [49].

# **1.3.2** Composite Properties

Achieving good mechanical properties in composites relates to how an external load is carried throughout the composite structure, and in particular, the reinforcing component from which the strength comes from [49]. This force is applied initially to the fibres that lie closest to the surface, then transfers from fibre to fibre via the matrix. The interface is therefore extremely important to ensure that this load transfer can occur and the fibre reinforcement can be effectively utilized [54]. Any voids or lack of adhesion at this interface will reduce the efficiency of load transfer, and subsequently reduce the ability of the material to withstand it. The resulting formulation and properties of a composite are heavily influenced by the properties of the individual components [55]. Both reinforcement and matrix components independently contribute their own properties, and their contribution is typically determined by the respective volume fractions which are present in the composite [56].

### **1.3.3** Textile composites

As mentioned in the previous section, pre-forms can take the form of a sheet or woven textile structure, the latter producing materials often referred to as textile composites. Research into textile composites has grown over the past few decades, drawing on many fundamental concepts within the disciplines of textile technology and materials science [57]. The flexibility of woven textiles means that they can be shaped into three-dimensional structures, as well as offer structural advantages and increased composite mechanical properties [58]. Textile structures can be considered a hierarchical system where the textile is formed from yarns that are themselves formed from fibres [59].

There are two main structural categories used in the textiles industry, woven and knitted. A woven structure is formed from warp and weft yarns which are interlaced perpendicular to each other [60]. The warp yarns are stretched in parallel on a loom and held under tension, and the weft yarns are run over and under them at 90° in a direction perpendicular to the warp yarns. There are a multitude of different ways the weft fibres can interlace the warp fibres, leading to different structures being formed. Plain weave, satin weave, and twill weave are the most common types of woven fabrics found in fashion [59]. Because the fibres can have a different in-plane arrangement, the properties of textile composites can be anisotropic, i.e. differ between the warp and weft axes.

Fibre and yarn properties can be highly influential in determining the properties of the textile they are used to create [60]. Fibre properties depend on intrinsic factors such a molecular weight and crystal orientation, for example. These fibre properties and the processing by which they are spun into yarns will in turn influence the yarn properties [60, 61].

# **1.3.3.1** Fibre orientation

It is generally understood that fibre orientation plays a crucial part in optimising the tensile properties of composites materials [62]. For instance, in unidirectional composites, where the fibres are straight, and aligned in one direction, they exhibit excellent tensile properties in the longitudinal direction of the fibres. There is, however, a drawback to unidirectional aligned reinforcement fibres where properties are significantly weaker in the transverse direction, due to fibre alignment along just one axis.

The orientation of fibres on two axes in the case of a woven fabric can provide more balanced properties in the fabric plane [63]. The use of woven textiles as a composite preform provides yarn orientation in two directions owing to the interlaced ends (warp yarns) and picks (weft yarns) aligning perpendicular to each other, thus providing a (0°, 90°) orientation. It can be said, therefore, that the warp yarns contribute to the longitudinal properties of a woven textile, and the weft yarns contribute to the transverse properties [64]. In many woven structures, particularly commercial clothing textiles, the warp yarns typically have a higher tensile strength than weft yarns [65]. As more tension is placed on the warp fibres during the weaving process, fabrics typically have more warp yarns per unit area than weft yarns which can increase strength. Stronger fibres may also be used to make warp yarns to ensure they withstand the weaving process. This imbalance can be more pronounced if there is an unequal number of yarns in the warp and weft directions. Textiles used for industrial applications typically use balanced fabrics, where there is an equal number of warp and weft yarns [66], and yarns are chosen for performance and strength.

When studying woven structures, it is useful to be aware of the arrangement and configuration of the weft and warp yarns within a unit length of fabric. This involves parameters such as yarn count, linear density, crimp, and yarn spacing, all of which can contribute to the resulting physical and mechanical properties of the fabric [67].

Yarn crimp occurs through the interlacing of warp and weft yarns within the fabric, leading to a portion of the yarn orientating out of the two-dimensional textile plane [68]. The yarn becomes wavy as it passes over and under the perpendicular yarn, and this is generally more pronounced in the weft yarns. Crimp can be quantified in terms of the crimp ratio, which is the ratio of the yarn length to the cloth length, as shown in Equation 1-1

#### **Equation 1-1**

$$crimp \ ratio = \frac{length \ of \ yarn}{length \ of \ cloth}$$

A yarn with a crimp ratio of above one will be longer than the length of fabric it forms in the same direction, and high crimp ratios will contain more yarn across the length leading to increased density and thickness.

The yarns within different weaves will exhibit different levels of crimp which in turn will affect the thickness of the fabric [59]. In plain weave, for example, a single
weft yarn will pass over and under one warp yarn, and thus the interlacement is at maximum. The crimp ratio of the yarns is therefore higher than that of satin weave, where four or more weft yarns pass over four or more warp yarns [68].





The fabric weaving process creates more alignment in the warp yarns as they are held under tension, and this means that warp yarns typically have a lower crimp level than the weft yarns. As such fabric tensile strength can typically be perceived as higher in the warp direction than the weft [65, 67]. When applying load to a textile, the initial load is used in straightening out the yarns, leading to reduced tensile properties in the direction of the weft yarns [69]. The strength of the textile will be transferred to the composite it reinforces, and so strength may not be equal in these directions.

The portion of yarn that passes over a given set of transverse yarns in known as a float, and twill and satin weaves, for example, exhibit higher floats. Fabrics with yarns of a higher float offer a fabric surface that is less 'broken' than a fabric with a lower float [60], and so the unidirectional strength is provided by yarns with less

crimp, and continuity across a longer portion of the fabric in a given plane. Fabrics with longer floats can offer increased fabric strength and this is utilised in both fashion and materials design. Twill, for example is used in fashion to make sturdy denim products, and is also used in carbon fibre composites [60].

# **1.3.4** Natural Fibre Reinforced Composites (NFRCs)

As alluded to earlier, FRCs are typically reinforced with synthetic fibres such as glass, carbon, aramid and Kevlar [70]. Despite the suitability of these fibres to carry load and provide excellent properties to the composite, the desire to seek out more environmentally friendly reinforcements has led to a growing interest in the development of natural fibre reinforced composites (NFRCS), often shortened to NFCs. Here, a polymeric matrix encases a natural fibre, rather than a synthetic one, and cellulosic fibres such as flax, hemp and kenaf have garnered considerable attention [71-73]. Whilst the mechanical properties of natural fibres are typically not as favourable as synthetic fibres, in some applications they are able to compete on specific properties owing to their comparatively reduced density [14, 70, 74, 75]. Flax, for example, is used as an alternative to glass fibres to reinforce materials used by the automotive industry [14, 74, 75]. Despite the benefits of using natural fibres, NFRCs are nevertheless mixed component materials with a synthetic polymer matrix and so the difficulty in recycling remains. Additionally, there is always a challenge in creating a strong bond between the fibre and matrix phases.

## **1.3.5** Single Polymer Composites

Whilst consideration of the fibre component of composite materials is important in the context of cellulosic fibres, the matrix component is of equal importance to achieve the desired balance of material properties. The matrix component can take many forms in addition to polymers, for example, metals, and ceramics, however, polymers are most common matrix materials for composites [49], and is of particular relevance within the scope of this work. The matrix component of NFRCs commonly comprise thermoplastic polymers such as polypropylene (PP) and polyethylene (PE) or thermoset such as epoxy resin [76, 77].

One of the key challenges in composite production is making sure the individual components can truly combine and enhance one another, and this is highly dependent on the interfacial bonding that occurs at the interface between matrix and reinforcement. For composites with chemically different components this bonding is difficult to achieve and additional components need to be added such as surfactants or coupling agents [74]. The reduced adhesion at the interface between matrix and reinforcement phases can lead to reductions in mechanical performance as well as a risk of water uptake that will negatively affect the properties of the composite [7, 8, 56]. The heterogenous nature of a traditional mixed-material composite adds complexity to the recyclability of the material, as the two components will need to be liberated from each other before they can be reused [78].

These considerations led to the development of the single-polymer composite, where a polymer such as synthetic polypropylene (PP) forms both matrix and reinforcement phases. Here, the surface of an orientated polymer fibre is selectively melted under the application of heat to form the matrix fraction, through a process termed hot compaction [79]. This results in a material comprising two chemically identical phases that can be recycled easier after use.

Natural polymers such as cellulose could be used for both reinforcement and matrix as an alternative to fossil-derived polymers such as PP. The concept of using the same material for both component phases has been used in the development of homogeneous, natural polymer composites such as all-cellulose composites (ACCs) which will be discussed in the next section.

# 1.4 All cellulose composites (ACCs)

ACCs are a type of biocomposite where both the matrix and reinforcement are made of cellulose [7, 8]. This is a mono-component composite whereby the reinforcement is provided by the inherent high strength of cellulose and held together by a cellulosic matrix. This overcomes the issue faced with heterogeneous composites, where poor interfacial bonding and inefficient stress transfer can arise between chemically incompatible components [46, 80, 81]. The homogeneous nature of a ACCs is comparable to that of single-polymer composites mentioned in section 1.3.5, the key difference being that ACCs comprise a natural polymer, rather than a synthetic one. The preparation of ACCs was first reported in 2003 [7], and there has been much interest in the area since.

As the matrix and reinforcing components are chemically identical, they will bond well to one another [8], and this means that the interface can be reduced or even eliminated entirely [7, 82]. This reduces the need for extra treatments or added components used to reduce the interface, and can lead to composites with increased mechanical performance [7, 8]. The term composite can still be used however, because despite the components being chemically identical, there can be a significant difference in structural and physical morphology between the two phases [8, 46].

# **1.4.1** Formation of ACCs

The formation of the matrix fraction within the single-polymer composite is achieved by melting the surface of orientated polymer fibres [79]. Cellulose, however, does not melt [7, 83-86], and so the use of a dissolution process is required to generate a matrix phase from it. The continuous matrix phase of an ACC can be made by dissolving cellulosic material to form a solution that can surround and hold the cellulosic fibres that provide reinforcement. This was first demonstrated using a two-step dissolution process where cellulosic fibres were dissolved in a solvent to form a solution into which further cellulosic fibres were immersed [7], as illustrated in Figure 1-7. The dissolved cellulose regenerates to form a cellulose II matrix around the additional fibres, creating a composite of regenerated cellulose II around native cellulose I fibres.



Figure 1-7. Two-step method for forming ACCs.

A one-step process was later proposed by Gindl et al. [8], where one cellulose source (microcrystalline cellulose (MCC)), was partially dissolved, allowing it to form both reinforcement and matrix phases in the resulting ACC. On coagulation and solvent removal, the dissolved fraction formed the matrix component, leaving the undissolved fraction available to serve as the reinforcement. The principle of partial dissolution later inspired the concept of 'selective dissolving' the surface of a cellulosic fibre [87, 88]. The dissolved outer layer forms the matrix phase after coagulation, leaving the inner core undissolved to serve as reinforcement. This has also been referred to as 'surface-selective dissolution' [87], and nanowelding [89], and is illustrated in Figure 1-8.



Figure 1-8. One-step method for preparing ACCs.

The advantage of the single component, partial dissolution method is that it is less susceptible to the phenomenon of differential shrinkage [84, 90], which can occur during dissolution and regeneration. Cellulose is susceptible to swelling which can occur when put into contact with a compatible solvent that can dissolve it. The solvent works its way into the cellulose structure and initiates the breaking of certain hydrogen bonds in more accessible regions [91]. The bonds break and the solvent fills the space, pulling the chains away from each other, causing the cellulose to effectively 'swell'. This swelling can occur during dissolution in ACC formation, as the dissolution leads to a mix of dissolved and undissolved sections of cellulose which will swell to varying amounts. Differential shrinkage can then occur during regeneration due to the differences in swelling which causes voids to develop between the matrix and reinforcement sections [84].

Cellulose can be dissolved with, or without prior modification, the details of which are discussed more in section 1.6, however, on contact with a suitable solvent, dissolution occurs through a similar set of stages as observed for most polymeric systems [92]. The polymer network initially swells, allowing the solvent to diffuse into the polymer and polymer chains to disentangle and move into the solvent. After the dissolution process, solvent removal is carried out in a bath containing an antisolvent which essentially breaks the bonds formed during dissolution between the solvent and cellulose. Here, new hydrogen bonds are formed between the cellulose chains, resulting in the formation of the cellulose II allomorph [20, 28, 93]. This process is often referred to as coagulation [88, 94-96] and common coagulants used are water [95, 97, 98], ethanol [96], and methanol [7, 88].

## **1.4.2** Cellulose sources

Early literature on the subject of ACCs involved the use of cellulose at the nanoscale (~1-100 nm) as the reinforcing component, for example MCC [8, 99], and microfibrillated cellulose (MFC) [80, 100], and many cellulosic sources have since been used to generate the reinforcing and matrix components. Regarding the two-step method, the matrix has been formed from natural sources such as kraft pulp [7] and filter paper [11]. In the one-step method, natural sources used to form both matrix and reinforcement include nanowhiskers [101], filter paper [82], flax [97],

and ramie fibres [102], as well as man-made cellulose fibres such as unidirectionally aligned lyocell fibres [87] or lyocell fibres made into nonwoven mats [97].

#### Native fibres

The composition of natural fibres can influence the way they interact with a solvent during dissolution, which will influence how they remain in the final composite. As mentioned in section 1.2.1, the surface of native fibres consists of a less orientated crystalline region, with regions of higher orientation towards the centre. Cellulose fibres typically have five identified modes of dissolution depending on the quality of the solvent system used [91], which involve swelling and ballooning of the fibres. This, however, refers to the dissolution of cellulose fibres which are at a scale of approximately 10-25 microns [27, 103]. Cotton yarns for example, are made up of individual bundles of fibres, each bundle comprising many elementary cotton fibres. These bundles are twisted to form the cotton yarn used in textiles which, at a larger length scale (300-500 microns), swelling and ballooning mechanisms are not observed.

The use of cotton in ACC production has not been quite as common as other natural fibres and this is possibly due to the fact that the primary use for cotton fibres is established within clothing and textiles. Although the reinforcement potential of cotton has been investigated within polymer composites [104], its use within ACCs has not yet been thoroughly explored. Nevertheless, there has been some studies involving cotton fabric with promising observations, for example there is some evidence to suggest that cotton fabric can exhibit superior tensile properties and can maintain a higher elongation to break than wood timber in hot-pressed composites [105].

#### Man-made / regenerated fibres

Regenerated fibres can provide an effective reinforcement as a fibre. Indeed it has been shown that ACCs produced using lyocell fibres for example can exhibit better tensile properties (Young's modulus of  $7.2 \pm 1$  GPa and tensile strength of  $78 \pm 4$ MPa) than ACCs produced from natural flax fibres (Young's modulus of  $4.6 \pm 1$ GPa and tensile strength of  $34 \pm 2$  MPa) [97]. The use of regenerated fibres in ACC production was first demonstrated through the partial dissolution of lyocell fibres using NMMO [88], the solvent used in the production of lyocell fibres from wood pulp (as discussed in section 1.2.2).

The production process can influence the properties and morphology of different MMCFs, which in turn will affect the mechanism of how they will dissolve in a solvent. Lyocell fibres, for example, produced via direct dissolution in NMMO, have been shown to have notably different structure and properties to traditional regenerated cellulosic fibres produced via the derivatisation driven Viscose process [106, 107]. A dry jet-wet spinning process is employed in lyocell production, where a spinning dope is prepared from the dissolution of wood pulp in an NMMO-water mixture, and subsequently extruded into a precipitation bath at elevated temperature through an air gap [106]. The coagulated cellulose fibre will then typically undergo washing, drying and any post-treatments. The stages of processing can each contribute to the final structure and properties of the fibre.

It is largely understood that lyocell fibres possess a skin-core morphology [107-111]. The core consists of highly oriented, elementary fibrils of cellulose II crystallites in a parallel arrangement, connected in the fibre direction by amorphous regions as well as elongated voids [41, 109, 111]. This core is the origin of the high orientation possessed by lyocell, surrounded by a skin layer being of a lower orientation. This skin layer has been described as two distinct sub-layers consisting of a thin, semi-permeable outer skin of low orientation, and a porous mid-zone with more orientated cellulose chains [108, 109]. This seemingly heterogenous structure, however, has not been observed to provoke any significant differences in dissolution behaviour. Indeed, it has been suggested that lyocell fibres possess a more homogenous structure than viscose and Model [108], resulting in a uniform dissolution in solvent from the skin to the core [110, 112].

# **1.4.3** Textile reinforced ACCs

There is growing interest in the use of textiles made from cellulose sources such as cotton [81, 98, 105], and regenerated cellulose, most frequently Rayon [84, 96, 113-115], and lyocell [116]. Among the methods reported, partial dissolution of a textile in solvent [84, 98, 113] has been demonstrated, akin to the one-step process, as well as combining textiles with a pre-dissolved cellulose solution [115] as the two-step method.

# **1.4.4** Challenges in ACC formation

Most studies have so far produced all-cellulose composites in film form with thicknesses varying from 0.2-1 mm, and to broaden the range of potential applications of these composites it would be necessary to look at producing thicker, more three-dimensional structures [112]. This can be a challenge as creating a solid three-dimensional structure from a liquid requires the liquid to be cast in a mould.

When producing ACCs, the liquid solution formed after dissolution is composed of cellulose and the solvent. The solvent must be removed so that the dissolved cellulose can coagulate and regenerate to form the composite, and so the final volume of solution available to be put into a mould will be reduced.

The use of textiles offers a route to overcome this, where thickness could be built by stacking layers of textiles together, a concept not unlike the formation of laminate structures in traditional composite manufacturing mentioned earlier. Inspired by the lay-up method used in traditional infusion-based composite formation [48], the production of ACC laminates with thicknesses of 1.6-2.3 mm have been demonstrated using a variation of VARTM known as solvent infusion processing (SIP) [84, 113], where layers of viscose rayon textile were assembled inside a bag held under a vacuum, into which the solvent was introduced.

Whilst the use of textiles can help build thickness in ACCs, the issue of void formation in layered assemblies remains a challenge that must be addressed to improve performance and widen the practical applications of ACCs [117]. It is crucial for there to be excellent adhesion between the matrix and reinforcement phases of a composite material to achieve a desirable balance of mechanical properties. Having chemically identical matrix and reinforcing phases allows ACCs to overcome the issue of poor bonding at the fibre-matrix interface, however, obtaining strong interlayer bonding between the textile layers still requires sufficient matrix to be produced. It is well understood that sufficient matrix formation can support a strong fibre-matrix interface and help to efficiently transfer external loads to the fibres, thus getting the best out of the properties [102]. This is also the case in traditional laminate constructions, where thin sheets are stacked together to achieve the desired thickness.

The two-step process route relies on complete dissolution of the cellulose material, and as such, large amounts of solvent are needed which can elevate costs considerably. It is important to note that although one-step method can offset this with reduced solvent use, the volume fraction of the reinforcing component must be sufficient to avoid the reducing the properties of the outcome ACC [117]. This is because the dissolution itself creates significant change to the cellulose physical state. In the two-step method, fresh fibres are added to the dissolved solution and can therefore contribute their high strength without modification. By subjecting the entire starting material to dissolution in the case of one-step partial dissolution, the fibre reinforcement within the composite will need to undergo a sufficient amount of dissolution in order to create enough matrix to bind the undissolved fibres together. This will reduce the volume of undissolved cellulose remaining within the composite which will ultimately affect the properties.

Producing sufficient matrix to bond the fibres together is of further crucial importance when applied to laminate ACC constructions. Layered composite structures are susceptible to delamination [118] which can be caused by interlaminar voids and insufficient bonding between the layers. Despite attempts to create laminate ACC structures, avoiding the formation of voids between layers is still a challenge [84]. The one-step partial dissolution method requires balancing the production of sufficient matrix material, along with limiting fibre dissolution to ensure the fibres can adequately reinforce the composite. Obtaining adequate matrix and reducing voids is particularly challenging when using textile structures, and a reason for this can be suggested by looking at how bonding is achieved when thermoplastic polymer fibres are selectively melted during hot compaction. Here the outer skin of each polymeric fibre is selectively melted, which on cooling forms the matrix phase of the single polymer composite [119]. The fraction of melted polymer, however, is not always sufficient to adequately bond layers of woven polymer filaments, owing to the pockets of space that exist between the individual textile layers, due to the textile surface roughness. More material is therefore needed to produce a matrix that can achieve adequate bonding in the intra-textile layer, as in the absence of this, delamination can occur [113]. A similar situation can be attributed to the partial dissolution of cellulosic fibres within a textile, where a layer of dissolved material around each fibre surface is produced, forming the matrix to aid fibre-to-fibre bonding. The amount of cellulose that can be dissolved is highly influential in determining the matrix fraction of the resulting composite [84].

## **1.5 Interleaf films in ACC production / Novel ACC developments**

Recently, a method of forming ACCs has been presented that can potentially overcome the barriers associated with poor bonding and inadequate peel strength, offering potential to create three-dimensional structures. This patented [117] technique combines the advantages of the one and two-step methods by reducing the amount of solvent needed whilst still achieving an adequate ratio of matrix and reinforcement to bond fully.

Here, an interleaved cellulose film is placed between layers of woven cellulosic textile in a modified partial dissolution process. The key element of this method is at the preparation stage, and the formation of a pre-formed structure created from layers of two cellulose based materials; a cellulosic-based fabric and a film of regenerated cellulose [117], akin to the two-step method described previously. The incorporation of a chemically identical interlayer film to achieve sufficient matrix has been previously reported with regard to thermoplastic single polymer composites [119], resulting in increased interlayer strength without requiring significant reduction in the fraction of reinforcing fibres. It is suggested that the placement of matrix-forming material in-between the textile layers can target matrix production to where it is needed the most; the interlayer regions which can be a weak point in multiple layer composites. This then improves interlaminar adhesion, whilst limiting overall fibre dissolution, allowing the mechanical properties of the textile reinforcement to be utilised more efficiently. This structure is partially dissolved in solvent where the outer layers of both cellulose sources are dissolved to form the matrix in the same way as described previously. After dissolution, the cellulose undergoes regeneration by washing in a coagulant bath to form the composite.



#### Figure 1-9. ACC formation using layers and partial dissolution.

The resulting composite comprises a structure of three distinct phases, as shown in Figure 1-10:

- 1. A matrix of cellulose II and amorphous cellulose formed from the dissolved outer surface of the cellulosic textile and film.
- 2. Reinforcement phase of undissolved fibres from the cellulose textile made up of cellulose I and a small fraction of amorphous cellulose.
- 3. Undissolved film comprising regenerated cellulose (cellulose II). Ideally, the thin (~20  $\mu$ m) interlayer film completely dissolves and so is then indistinguishable from the dissolved outer layers of the cellulose source.



Figure 1-10. ACC layers after dissolution process. The image to the left represents the cross-sectional view of layers within the ACC, and a larger view of the layers is shown to the right.

Bonding between the textile layers is improved using this method and this is because the two phases at the interface are chemically compatible, owing to partial dissolution of two cellulosic materials. The matrix is formed from the dissolution of both materials, creating a chemically compatible phase of cellulose. Many layers can be built up for dissolution allowing thicker composites to be produced, and with the strong internal structure present, they are more able to withstand the strain and stresses incurred during processes such as moulding. This creates light, stiff and strong materials that can be shaped into three-dimensional objects [117]. The advantage of using textile pre-forms in ACC preparation allows the resulting material to possess a structural form without the need for casting which would be required when free floating fibres are added to a cellulose solution [117].

This method offers a way to overcome the challenge of partial dissolution described in section 1.4.4, where producing sufficient matrix for the composite may mean a compromise with the amount of reinforcing fibre fraction remaining to give the ACC strength. The addition of a cellulose film layer between fabric layers leads to the generation of adequate fibre and matrix components to support interlaminar bonding, in a single-polymer composition that supports interfacial compatibility. Improved strength can be achieved with the film reinforcement to offset the loss of fibre volume that arises through partial dissolution.

## **1.6 Cellulose solvents**

As mentioned previously, cellulose must be dissolved in a solvent rather than melted to produce ACCs [7, 8]. It is known that cellulose is insoluble in water and many organic solvents [91, 120], and the reasons for this have been widely debated in literature [20, 121, 122].

The underpinning concept of dissolution mechanics states that for two given components, if the mixed state is of a lower free energy than the separate phases, dissolution will occur [121]. Dissolution may still be too slow, however, requiring heating or agitation, which is easier for low molecular weight (M<sub>w</sub>) solutes. In the case of polymers, achieving fast dissolution is still difficult, and this relates to the multi-step process of polymer dissolution. Initially, the solvent diffuses to the polymer surface, causing the outer layer to swell, and the polymer transforms into a gel-like medium. The polymer chains will then start to move into the bulk solvent solution which can be a slow process because before they can move, they must first disentangle. This process is even slower for semi-crystalline polymers like cellulose.

In early literature, one frequently cited notion to explain cellulose solubility was related to the extensive network of intermolecular hydrogen bonding within its structure, and the understanding that an effective solvent needs to be able to firstly break these bonds, and then form new hydrogen bonds with the solute [120, 121, 123, 124]. However, this alone did not fully explain why some solvents could dissolve cellulose while others could not. For example, cellulose is not soluble in water, and since solubility is often determined by a solvent's ability to form hydrogen bonds, one might expect cellulose to dissolve in water, given water's strong hydrogen bonding properties. As this is not the case, it soon became clear that the mechanisms surrounding cellulose solubility and the structure of cellulose itself warranted new perspectives to aid the discovery of new cellulose solvents [121]. In 2010, Björn Lindman proposed that other factors, particularly hydrophobic molecular interactions, also play a role in cellulose's solubility, challenging the previous theory that focused solely on hydrogen bonding [121]. The Lindman hypothesis, as it has come to be known [125], discusses the amphiphilic nature of

cellulose; amphiphilic being a term given to molecules that have both polar (hydrophilic) and non-polar (hydrophobic) regions. Amphiphilic polymers tend to organize themselves into structured formations when placed in a solvent such as water, a process known as self-assembly. It is suggested that the hydrophobic sides of cellulose will stick together in an aqueous environment, lowering its solubility in aqueous environments [121]. The Lindman hypothesis has been challenged, however, with suggestions that the dissolution behaviour of cellulose has other potentially influential factors [125]. For instance, it has been proposed that the interaction between hydrogen bonds, Van der Waals forces, and hydrophobic effects should be considered during the dissolution process.

Whilst the complexity of cellulose dissolution is evident and our understanding far from complete, there are several well-documented cellulose solvents in use that we have a good understanding of. The two main types of solvents for cellulose can be characterized by the way in which they achieve dissolution, and these are known as derivatizing, and non-derivatizing solvents.

# **1.6.1 Derivatising solvents**

Derivatizing solvents work by modifying the cellulose at a molecular level to produce an intermediate that can then be dissolved [126]. By interacting with its hydroxyl groups, it forms a cellulose derivative which, after dissolution, is either used as the derivative, or chemically converted back to cellulose. The chemical conversion process is known as regeneration [124], the term used to describe fibres produced though dissolution-based processes as discussed in section 1.2.2. The Viscose process was one of the first commercial applications of cellulose derivatives, producing viscose fibres mentioned previously. In this process, cellulose is reacted with carbon sulphide to produce cellulose xanthate which can then be dissolved in sodium hydroxide. In this process the viscose is then converted back to cellulose and spun into fibres using sulphuric acid and zinc sulphate. This process is complex in terms of the steps required to create the derivative and consequently revert it back to cellulose. Several steps are required before dissolution, and the chemicals required to chemically modify cellulose and convert it back, can lead to the creation of unwanted based by-products [84]. In addition to this, a large amount of solvent is required to achieve this modification and produce the derivative [126].

# **1.6.2** Non-derivatising solvents

Non-derivatizing solvents are able to directly dissolve cellulose without any intermediate derivation steps [46], and they do this by breaking the hydrogen bonds within the cellulose supramolecular structure, so that new hydrogen bonds can be made with the solvent [127]. These can also be referred to as direct solvents, and there are many examples of such solvents being used to produce ACCs, the most common solvents being N,N-dimethylacetamide/lithium chloride (DMAc/LiCl), N-methylmorpholine-N-oxide monohydrate (NMMO), and Ionic Liquids [7, 8, 11]. Some of these non-derivatizing solvents will be discussed in more detail in the following section.

The first ACCs were produced using a DMAc/LiCl solvent system [7]. This is an example of a non-derivatizing direct solvent, however, in this system the cellulose is not converted into a soluble derivative prior to dissolution. Instead, the cellulose is

'activated' to make it soluble [124]. Cellulose fibres are pre-treated using water, acetone and DMAc [7, 8, 87] after which the fibres can then be immersed into the solvent. The reasoning behind this activation step relates to the mechanism of cellulose dissolution which, as mentioned previously, has been discussed extensively throughout literature [20, 91, 123, 124]. It is understood that one of the factors influencing cellulose dissolution is the breaking of hydrogen bonds between the cellulose chains, allowing the hydroxyl groups to subsequently make new hydrogen bonds with the solvent. It has been suggested that this is linked to a swelling mechanism that cellulose undergoes during dissolution, [124] which influences the accessibility of the hydroxyl groups present in its structure and their subsequent availability to make bonds with the solvent [128]. The abundance of strong hydrogen bonding between cellulose chains makes this a challenge for any solvent system, and the activation step initiates swelling via the breaking of these bonds, making them available to bond with the solvent molecules [32]. Once activated, the cellulose can then be dissolved using DMAc/LiCl. The DMAc forms a complex with lithium, releasing chloride as an anion that can readily interact with hydroxyl groups [127]. Dissolution of cellulose using the DMAc/LiCl system can be carried out at ambient temperatures however, the process can be lengthy, with up to 12 hrs before formation of composites [7]. Additionally, DMAc and LiCl together form a toxic combination that is both volatile and corrosive [100, 129], and these health and safety concerns are a barrier for its industrial potential.

NMMO is a direct solvent used in the industrial production of lyocell fibres and is considered a more environmentally sound alternative to the Viscose process [130], mainly because it is non-toxic, biodegradable, and can be recycled up to 99 % in industrial processes [36]. NMMO is amphiphilic, supporting the theory that

cellulose is also amphiphilic [131], and has a high dissolution capacity for cellulose [132]. Although the use of NMMO has seen industrial success for fibre production, there are still challenges in its use, such as the high costs associated with the process [133]. In addition to the economic drawbacks, there are some safety concerns that relate back to the chemistry of the process reactions. Side reactions such as oxidation and free-radical generating homolytic fissions can lead to by-products that cause NMMO degradation, as well as chemical alteration of the pulp [36]. To avoid this, large amounts of stabilizers are needed which increase cost and complexity of the process [132]. Other heterolytic reactions can occur which cause the temperature to increase uncontrollably, known as 'thermal runaway' reactions, and these can be particularly dangerous to control. In addition to this, the cellulose itself can degrade which ultimately affects the properties of the ensuing material. In the case of the lyocell process the fibre produced can be discoloured and suffer from fibrillation which ultimately affects the dying capabilities [134]. It is therefore important to carefully consider the solvent to be used for cellulose dissolution, to ensure the properties of the cellulose can be maintained. Consequently, there is an interest in looking for alternatives to NMMO as a solvent for cellulosic materials for fibre production [83]. The use of 1,5-diazabicyclo[4.3.0]non-5-enium acetate ([DBNH]OAc) for example, has been reported as a less harmful solvent to convert cellulosic material into regenerated fibres for spinning [135]. [DBNH]OAc belongs to the family of chemicals known as ionic liquids, and their potential for cellulose dissolution will be discussed in more detail in the next section.

#### **1.7 Ionic Liquids**

Ionic Liquids (ILs) are salts with a wide liquid range [80, 136], composed of a combination of one anion and one cation. The term ionic liquid is given to salts with relatively low melting points, but more specifically below 100°C [137], existing as liquids at comparatively low temperatures, and can also be referred to as room temperature ionic liquids (RTILs) [138]. They are stable at high temperatures and have low vapour pressures [139], meaning that they typically have low volatility, and have been seen as favourable alternatives when compared to traditional volatile solvents [123]. ILs have also been shown to be highly effective at dissolving cellulose, with dissolution capacities comparable to NMMO [126].

Owing to the vast combinations of cations and anions that can be present, it is possible to form an IL for a specific purpose, such as to increase the yield of a particular reaction. ILs are therefore highly tuneable and have been labelled as 'Designer Solvents' [140, 141]. Many ILs have been found to have strong dissolving power with regard to cellulose and are able to form fully dissolved solutions with cellulose concentrations of 5-10 wt.% with ease [127]. At 10 %, a viscous liquid crystal solution can be formed, and this has potential for high strength materials applications if the crystallinity can be retained in the solid state [127].

The combination of cation and anion within an IL is important in determining whether a particular IL will dissolve cellulose. It has been found that imidazolium and pyridinium based ILs with chloride [123] [Cl]<sup>-</sup>, or acetate [142] [Ac]<sup>-</sup>, anions can dissolve up to 20 % w/w cellulose [127]. The ability of ILs to dissolve cellulose comes primarily from the hydrogen-bond accepting ability of the anions, and so the choice of anion is a particularly important factor. Chloride and acetate ions are

strong hydrogen-bond acceptors (HBAs), capable of achieving the initial bond breaking step. This allows direct dissolution of cellulose without prior derivatization.

Another distinct advantage with using ILs with these anions is that there is no need to activate the cellulose as in the case for DMAc/LiCl. With the DMAc/LiCl system, the chloride ion needs releasing first, which occurs after the DMAc has formed a complex with the lithium atom. The concentration made available, however, is not sufficient to break the hydrogen bonds between the cellulose chains and this means that pre-activation is needed as mentioned previously [127]. In ILs, the HBA ion is already free and does not need a second compound to facilitate its release. Its concentration can be three times as much as from the DMAc/LiCl system (20 % compared to 6.7 %) [127]. At these concentrations, the anions can break the hydrogen bonds holding the cellulose chains together and further make new bonds with the hydroxyl groups. The cation is favourably displaced by the cellulose hydroxyl groups which then forms new bonds with the anion [142].

## **1.7.1 1-Ethyl-3-methylimidazolium Acetate**

The IL used in this work is 1-Ethyl-3-methylimidazolium Acetate ([C2MIM][OAc]), often abbreviated to EMIMAc. [C2MIM][OAc] has an imidazolium-based cation, and an acetate anion, and has been found to be one of the most efficient solvents for cellulose [143], capable of dissolving up to 27 % w/w cellulose [142].

Figure 1-11. Structure of ionic liquid 1-Ethyl-3-methylimidazolium ([C2MIM][OAc] ). Right: 1-Ethyl-3-methylimidazolium cation Left: acetate anion

# **1.7.2** Use of Dimethyl Sulfoxide as a co-solvent for EMIMAc.

ILs typically possess a high viscosity, which increases further when introduced to a polymer such as cellulose [144]. This poses a significant challenge for dissolution, as increased solvent viscosity can restrict mass transport and subsequently limit the amount of dissolution that can occur [145]. To overcome this, co-solvents have been used to modify the viscosity of ILs and improve cellulose dissolution [146, 147].

Dimethyl sulfoxide (DMSO) is produced as a by-product from the production process used to make paper from wood pulp [148]. It is a colourless, aprotic solvent, often cited in literature as a co-solvent that, when mixed with ILs to dissolve cellulose, can reduce IL viscosity without compromising its ability to form solventsolute bonds with cellulose [144, 149, 150]. It is also acknowledged as having the ability to improve the solvation power of ILs and there are different reasons behind this cited in literature. One reason relates to its ability to reduce IL viscosity which assists mass transport [145], this has likewise been related to how DMSO can modify the diffusion coefficients of the IL's ions [149]. This makes it an ideal choice over co-solvents such as water that interact with the IL, and interrupt the solute-solvent interactions required for dissolution [145].

# **1.8** A design of experiments approach to optimise ACC processing parameters.

From a sustainable manufacturing point of view, finding a balance between product functionality and process feasibility is extremely important to ensure the best quality product can be achieved whilst minimising costs and processing times [151].

It is well known that processing parameters play an important role in the resulting properties of composite materials [152, 153], indeed many industrial systems comprise multiple factors that may influence the required output.

In the production of ACCs, for example, there variables such as processing time, temperature, and pressure, as well as solvent composition and raw materials. Understanding the relationships between these various system factors and a given output, as well as the interactions between factors, often requires a systematic approach to experimentation to analyse all possible combinations in the most time-efficient way. A systematic approach to planning appropriate experiments can provide a rich source of information, and help understanding the complexity of a given system seem less of a daunting task [154].

Design of Experiments (DoE) is a powerful and well-established statistical approach to process understanding, improvement and optimisation, and offers a route to obtain a large amount of insightful information with a relatively small amount of experimental effort [154-159]. It allows multiple influential factors to be analysed simultaneously, whilst keeping the total number of experimental runs to a minimum [154, 156-158, 160]. DoE is often to referred to as statistical experimental design [159, 160] where probabilities are applied to experimental data rather than theory [154, 159], and factors are analysed in terms of their statistical significance to a given system [156]. In other words, DoE doesn't rely solely on theoretical assumptions of predictions and instead, interprets the data obtained from experiments using statistical principles and probabilities. Decisions are data-driven based on empirical evidence rather than just theoretical models. Factor combinations are chosen such that a rich amount of information can be obtained about a given process or system, to ascertain the significance of each factor or factor combination on a particular response [156, 159]. A great deal of insight can be gained from a carefully structured set of factor combinations, allowing interactions between factors to be identified, and conclusions to be drawn about the influence of factors on a specific output parameter [154, 156, 158].

#### **1.8.1** Benefits of DoE

DoE offers a more desirable route to process understanding than traditional trial and error or one-factor-at-a-time (OFAT) methods, where all factors are fixed except for the one being varied [158-160]. Once optimized, this factor is fixed for subsequent experiments where another factor is then varied, and the process continues until all factors have been optimized [155, 156, 158]. In addition to being time-consuming and resource heavy, this approach is unable to differentiate between the inherent variation in runs (the 'noise') and genuine improvements in the system outputs [156, 158]. Noise factors are difficult to avoid or control and in the absence of systematic planning with OFAT, there is less control over the process conditions, and so it is harder to know for sure if notable changes in the response are exclusively due to key factors, and not simply a consequence of uncontrollable noise [156]. Consequently, the quality of information generated from OFAT may not be sufficient for the desired objective [155], and additional experiments may be needed which contributes to extra time and resource use [153, 154]. Figure 1-12 shows an experimental design space for a system with three factors and the runs involved in an OFAT design, as compared to what a typical DoE study may look like. The runs in the OFAT cube are closely related to each other, with little information available for other regions of the cube. With a DoE study, the entire domain is reasonably covered by the experimental runs.



Figure 1-12: Distribution of experimental runs in OFAT compared to DoE.

Additionally, in the absence of a pre-planned set of experiments, the ability to truly optimise a process using the OFAT approach is inhibited by researcher bias and initial decisions driving the starting point of factors to fix, and those to vary [156, 158]. In DoE, all experimental runs are established at the beginning, rather than being built upon throughout. With a well-designed experiment, there is no initial bias driving how and what runs are conducted, allowing for optimum conditions to be found that may not have been thought of before [156]. Factors are evaluated independently of each other whilst being systematically varied at the same time as

others [154]. Single-factor (main) effects can be identified, as well as synergistic effects between factors which otherwise might be missed with an OFAT approach [155, 156, 158].

The insights gained from DoE can lead to improvements in product quality, performance and consistency, and minimize risks that could potentially reduce costs [160, 161]. Sustainable manufacturing is becoming increasingly important within the research field and more decisions are being needed with respect to green processing [156]. Understanding processes better can help to reduce waste and improve resource efficiency, making it desirable for future innovations and product development.

## **1.8.2** Applications of DoE

DoE has been used widely across the pharmaceutical industry to optimise product formulations and improve product quality [154, 162-164]. The versatility of DoE, however, allows its applications to extend into a wide range of industries such as food production [165], steel processing [166, 167], biomass extraction [157, 168] and biofuel production [169]. In addition to simply reporting the application of DoE, these examples highlights the benefits of the approach over the traditional OFAT methods, for example in reducing costs of running multiple experiments [163], and supporting the application of statistical analysis at the planning stage of research to obtain the most appropriate data for analysis [163, 167].

In the materials industry, the use of DoE has been applied to optimise composite performance in various manufacturing processes such as resin transfer moulding (RTM) [170] and heat press forming [153, 171]. Composites with traditional reinforcements such as carbon fibre [170] and glass fibre [172] have been studied, as well as natural fibre reinforced composites (NFRCs) reinforced with flax [153], coir [173], and kenaf [171, 174]. It has been possible to optimise continuous factors such as fibre content through the application of DoE, a task that, through OFAT, would have required a larger experimental burden [171, 173]. Hot compaction is used widely in composites production [175] where process factors such as temperature, pressure, and time can be influential in the resulting mechanical properties [153, 172]. It has been the subject of several experimental design studies with respect to the production of composites comprising wood/rubber [176], glass/PP [172], flax/PLA [153], and kenaf/PP [171]. These studies highlight the ability of DoE to identify significant process parameters in materials manufacture, where there are many to choose from. One of the most significant benefits of DoE over OFAT, however, is in its ability to identify interactions between factors that would not be identified as easily through OFAT. For example, in the manufacture of wood-rubber composite panels, interactions between pressing time and temperature, and board density have been identified through the use of DoE [176]. The identification of significant interactions has helped predictive models to be developed in the machining of steel [167], and greater process behaviour understanding to be gained in the manufacture of flax/PLA [153], and kenaf/PP [171] composites.

DoE can play a crucial role in accelerating process understanding in the materials industry, particularly in the field of novel material developments such as ACCs where insights are only just developing. However, despite the growing interest in applying DoE to the manufacture of composite materials, its application in the field of ACCs is in its infancy, with only two known reported studies [9, 177] to the best of available knowledge. It is, therefore, worthwhile to investigate the application of DoE in this work and develop insights that can contribute to the field of ACCs.

## **1.8.3** Statistical analysis

In statistical DoE the aim is to generate a numerical model that describes the relationship between the response variable of interest, and the input factors that were varied in each run [161]. The primary tool for analysing data from designed experiments is linear modelling, a statistical technique used to understand relationships between variables, however, this is not limited to data following a perfect straight line [159]. Linear models assume a straight-line relationship in the sense that as one variable changes, the other variable changes in a consistent way. It is generally accepted that linear models can describe many industrial processes and systems within a specified range of conditions. Here, the behaviour is assumed to be smooth enough to be sufficiently described by a Taylor polynomial on which data analysis in DoE is based [159], where a response variable Y is written as a linear combination of the factors X1, X2...Xi... for each experimental observation.

In linear modelling, the way a response Y changes in relation to adjustments in fitting parameters (experimental settings) does not depend on the values of those parameters themselves, making the response predictable as the parameters change [159]. Multiple linear regression is the term used when there are more than one explanatory variable (factor) influencing a given response [159]. This contrasts with model-based DoE which uses complex equations to describe systems that are not straightforward (non-linear models).

The response variable is written as a product of each significant system factor. Each factor in the model has a numerical coefficient that is solved by applying least squares analysis. A simple linear model with only first order (main effects) would have terms for each single factor only, whereas second order terms such as two-factor interactions or quadratic (square) terms would have more terms. The final model will contain only the statistically significant factors as identified from statistical analysis of their significance using Analysis of Variance (ANOVA) [156].

#### **1.8.3.1** Analysis of Variance (ANOVA)

ANOVA is a widely used statistical method used in hypothesis testing to compare the means of different groups to find out if they are significantly different from each other [160, 178]. It works on the principle of the law of total variance, in which the total variance within a data set can be separated into components relating to different sources of variation; the sum of squares between groups, and the sum of squares within groups [160]. Here, the sum of squares between groups relates to explained variation due to factor effects, and the sum of squares within groups relates to unexplained variation due to random error. There are many different types of ANOVA techniques, and the appropriateness of one type over another will depend on the specific scenario and the way the study is designed [179]. ANOVA can be applied to complex experimental designs and data sets, and as such is used in DoE to determine the level of significance of multiple factors in affecting particular response variable [154, 178]. When applied to a DoE generated data set, ANOVA presents a set of values and test statistics to help identify the factors that have the most influence on the response:

#### Sum of Squares (SS)

This is a measure of variation relating to different components of a model, for example each factor or combination of factors (within groups), and variation in the data that cannot be explained (between groups). Adding all the SS values together results in the total SS (also known as the total variance) which is a measure of how different the data points in a data set are from each other. This is often presented as an Adjusted Sum of Squares (Adj SS), which is independent of the order in which the factors are added to the model. As such, it allows the unique contribution of each factor (independent of other factors) to be identified and interpreted.

#### Degrees of freedom (DF)

This is the number of independent values that can vary. For example, in a data set of 10 values with a given mean, all but one value has the freedom to be any number, but the final value is fixed so that the sum of the data divided by the number of data points equals the mean [180]. Each SS value will have a specific DF depending on the terms involved, and for n experimental runs, the total DF is n-1 [178].

#### Mean Square (MS)

MS is calculated by dividing the sum of squares (SS) by the degrees of freedom (DF), for each respective component of the model. It is a measure of average variability.

## F-value

This is a test statistic that helps determine whether the relationships in the data are strong or weak [160] and is calculated by dividing the MS of the respective component by the MS of the error (the average difference between predicted and measured values in the model). It compares how much a derived model can explain the variation in the data, compared to how much it cannot explain. A higher F-value suggests that the model can explain the data well, whereas a lower F-value means the model may not be very useful.

#### P-value

This is a test statistic that indicates the significance of a factor and the probability that there are no significant differences between the settings of each factor. In other words, it assesses the likelihood that obtained results happened by chance, rather than by a real effect. The P-value is calculated using the F-value within a given significance level, usually 0.05. A P-value under 0.05 indicates that the results are unlikely to be due to chance, suggesting that the observed effect is likely real [180]. A high P-value (> 0.05) indicates that the observed effect may not be significant, and the results are more likely to be due to chance.

Factors are disregarded based on their significance to the response variable, and only the significant factors are included in the final model. The model not only provides information on the factors influencing the process, but it also helps to describe the interactions between factors and highlight any conflicting factors present in the process can be identified and managed [155, 181]. The suitability of the final model can be supported by looking at the coefficient of determination,  $\mathbb{R}^2$ , which is an indicator of how well the experimental data fits the model and how well the variables in the model can explain the variation in the data [160, 182]. It ranges from 0 to 1, where 1 indicates that the model explains all the variability, and 0 indicates that it explains none of the variability. This value alone, however, is not an adequate indicator of a good regression model as it can be inflated with increased number of variables in the model, so it good practice to look at this alongside the adjusted, and predicted coefficients of determination, known as  $R^{2}_{(adj)}$  and  $R^{2}_{(pred)}$  respectively.  $R^{2}_{(adj)}$  reflects the number of variables in the model and is an adjustment of  $R^{2}$  to prevent it from increasing just because more terms are added. It can be useful in assessing how much of an impact the number of terms has on the fit of a model, and whether it might be overfit. If there is a notable difference between  $R^{2}$  and  $R^{2}_{(adj)}$ , this is another indication that there are insignificant terms in the model [160].  $R^{2}_{(pred)}$  provides a useful measure of how well the model obtained can predict responses for new, unseen data and is calculated by removing each observation in the data and re-estimating the model equation. The re-estimated model is then used to predict the response of that removed observation.

## **1.8.4** Experimental runs and design space

The first step in a DoE driven study is to generate a set of experimental runs for which to perform experiments. There are different ways to approach experimental design depending on the desired objectives, whether it be to screen multiple factors, optimise a process or make predictions [158], for example. Whilst different designs can differ in the information they can provide, they all share similar characteristics. A series of experimental runs or tests are planned, where each run is a combination of all input factors at varying settings (also referred to as levels), and the upper and lower limits of these levels are kept within the boundaries of the design space, also known as the experimental domain. The experimental domain is the region of experimental analysis specified at the initial stages of planning [155], confirming the boundaries within which to maintain factor levels. Experimental runs can be visualized as points within that space, located according to the factor combination and specific to the design. Commonly used design points in experimental designs include centre points, factorial points, and axial points. Centre points (CPs) are included in most designs and lie at the midpoint of all factor ranges, typically replicated provide a balanced estimation of error and assessment of repeatability [155, 159]. Factorial points (also known as corner points) are located at the extreme levels of all factors and are typically used in factorial designs. Axial points (also known as star points) are used to estimate curvature through quadratic effects in response surface designs [158, 160] and are typically located at expanded boundaries of the factorial space, but this can vary depending on the design (as elaborated on in section 1.8.6 later). The number of axial points used in a design equal the number of factors multiplied by two [160, 183]. For a system of three factors, the experimental domain can be visualized in terms of cube as shown in Figure 1-13.



Figure 1-13: Geometry of a 3-factor experimental domain shown as a cube, with some common points defined by factor combinations.

Choosing an appropriate design space is a key element of a well-designed set of experimental runs that can provide the most information [164]. A balance must be struck between opting for a design space large enough to avoid missing the optimum conditions [155], whilst remaining within an acceptable range to allow ease of operation, avoid any loss in product quality [155, 161]. The runs are designed such that the factors are varied simultaneously ensure that on analysis, the most information can be drawn from them [159, 164].

## **1.8.5** Types of design

As mentioned previously, a major advantage of DoE is the ability to gather a lot of useful data on a process with a relatively small amount of experimentation and obtain statically powerful experiments that can give the best quality data [159]. That said, the number of runs must be sufficient to obtain the data required, and this will vary depending on the design employed. There are many types of design from which a series of experimental runs can be generated, and the choice of design will be driven by the objectives of the work, and knowledge of the system under investigation. Broadly speaking, designs can be categorised based on two goals: screening and optimisation.

# **1.8.5.1** Screening designs

Screening designs are a useful starting point to efficiently gain information about a system and ascertain an appropriate experimental domain [154, 159]. They can be beneficial at the early stages of new product development to help screen factors and their relative influence on a specific response, identifying the most important ones in a cost and time-effective way [155, 156, 158]. Screening designs can model first
order main effects, i.e. main effects and interactions, and there are various methods such as definitive screening designs (DSD), Plackett-Burmen and factorial designs. Within the scope of this work, factorial designs will be discussed in more detail.

## **1.8.5.2** Full factorial designs

Full factorial designs are commonly used as a screening stage [160], and have been applied to the exploration of different materials in the composites industry to explore responses such as mechanical properties [171], impact behaviour [182], and machinability [174]. A full factorial design consists of factorial points, where experimental runs are carried out at all the highest-level settings, all the lowest level settings, as well as combinations of both, allowing all possible combinations of factors and levels to be tested [155, 159, 160]. This helps to assess the feasibility of the extreme conditions of a process and confirm that the design space within which they lie is acceptable. In addition, center points (CPs) are typically included in the factorial design. Figure 1-14 shows the full factorial design domain for a two-factor factorial design, and three-factor factorial design.



As well as main effects, exploring interactions between factors can be done using a factorial design approach, which allows you to understand the causal relationships of several continuous factors in a process system and makes the most efficient use of the data collected [160]. Factorial designs are good for exploring continuous factors as priority is assigned to the high- and low-level settings, rather than investigating several discrete values within a range.

Factorial designs are named as such based on how the number of required runs is calculated, for example a system with M factors each with k levels would need  $M = L^k$  runs. The most common factorial design is the 2<sup>k</sup> factorial, used for factors with two levels. Figure 1-14(a) and Figure 1-14(b) are a 2<sup>2</sup> and 2<sup>3</sup> factorial designs, respectively. Experimental data from a full factorial is fitted to linear model with main effects and interactions, where the predicted mean response variable  $\hat{y}_t$ , is written as a linear combination of the factors. The model is shown in the Equation 1-2 below for *M* number of independent factors [159], where x<sub>j</sub>, and x<sub>i</sub>x<sub>j</sub> denote the linear and interaction terms of the independent factor variables, and the coefficients determined when fitting the model for the intercept, linear and interaction terms are represented by  $\beta_0$ ,  $\beta_j$ , and  $\beta_{ij}$ , respectively.

**Equation 1-2** 

$$\widehat{y}_i = \beta_0 + \sum_{j=1}^M \beta_j x_j + \sum_{i< j}^M \sum_{j=2}^M \beta_{ij} x_i x_j$$

Full factorial designs are better placed for systems with only a small number of factors, as the number of experimental runs required increases considerably as the number of factors increases, rendering it unfeasible [155, 159]. For the same reasons, two-level factors are preferred, and whilst it is possible to conduct factorial designs for multi-level factors, the number of required runs would increase significantly and be impractical for many industries [155, 159]. Whilst it is possible to explore interactions between factors, the strength of factorial designs lies primarily in estimating linear main effects and this is due to the experimental runs being based on upper and lower limits and a single centre point [184]. They are, therefore, less powerful for estimating higher order effects such as quadratic effects [158, 174, 184] and so if curvature is suspected with a system, further experimentation is recommended after initial screening of the design space such as utilising response surface methodology (RSM).

#### **1.8.6** Response surface methodology (RSM)

Factorial and screening designs are powerful tools for understanding a process and identifying key influential factors, but their estimation power for effects beyond first order can be limited. An optimum response may lie in a region that has some curvature and so to estimate higher order terms with more confidence, RSM is often applied to obtain a second order model where all terms can be estimated [185, 186]. RSM is an approach that allows the estimation of second order (quadratic) effects through the inclusion of additional experimental runs within the experimental domain [159, 185, 187]. These designs are useful if curvature is suspected within a system, that a full factorial design cannot accurately estimate with factorial points alone. With the ability to estimate curvature, response surface models have some

predictive power, making them ideal for optimisation [159, 177, 188] which can be extremely beneficial for understanding systems that may have more than one area of optimum response as a result of different combinations of factor response [159].

RSM models are based on a polynomial model which is essentially the linear main effects model with added interactions and quadratic terms [159]. The response surface model is shown in the Equation 1-3 below where  $x_i^2$  denotes the additional quadratic term of the independent factor variables, and  $\beta_{ii}$  represents the coefficients determined when fitting the model for quadratic terms.

#### **Equation 1-3**

$$\widehat{y}_{i} = \beta_{0} + \sum_{j=1}^{M} \beta_{j} x_{j} + \sum_{i < j}^{M} \sum_{j=2}^{M} \beta_{ij} x_{i} x_{j} + \sum_{i=1}^{M} \beta_{ii} x_{i}^{2}$$

Crucially, numerical factors need to have more than two levels for an RSM model to be able to predict quadratic effects [159, 185]. For systems with a small number of factors, RSM is appropriate choice of approach, but beyond 6 factors, and RSM can become difficult to implement owing to the increased number of runs required [188]. Typically, a response surface design is applied after an initial screening stage has been used to locate an optimum region. RSM can then provide the best estimate of key factor interactions. It can, however, be applied as a main step for systems with a small number of factors to start with.

#### Central Composite Designs

There are different ways to approach RSM design, depending on the system under investigation. Central composite designs (CCD), are a popular form of response surface methodology (RSM) proposed by Box and Wilson in 1951 [187]. As mentioned in section 1.8.4, factorial design can be augmented through the addition of axial points positioned at a distance,  $\alpha$ , from the centre of the experimental space [189]. Axial points are typically positioned to ensure rotatability in the design, which is a desirable property for response surface designs. Rotatability allows the variance of predicted responses at points within the design space to be consistent and stable [160]. In other words, a rotatable design ensures that the variance of predicted responses is the same at all points at an equal distance from the centre. This means that no area of the design space is inherently more uncertain than another, and the uncertainty in predictions is constant, irrespective of where they are in the design space. The value of  $\alpha$  is typically determined based on the number of factors in a design and the requirements of the design. A general rule of thumb to maintain rotatability is to calculate  $\alpha$  as shown in Equation 1-4 [160].

#### **Equation 1-4**

## $\propto = [Number of factorial runs, 2^k]^{\frac{1}{4}}$

Figure 1-15 shows three common CCDs and the positions of the various points in the design space for two-factor designs, and three-factor designs. The original form of the central composite design is the central composite circumscribed (CCC) shown in Figure 1-15 (a) and Figure 1-15 (d). A CCC is a five-level rotatable design where the axial points extend beyond the original limits set by the full factorial and establish new extreme settings for the factors under investigation [189]. For example, if the distance from the centre of the design space is +1 or -1 for each

factor, then an axial point would be larger than +1 or less than -1. The advantage of this type of design is that the original runs from a full factorial can be preserved and used in the design, provided the design domain has not been altered following the full factorial screening.



Figure 1-15: Various types of central composite design (CCD) for two factors (ac) and three factors (d-f) including the central composite circumscribed (a),(d), central composite face-centred (b),(e) and central composite inscribed (c),(f). The yellow dots represent the centre points (CPs) of each design, and the red dots represent the axial points added to a factorial design to form the CCD. The blue dots represent the corner (factorial points) of a factorial design. Whilst useful for exploring a wider experimental space, it is not always appropriate or possible to extend the original factor limits. For example, if the new extreme settings were impractical for a particular process or might cause quality degradation [189, 190]. A way to overcome this would be using an inscribed central composite design (CCI) (Figure 1-15(c) and Figure 1-15(f)), where each factor has five levels, and the upper limits of the original full factorial represent the limits of the CCI design. This creates a rotatable design where the face of the original factorial space defines new boundaries at which the axial points are positioned, and as such, a new (smaller) factorial design is essentially created within this new boundary. This means that the extreme settings of the original factorial design are not exceeded, avoiding any loss in product quality from unsuitable process conditions [189]. This does, however, mean that the only runs preserved from the full factorial are the centre points.

Another form of central composite design is the face-centred central composite (CCF) shown in Figure 1-15(b) and Figure 1-15(e). CCF designs are a type of response surface design that are made up of factorial points, centre points, and axial points, meaning they can build on existing factorial designs in the same way that CCC designs can, whilst preserving the upper and lower limits of the original factorial design like the CCI designs do. In CFF designs,  $\alpha = \pm 1$ , and as such the axial points are located at the centre of each face of the design cube space as a combination of one extreme and two midpoints of the other factors [191]. This type of design maintains each factor at 3 levels; however, the position of the extra points does provide information to explore second order effects. One key limitation with this approach, however, is that the positioning of the star points in a CCF designs deems the design non-rotatable, in that all points in the design are not equidistant

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from the centre. As mentioned previously, rotatability is desirable to ensure consistent variance of predicted responses, and so in the case of CCF, there may be regions of the design space than are more uncertain than others. It is, however, an efficient way to gather additional information beyond that provided by the factorial design. With only three levels, this design is arguably less susceptible to errors associated with the execution of additional factor settings beyond the original three, and it is often easier to maintain three levels in practice [160].

## **1.8.7 Optimisation and Validation**

As mentioned previously, the application of DoE can lead to enhanced process understanding through identification of significant factors and their interactions, and the effect they have on a specific response. The relationships between factors and responses are represented through numerical models as discussed in Section 1.8.5 and Section 1.8.6, obtained through the analysis of experimental data. The predictive model obtained from an RSM stage can be used to predict the factor settings required to optimise the response [158, 192].

The desirability function is a mathematical approach used in optimisation, whereby the value of response variable is transformed into a scale-free value referred to as desirability [192, 193]. This value essentially 'scores' the desirability between 0 and 1, where 0 is completely undesirable and 1 is fully desirable. The best process conditions are identified to optimise the response and obtain a desirability function close to 1, the objective for optimisation being to maximise, minimise, or meet a target value for a response [194]. The concept of desirability was first proposed by Harrington in 1965 [195], for single objective optimisation, and later modified by

Derringer and Suich [196] for the optimisation of multiple responses, where a compromise may be needed to ensure both responses are adequately optimised to achieve overall desirability [193]. This means that the significance of many different variables can be balanced, which allows more control over the region between 0 and 1, rather than having emphasis on the extreme desirability values of 0 and 1, which would be difficult to achieve for multiple responses with varying dependencies on significant factors.

The use of Derringer's desirability function has been used to support optimisation in the production of sugar [194], bioplastics [157, 197], and concrete [198]. With regard to the field of bioplastics, its use in optimising formulations for producing alginate-based composite films has been reported [197]. Used in combination with RSM, an optimum combination of additive concentrations was identified to optimise Young's modulus, resulting in alginate films with barrier and mechanical properties comparable to commercial HDPE, PET and PLA films. Desirability analysis can be particularly useful when applied to systems comprising multiple continuous process variables, for example, extraction processes that can involve multiple extraction parameters having significant effects on extract quality. The yield and purity of sodium alginate extracted from seaweed biomass has been optimised using RSM and Derringers desirability function, leading to improved process efficiency and process understanding [157]. Desirability can also support economic considerations in manufacturing, for example in the optimisation of concrete performance from analysis of mixture compositions. Here, a number of desirable options are generated on which cost analysis can be performed, helping to balance cost and performance [198].

Depending on whether a response  $Y_i$  is to be maximised, minimised, or matched to a target value, various functions can be applied to obtain the desirability function,  $d_i(\hat{Y}_i)$ . For example, to maximise a response, Equation 1-5 can used to calculate desirability for each response  $\hat{Y}_i$ , where  $T_i$  and  $L_i$  denote the target value (the upper limit in this case) and lower limit of the measured responses, respectively.

#### **Equation 1-5**

$$d_i(\widehat{Y_I}) = \left(\frac{\widehat{Y}_i(x) - L_i}{T_i - L_i}\right)$$

Overall desirability, D is calculated by combining each individual desirability using the geometric mean as shown in Equation 1-6, where k is the number of responses.

#### **Equation 1-6**

$$D = (d_1(Y_1) d_2(Y_2) \dots d_k(Y_k))^{\frac{1}{k}}$$

The application of DoE methodology is a worthwhile endeavour in the development of ACCs. With a wide range of process factors that could influence the properties of ACCs, it is of interest to explore whether DoE can support ACC optimisation and accelerate understanding of how to prepare these materials.

## **1.9 Summary**

ACCs have the potential to provide sustainable alternatives to many fossil-derived composite materials, however, as discussed in this chapter, there are some

challenges when it comes to accelerating the development of these materials. Primarily the performance of ACCs must compete with existing materials, and this includes finding ways to enhance mechanical properties and achieve strong bonding within the material structure. Secondly, it is necessary to look at accelerating research and development to allow ACCs to be optimised across multiple process and material variables in the most resource efficient way.

This thesis intends to address the above challenges, with an investigation into the use of cellulose-based textiles and interleaved cellulosic films in ACC preparation, and an exploration into the use of experimental design as a more efficient alternative to traditional iterative, OFAT methods. There is potential for the resulting properties of ACCs to be tuned through the variation of several factors present in the processing system. This includes dissolution conditions such as time, temperature, and pressure, the solvent configuration as a combination of IL and DMSO, and raw material parameters such as textile fibre source and the use of interleaf films.

It is of interest to explore whether an optimum combination of process conditions can be found using an iterative experimental approach, and if a DoE strategy can help reach the same conclusions, or improved outcomes more efficiently. It is also of interest to investigate ACCs production using different cellulose sources, for example, when using textiles made from virgin plant fibres compared to regenerated fibres, and find out if they optimise differently, and how the optimum samples compare between the two sources.

#### 1.10 Thesis plan

This work focuses research on the following aspects:

- I. The use of interleaved films to enhance interlaminar bonding in ACCs produced from woven natural cellulosic yarns (cotton).
- II. The application of DoE to optimise ACC processing produced from woven natural cellulosic yarns (cotton).
- III. A DoE investigation into the preparation of ACCs using woven regenerated cellulose-based textiles (Tencel).

The remaining chapters are structured as follows:

Chapter 2 outlines the core experimental methods employed in terms of the ACC preparation method, ACC mechanical testing, and characterisation of prepared ACCs. The stages of analysis involved in performing statistical design of experiments is also included in this chapter.

Chapter 3 builds on existing ACC knowledge and explores the benefits of using an interleaved cellulose film in combination with cotton textiles to produce ACCs. A key aim of this study is to independently validate the patented process described in section 1.5, and explore the benefits when applied to cotton textiles. Solvent configuration and the use of DMSO in conjunction with [C2MIM][OAc] is additionally studied.

Chapter 4 builds on the cotton-based ACC system and applies DoE methodology to the ACC process, as a route to process understanding and optimisation.

Chapter 6 summarises the research outcomes and key findings of this work. The wider implications of the work are also discussed, along with suggested directions for future work regarding how ACCs could be positioned within a circular economy.

## Chapter 2. Experimental Methods

## 2.1 Materials

For the work conducted in Chapter 3, commercially available bleached 100 % cotton with a plain weave obtained from Oh Sew Crafty, Kidderminster, UK, was used as the cellulosic textile precursor. The textile had an areal density of 136 g/m<sup>2</sup> and a thread count of 120 in both directions.

For the work in Chapter 4, bleached 100 % cotton with a plain weave was used as the cellulosic textile precursor, purchased from Minerva fabrics, UK. The textile had an areal density of 135 g/m<sup>2</sup> and a thread count of 120 in both directions.

Regenerated cellulose (Tencel) was used for the work conducted in Chapter 5, purchased from Ecological Textiles, Netherlands. The textile had an areal density of  $140 \text{ g/m}^2$  and a thread count of 144 in both directions.

Natureflex 23NP cellulose film supplied by The Futamura Group, was used as the cellulosic interleaf layer for all the studies in this thesis and has a thickness of 23  $\mu$ m. The films were supplied containing small amounts of additives that were not removed prior to processing; it is assumed that these additives do not disturb the dissolution process. Ionic liquid [C2MIM][OAc] with a purity of  $\geq$  95 % was purchased from ProIonic, and co-solvent dimethyl sulfoxide (DMSO) with a purity of  $\geq$  99.9 % was purchased from Fisher Scientific.

## 2.2 ACC Processing

ACCs were prepared by introducing a solution of [C2MIM][OAc] and DMSO to a layered stack of cotton or Tencel fabric and Natureflex film, and heating under pressure in a laboratory heat press. The stack consisted of two layers of textile with a single layer of interleaf film in between. Squares of textile and film were cut and sized to produce ACCs of dimensions 10 cm x 10 cm. Solvent was applied to the first textile layer using a brush, after which the layer of cellulose film was added and pressed down. The second textile layer was then added and the remaining solvent applied. Each textile layer was treated with equal amounts of solvent to ensure even distribution of the solution. A schematic of the process is shown in Figure 2-1.



Figure 2-1: Schematic outlining the various stages in the manufacture of ACC samples using textile and cellulosic film layers.

Textile layers were cut and weighed to obtain an overall mass of cellulose to be processed, and the mass of solvent solution to apply was then determined and expressed as a solvent to cellulose (S/C) weight ratio. The solvent solution comprised a combination of ionic liquid [C2MIM][OAc] and DMSO, and the percentage by weight of [C2MIM][OAc] in DMSO was determined according to each chapter. To summarise for clarity, the percentage by weight of [C2MIM][OAc] in DMSO was fixed at 80% for the first part of Chapter 3, and for the work of Chapter 4. For the second part of Chapter 3 and the work of Chapter 5, the percentage by weight of [C2MIM][OAc] in DMSO was varied (between 20 % and 80 %). Further details are provided in the experimental chapters.

The layered stack was then placed in a laboratory heat press at temperature and pressure settings as determined in the subsequent experimental chapters, and left for a variety of processing times. Further details of each experiment are provided in each chapter. After dissolution, the samples were placed in a coagulation bath of distilled water at room temperature and left for 1200 minutes (20 hours) to remove the solvent. After coagulation and solvent removal, the stack was placed in the heat press once more to be dried. The drying stage was fixed at a temperature, pressure, and time of 125 °C, 2 MPa and 60 minutes respectively, in accordance with initial development of the process [117].

#### 2.3 Characterisation

## 2.3.1 Mechanical Testing

The tensile strength (ASTM D1846) and Young's modulus (ASTM D1846) of the ACCs were evaluated using an Instron 5584 universal test machine. To determine Young's modulus and tensile strength, sample specimens of width 5 mm and a

central gauge length of 30 mm were tested using a crosshead speed of 10 mm/min. Two small sheets of silicon carbide paper were placed around the grip sites of the specimen to avoid any slipping between the specimen and the grips. Five specimens were cut from each composite sample from which an average value and corresponding standard error could be calculated. In Chapter 3 and Chapter 4, cotton-based ACC Chapter 5, specimens were cut into strips for testing, which was appropriate to allow the specimens to break in the centre. For Chapter 5 where Tencel-based ACCs were produced, a dumbbell-shaped specimen was used. Samples were cut and tested in the warp direction in all experimental chapters, however, additional samples were cut and tested in the weft direction in Chapter 3. Data from the tensile test is presented in the form of load and displacement from which stress and strain can be calculated using Equation 2-1 as Equation 2-2 as shown below.

#### **Equation 2-1**

Stress, 
$$\sigma\left(\frac{N}{m^2}\right) = \frac{Load(N)}{Cross-sectional area(m^2)}$$

#### **Equation 2-2**

$$Strain, \varepsilon = \frac{Extension \Delta L (mm)}{Original \ length \ L_o \ (mm)}$$

The cross-sectional area of the test specimen was determined by measuring thickness and width using RS PRO digital calipers. For unprocessed yarn testing, the cross-sectional area of the yarn was determined using the mass of the yarn along with the density of cellulose. The density of cellulose is reported from previous literature to be between 1.4-1.5 g/cc for plant fibres [199] and 1.530 g/cc for cellulose II [200].

From here, a stress/strain plot was produced from which Young's modulus, tensile strength and strain-to-failure were determined as shown in Figure 2-2. To summarise, the gradient of the initial linear section of the stress-strain plot determines Young's modulus (stress / strain), and Tensile strength is the maximum stress to which the specimen was subjected to. Strain-to-failure is determined from the extension at the point of specimen break. An average and a standard error was determined for each set of five measurements. Tensile tests were conducted at room temperature and relative humidity of approximately 50 %.



Figure 2-2 Stress-strain plot from which mechanical properties are determined.

## 2.3.2 Peel Strength Test

Peel strength is a metric used to measure the level of adhesion between ACC layers in laminate materials and is tested through a T-peel test according to the British Standard ASTM D1876. Peel strength is calculated as the average load  $(\hat{F})$  per unit width (W) required to separate bonded materials, at an angle of separation of 180 degrees. The unit of width refers to the bonded region between the materials, and thus the width of the specimen being tested.

#### **Equation 2-3**

$$Peel strength (N/m) = \frac{Average \ load \ during \ peel \ test, \ \hat{F}(N)}{Width \ of \ sample, \ W(m)}$$

An Instron 5584 universal tensile tester was used to evaluate peel strength, using specimens of width 10 mm and a length of 80 mm, and testing at a speed of 80 mm/min as specified by the standard (the test should take 1 minute in total). All specimens were tested in the longitudinal direction, parallel to the direction of the warp yarns. Prior to the dissolution process, a thin layer of foil was placed in between the two textile layers at the edge to provide an unbonded region from which to start the peel test. The length of sample and associated load to separate the layers was recorded, and the measured peel force was averaged between 20 mm and 160 mm on the sample. Peel strength results are presented as an average force for a one metre bonded width. One specimen was tested for each sample, across which the mean and standard deviation were calculated. Peel tests were conducted at room temperature and relative humidity of approximately 50 %.



Figure 2-3 A typical peel test plot of load versus extension showing the region from which to take the average value of peel strength in N/m (shown as vertical dashed red lines at 20 mm and 160 mm). This typical result was for a 10mm wide sample giving an average peel load of  $667 \pm 61$  N/m.

## **2.3.3 Density Measurements**

Densities of the optimised ACCs were determined using a gravimetric method. Three ACC specimens were cut and measured using an RS PRO digital caliper to obtain accurate width and length measurements. Using thickness measurements as described above, specimen volume was calculated prior to weighing to obtain density measurements of the ACCs. To ensure accuracy in the density measurements, the specimens were taken from three different points within the ACC sample, and dimensions were measured at three different points along the length and width. From previous literature, the absolute density of plant fibres is reported to be between 1.4-1.5 g/cc [199], the density of cellulose II is estimated as 1.530 g/cc [200], and bulk density of amorphous cellulose has been reported to be 1.48-1.5g/cc [201]. It was therefore proposed that a value of 1.5 g/cc would be used for the density of the cellulose components within the ACC, for comparison purposes.

## 2.3.4 Optical Microscopy

Surface images of the prepared ACC samples were obtained using a Swift 350B optical microscope in transmission mode. An Olympus BH2 microscope in reflection mode was used to observe the cross-sections of the prepared ACCs, and measurements of composite thickness were taken from these images using ImageJ. To allow a clear image to be obtained, samples were embedded in epoxy resin and polished. To ensure a consistent and representative view of each sample was obtained, multiple images were collected and used for measurements. An average value for thickness and corresponding standard error was calculated for each ACC sample from six measurements.

## 2.3.5 X-Ray Diffraction (Digital)

Quantitative analysis of crystalline structure was conducted through X-Ray Diffraction (XRD). A Bruker D8 Diffractometer with monochromated CuK $\alpha$ radiation was used, running scans in Gonio (Bragg-Brentano) mode to get a diffraction pattern. 2 $\theta$  line scans were run from 5° to 70° with a step change of 0.013°. Data were analysed in the 2 $\theta$  range of 5° to 30° as the most intense peaks in crystalline cellulose are found below 30° [202]. Samples were scanned in their solid form to perform the analysis on the most representative version of the ACC structure, and to avoid any potential degradation or crystal modification that might arise through grinding. To ensure a homogenous representation of the sample was seen, the sample stage was spinning at 2 revolutions per second. Specimens were cut from three different locations within the sample to allow average values and a corresponding standard error to be calculated. The intensity of signal obtained at each  $2\theta$  value was collected from which a plot could be made of  $2\theta$  versus intensity as shown in Figure 2-4.



Figure 2-4 X-ray diffraction profile obtained from a scan of raw cotton textile.

Each peak in a diffraction profile refers to the diffraction of X-rays by the crystal lattice of a given material, corresponding to specific plane in the crystal lattice. Knowledge of peak positions for the components under analysis, therefore, is required to analyse the obtained diffraction patterns from XRD. In this work, cellulose I, cellulose II and the amorphous component are of primary interest and the peak positions of cellulose I, II crystals, and amorphous cellulose are well documented as follows. Cellulose I is known to show peaks at 14.8°, 16.3°, 20.6° and 22.4° and cellulose II has peaks at 12.4°, 20.2° and 21.8° [103, 203]. Amorphous cellulose has a broad peak located around 18° [203, 204]. It is worth noting that the 20.6° peak for cellulose I is only observed in ground samples, and does not appear on the equator if the sample is orientated, as is the case for this thesis [205].

Depending on the cellulose source, however, a mixture of these polymorphs may be present in the obtained diffraction profile. The profile shown in Figure 2-4 from raw cotton for example, is formed from the individual peaks for cellulose I and amorphous domains contained in native cellulose [17]. These components need to be isolated to be analysed effectively, and as such a deconvolution method was used [103]. Deconvolution is a technique used to separate overlapping signals (in this case, peaks) so that the individual components of the specimen can be isolated and identified with more clarity. Using the above knowledge of peak positions, estimated fractions of cellulose I, cellulose II and the amorphous component were calculated using this method, where the sub peaks of each allomorph are fitted to a Gaussian curve.



Figure 2-5 Peaks in isolation for amorphous (a), cellulose I (b) and cellulose II (c)

A least squares approach was employed to fit the data to the peaks of cellulose I, cellulose II and amorphous cellulose using their 2 $\theta$  locations as outlined above as a guide, with an allowance of  $\pm 2^{\circ}$  at either side to aid the best fit. Peak heights and widths were left unconstrained, however peak width was a single value common to all peaks. Using this information for the individual peaks, the optimum fit of the peaks could be determined by fitting the data to a combination of each allomorph in superposition. With the peaks now isolated, the estimated fractions of each allomorph could then be determined. Figure 2-6 shows a deconvoluted diffraction profile of an ACC comprising a combination of cellulose I, cellulose II and amorphous cellulose.



Figure 2-6 Example of a deconvoluted diffraction profile of cellulose I (orange), cellulose II (green) and amorphous (red) peaks. The dashed black line represents the measured data, and the solid black line represents the resultant fit.

#### 2.3.6 Viscosity Measurements

Viscosity measurements of the [C2MIM][OAc]/DMSO mixtures were taken using an Anton Paar MCR 302 Rheometer with a plate-plate geometry, at 25 °C and 100 °C. Data were obtained in the form of viscosity-shear flow curves for each mixture under investigation, to provide a profile of how the viscosity of the mixture changed with shear rate. All mixtures under investigation exhibited Newtonian behaviour indicated by a horizontal line on the flow curve, from which an average value for Newtonian viscosity was taken. Two measurements were taken to obtain an average and corresponding standard error.

#### 2.4 Experimental Design

Chapters 4 and 5 explore the application of statistical design of experiments (DoE) to gain further insight into the ACC process and attempt to identify any relationships between process conditions and ACC mechanical properties. A description of the stages involved in applying DoE methodology is provided below. Details of the specific designs used are provided in the relevant experimental chapters, but the following section outlines the methodology.

The first stage of experimental design was to establish the experimental design space and the variables to investigate; independent variables (referred to as factors in this thesis), and the dependant variables, referred to as responses. The upper and lower limits of each factor were chosen, based on knowledge of the process, and to ensure the quality of the ACC is not compromised. This involved some initial sampling of ACCs to determine an appropriate region at which ACC quality remained acceptable, and further details are included in the subsequent chapters. An appropriate design was chosen from which the experimental runs could be designed, with each experimental run being a combination of each factor. Once a full data set was collected, a table was created for each experimental run including processing factors and measured response which could then be analysed. Three factors were explored for both Chapters 4 and 5, and thus  $\alpha$  was determined for rotatability as 1.68.

#### 2.4.1 Statistical Analysis

The software package Minitab was used to generate the designs and corresponding experimental runs, as well as conduct statistical analysis on the experimental data obtained. Least squares regression was used to fit a linear model to the experimental data, providing estimates of the effect of each factor and factor combination in the form of coefficients. This model essentially provides a prediction for the response based on the factors involved and their effect. ANOVA was then applied to the results of the linear regression to calculate the variation in the data and test for significance of each factor and its interactions. A backward elimination approach was applied, whereby all possible factors and factor combinations were included initially in the model fitting. The factors deemed insignificant (p-value  $\geq 0.05$ ) through the ANOVA were then disregarded, and linear regression applied to fit a new model. The process was repeated until a model was generated that included only significant terms.

An evaluation of test statistics was then performed to confirm whether the derived model was meaningful. This includes the F-value to assess how well the factor or factor combinations of the model can explain the variation in the response, with higher values being a marker that it can do this well. The p-value for each factor/ term in the model assesses how significant each factor is, and if it has had a real impact on the response. A p-value below 0.05 indicates significance of a factor or factor combinations.

The goodness of fit of the model to the experimental data was assessed from calculation of coefficient of determination,  $R^2$  [182, 197, 206]. This was supported by calculation of adjusted coefficient of determination,  $R^2_{(adj)}$ , used to validate the strength of model with respect to the number of model terms. The predictive power of the resulting model was gauged through calculation of predicted coefficient of determination,  $R^2_{(pred)}$  [157]. The value of  $R^2$  is expressed as a decimal between 0 and 1, representing the percentage of data that the model can explain. For example, an  $R^2$  of 0.21 would mean that 21 % of the data can be explained by the model.

When applying least squares regression, it is important to be aware of underlying assumptions, for example, the assumption that residuals (errors) are normally distributed and have no obvious patterns or structure between them. This can be validated during the statistical analysis through observation of residual plots such as normal probability plots and residual histograms, for example. A key assumption to be aware of is that the independent variables are truly independent and not correlated in any way. If multicollinearity exists between two or more variables, the regression model cannot distinguish their individual effects [160]. In many thermodynamic systems, temperature and pressure are inherently linked for example through the ideal gas law. In the context of this work, ACC processing is carried out using heat press which functions as an open system where factors of temperature

and pressure can be controlled independently. Whilst a relationship may exist between these variables in other settings, the ability to adjust them separately ensures that multicollinearity is not a significant issue. The regression model, therefore, can still provide meaningful insights into the individual effects on the output variable.

## 2.4.2 **Optimisation and Validation**

Derringers desirability function [196] (as introduced in Section 1.8.7) was used to identify the optimum process conditions to yield the most desirable response. This optimisation approach can be applied when optimising on a single response of key interest as conducted in Chapter 4, and is highly beneficial for multiple response optimisation explored in Chapter 5.

Using the obtained model, each theoretical response  $Y_i$ , (obtained from all experimental runs) was converted into a desirability function  $d_i(\hat{Y}_i)$ . Recall from section 1.8.7, that  $d_i(\hat{Y}_i)$  is a value between 0 and 1, and as the response moves further away from the goal,  $d_i(\hat{Y}_i)$  gets closer to 0. Desirability function for each theoretical response  $\hat{Y}_i$  was calculated using Equation 2-4, where  $T_i$  and  $L_i$  denote the upper limit and lower limit of the measured responses, respectively. Independent variable (factor) settings were then chosen to maximise the overall desirability, D.

#### **Equation 2-4**

$$d_i(\widehat{Y_I}) = \left(\frac{\widehat{Y}_i(x) - L_i}{T_i - L_i}\right)$$

The desirability function was determined using the Minitab software; however, this approach can be conducted using Excel. To set up the calculation and solidify the understanding, Excel was used simulateously alongside Minitab. From this, a desirable set of processing conditions was determined along with a predicted response.

Experimental samples were prepared at the processing conditions identified during the desirability analysis. An unpaired student t-test was used to compare the average response from the in-lab samples with the prediction, to determine whether the difference between the two responses was statistically significant or not. To conduct a student t-test, the mean ( $\bar{Y}$ ) and standard deviation (SD) of the experimental sample data are calculated. The t-statistic is then calculated according to Equation 2-5, where  $\mu_0$  is the model prediction and *n* in the number of experimental runs.

#### **Equation 2-5**

$$t = \frac{\bar{Y} - \mu_0}{SD/\sqrt{n}}$$

A t-distribution table can then be consulted to locate the critical t-value associated with the degrees of freedom (DF = n-1), for the desired significance level. In this work, a significance level of 0.05 was used. If the calculated t-value is more than the critical value, this indicates a significant difference between the experimental samples and model prediction. Conversely, the difference can be deemed insignificant if the calculated t-value is less than the critical value.



# Chapter 3. Use of interleaf films in the production of all-cellulose composites.

## **3.1 Introduction**

As described in Chapter 1, manufacturing a well-bonded ACC from woven textile layers requires two distinct regions of matrix. A region within each textile layer to bind all the yarns together, and a region between each layer to bind the layers together. The approach used in this work involves the partial dissolution of the yarns within a textile. This method is ideal for producing the matrix within each textile layer, as the distances between each yarn are relatively small and can be filled easily, and the one-component nature of the ACCs lends itself to good adhesion at the fibre-matrix interface. Achieving sufficient bonding between the textile layers, however, can be more challenging when only partially dissolving the yarns. The uneven surface of a textile layer requires significantly more matrix to fill the space between two adjacent layers and achieve adequate bonding. It is, therefore, of interest to explore how the matrix fraction can be increased in this region to enhance interlaminar bonding.

The following chapter seeks to validate the patented method [117] for adding an interleaf film for ACC production described in section 1.5, and ascertain how the addition of the film benefits the mechanical properties of ACCs produced using cotton textiles. There are three parts to this chapter as outlined below.

#### Comparison of ACCs prepared with and without film.

Here, the patent claims are validated, and the effectiveness of the interleaf film when placed between two layers of cotton textile is assessed. ACCs are produced with and without film, at fixed process conditions, using varied amounts of solvent solution. Solvent to cellulose (S/C) weight ratio is varied to establish the most preferable solvent quantity to use that allows it to distribute effectively into the textile layers. The percentage weight of [C2MIM][OAc] with DMSO is fixed at 80 %.

#### Addition of DMSO in [C2MIM][OAc].

The percentage weight of [C2MIM][OAc] in DMSO is now varied from the original fixed 80 %, to establish whether the addition of DMSO as a co-solvent affects ACC production when processing at elevated temperature and pressure, and observe any effects on the resulting ACCs portfolio of mechanical properties. While the addition of DMSO might favourably adjust the diffusive mechanisms of the ions, there is also a cost benefit to its use as ILs are typically expensive to synthesise [139]. To use a dilution in DMSO would be of additional benefit in lowering processing costs associated with their use. The addition of DMSO, however, also dilutes the IL ([C2MIM][OAc]) and so at some percentage fraction the dissolving power will fall below a useful threshold. Additionally, the reduction in viscosity may indeed cause solvent to be lost under pressure, reducing the presence of dissolved cellulose and subsequent matrix.

#### Multi-axial properties of ACCs prepared with interleaf film.

The final part of the chapter involves the exploration into the effect of the interleaf film on multi-axial properties. As mentioned in 1.3.3, commercially obtained fabrics

such as the cotton used in this study can have an imbalance of properties. It is proposed that by using an interleaved film, the additional matrix produced will improve the efficiency of the stress transfer between longitudinal and transverse orientated yarns by stabilizing the reinforcement yarns and improving the overall level of adhesion throughout the composite structure.

The content of this chapter led to my first publication entitled "Use of interleaved films to enhance the properties of all-cellulose composites" published in Composites Part A: Applied Science and Manufacturing (Victoria, A., et al., Use of interleaved films to enhance the properties of all-cellulose composites. Composites Part A: Applied Science and Manufacturing, 2022: p. 107062).

#### **3.2 Materials and Methods**

## 3.2.1 Materials

Bleached 100 % cotton with a plain weave was used as the cellulosic textile in this study, details of which are provided in section 2.1.

## 3.2.2 Composite processing

Details of the procedure for preparing ACCs can be found in section 2.2, where a schematic of the process can also be found.

For the first part of the work, three different solvent to cellulose (S/C) weight ratios were explored; equal solvent to cellulose (1:1), two-fold solvent to cellulose (2:1)

and threefold solvent to cellulose (3:1). A solvent solution comprising 80 % by weight [C2MIM][OAc] and 20 % DMSO was prepared.

For the second part, five preparations of [C2MIM][OAc] and DMSO were prepared, varying the percentage of [C2MIM][OAc] in DMSO from 20 % up to 100 % (100% being neat [C2MIM][OAc]).

## **3.2.3 Processing conditions**

Once the layered stack was introduced to the solvent solution, it was placed in a laboratory heat press at 100 °C with an applied pressure of 2 MPa for 10 minutes. The samples were then left overnight in a coagulation bath as outlined in section 2.2.

## **3.2.4** Cloth Orientation during sample preparation

For the first set of iterations, samples were made with both cotton textile layers stacked at  $0^{\circ}$  with respect to the warp yarns, giving a stacking sequence of (0,0).

Once the appropriate solvent configuration had been established, additional ACC samples were made with the interleaf film using additional stacking arrangements, to explore how the cloth orientation within the stack influenced mechanical properties. A two-layer sample was prepared with one layer of cloth orientated 0° relative to the warp yarn direction, and the second layer orientated 0° relative to the weft yarn direction (0,90). A fully symmetric sample was prepared using 4 layers of cloth, with the warp yarns aligned 0°, 90°, 90°, 0° from bottom to top (0,90,90,0). The

different stacking arrangements used throughout this study are summarised in Figure 3-1.



Figure 3-1. Stacking sequences of cloth textile layers used in the study. a) shows a 0,0 stacking arrangement where the warp yarns of both layers are aligned in the same direction, b) shows a 0,90 stacking arrangement where the first and second layers are aligned at  $0^{\circ}$  and  $90^{\circ}$  respectively, and c) shows a 0,90,90,0 symmetric stacking arrangement where the upper and lower textile layers are aligned at  $0^{\circ}$ , and the middle layers are aligned at  $90^{\circ}$ .

#### **3.2.5** Mechanical Testing

Details of the mechanical testing caried out on these samples are provided in section 2.3.1. For this work, ACCs were initially tested in the direction of the warp yarns (longitudinal), with subsequent tests carried out in the direction of the weft yarns (transverse), and  $45^{\circ}$  to the warp yarns.

## **3.2.6** Estimation of cellulose content of processed ACCs

There are some challenges faced when estimating fibre volume fraction of ACCs produced via partial dissolution methods. Unlike traditional fibre reinforced

composites, the volume of fibres used to prepare ACCs will not be the same after processing, as a certain amount of fibre will have dissolved to subsequently form the matrix. Additionally, with the dissolution process being carried out under pressure, there will be some dissolved cellulose pushed out from the mould plates, and this is known as 'flashing'. Estimating the fibre volume fraction of the ACCs is therefore more complex, and so a semi-quantitative analysis of crystalline structure using X-Ray Diffraction (XRD) was employed.

Before dissolution, the majority of cellulose I and cellulose II will be present in the cotton cloth and interleaf film respectively, together with an amorphous fraction. After partial dissolution, the dissolved fractions of cotton and film will be converted to amorphous cellulose and cellulose II. Using this knowledge, XRD was employed to characterize the change in the crystalline structure of the ACC samples made with and without interleaved film and provide estimations of the cellulose I, cellulose II and amorphous cellulose fractions present in the ACCs. Details of the methodology is provided in section 2.3.5.

It is appreciated that the absolute crystallinity cannot be determined just from an equatorial line scan, as some crystal reflections can appear away from the equator. However, these are generally only small intensity reflections, and, therefore, are expected to have at most, a small contribution to the total crystallinity. This technique was, therefore, deemed appropriate to assess the change in the cellulose I fraction when using interleaved films.
#### **3.3 Results and Discussion**

#### **3.3.1** Influence of Interleaf Film

Mechanical properties in the longitudinal (warp direction) of the prepared ACCs are presented in Figure 3-2, using various S/C weight ratios for preparation with and without interleaf film. The error bars shown in Figure 3-2(a) and Figure 3-2(b) reflect the standard error, which was calculated across the five tested specimens. The errors bars in Figure 3-2(c) reflect the variation in the measured peel strength along the sample using standard deviation.



Figure 3-2 Young's modulus (a), tensile strength (b), and peel strength (c) of allcellulose composites prepared with interleaf film and without interleaf film using various S/C weight ratios. Samples were processed for 10 minutes using an 80/20 ratio of [C2MIM][OAc]. Mechanical properties were tested in the longitudinal direction.

Surface and cross-sectional images of the prepared ACCs are presented in Figure 3-3, with the original raw cotton textile included for comparison. Thickness, density, and yarn cross-sectional area (CSA) of the ACCs are presented in Table 3-1 along with the thickness and density of the unprocessed cotton textile and interleaf film.



Figure 3-3 Optical microscopy images of ACCs prepared without film (a, b, e, f, i, j) and with film (c, d, g, h, k, l) using various S/C weight ratios of 1:1, 2:1 and 3:1. Raw cotton (m) and (n) is also shown for comparison. Surface images and cross-sections are displayed for each sample. The darker regions within the sample cross-section indicate the presence of void space, as indicated by the red arrows.

It was found that during preparation, an equal weight of solvent to cellulose (1:1), provided scarcely enough solvent to distribute to the textile layers. Consequently, the difference in properties between the samples made with film, and those made without film, was not significant. Furthermore, across the five test specimens for these samples, the errors were large, indicating a variation in properties across the sample caused by inconsistent solvent distribution. In addition to pockets of air within the yarns, the yarns in the cotton cloth are not tightly woven, in that the warp and weft yarns are sufficiently spaced out as to leave small pockets of space between them as they interlink. This allows for rapid absorption of the solvent into this space that when using less solvent, leaving little opportunity for the solvent to evenly distribute throughout the textile. It is suggested that there is insufficient solvent to introduce across the full area of the textile and, furthermore, insufficient solvent to partially dissolve enough fibre and film to produce the necessary matrix for the composite structure. This is further evidenced through observation of the inconsistent appearance seen across the ACC cross-section in Figure 3-3 (b). Whilst this may result in a higher fibre volume fraction, the lack of useful matrix leads to inefficient stress transfer to the reinforcing component and decreased mechanical properties. Additionally, as shown in Figure 3-3(d), the interleaf film can still be clearly seen, and aside from a flattening of the yarns occurring through compaction, there is little difference between the ACC surfaces from using the film or not. Film thickness in this sample was measured to be  $0.0087 \pm 0.0003$  mm; this suggests that over 50 % of the film has dissolved given the original thickness of the film is 0.023 mm). However, the matrix production is not enough to distribute through the textile and create the smoother appearance seen in Figure 3-3(g) and Figure 3-3(k) when using more solvent (2:1 and 3:1 S/C weight ratios). Using more solvent allows the film to dissolve completely, which contributes to matrix production. There is then more matrix to distribute through the fibre assembly and coat the partially dissolved fibres, contributing to a stronger interface between both reinforcement and matrix, and the textile layers. This strong fibre-matrix interface promotes effective transfer of external loads to the reinforcing fibres [84, 207], which leads to an increase in modulus as evidenced in Figure 3-2(a).

The significant increase in the peel strength when using a 3:1 S/C weight ratio, however, highlights the positive influence of solvent amount on maximising the

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benefits of using the interleaf film. From Figure 3-3(k), the fibres appear smoother, and the pockets of space between interlinking fibres are filled in more, creating a more consistent surface. As mentioned in section 3.2.6, there is a tendency for flashing to occur under applied pressure when processing at elevated temperatures, and dissolved cellulose being removed from the stack. When applying less solvent to the textile, there is a risk that any cellulose that dissolves will be removed through flashing, leaving little left to form the matrix. If more solvent is used, any flash expelled from the sides of the stack may be compensated for, and this will prevent the loss of too much potential matrix.

Whilst similar tensile behaviour is exhibited in the samples produced at both 2:1 and 3:1 S/C weight ratios, the increase in peel strength when using the 3:1 S/C weight ratio suggests that for this process it may be beneficial to opt for extra solvent to ensure sufficient matrix can form under compaction. A 3:1 S/C ratio provides an excess of solvent to penetrate the cellulose textile stack evenly such that the cellulose lost through flashing is offset through increased dissolution. This helps to provide the matrix needed to promote excellent interlaminar adhesion by effectively surrounding the fibres to create a stronger fibre-matrix interface. As shown in Figure 3-3(1) a more consolidated ACC can result that yields the most favourable peel strength and modulus without a significant drop in tensile strength. When compared to the sample produced without film, there is a significant increase in Young's modulus and peel strength from 2.18  $\pm$  0.20 GPa to 4.20  $\pm$  0.16 GPa, and 62  $\pm$  10 N/m to 917  $\pm$  73 N/m respectively. It is interesting to note that the tensile strength of the ACC is not affected by the incorporation of the film and, therefore, it is less affected by the level of interlayer adhesion. It is hypothesised that all the ACCs

Table 3-1 Calculated values of thickness (mm), density (g/cc), and yarn CSA (mm<sup>2</sup>) for ACCs prepared with and without interleaf film using various S/C weight ratios. Properties of the unprocessed raw materials are also presented.

S/C Ratio	Preparation	Thickness (mm)	Density (g/cc)	Yarn CSA (mm <sup>2</sup> )
(1.1)	No film	$0.30\pm0.01$	$0.96\pm0.02$	$0.025 \pm 0.002$
(1.1)	With film	$0.36\pm0.01$	$0.87\pm0.02$	$0.0243 \pm 0.0002$
(2:1)	No film	$0.29\pm0.01$	$1.04\pm0.01$	$0.028\pm0.001$
	With film	$0.34\pm0.01$	$0.92\pm0.04$	$0.027\pm0.001$
(2,1)	No film	$0.31\pm0.01$	$0.91 \pm 0.02$	$0.029 \pm 0.004$
(3.1)	With film	$0.220\pm0.005$	$1.31\pm0.02$	$0.015\pm0.004$
Raw material	s	Thickness (mm)	Density (g/cc)	
Raw cotton te	extile	0.229	1.5	
NatureFlex 2	3NP film	0.023	1.5	

Figure 3-3 (n) shows the unprocessed cotton yarns within the textile, which comprise an arrangement of loose smaller fibres that, unbonded, may move about more freely and cause the yarn to expand in the epoxy resin [103]. The overall area of the yarn cross-section will therefore be a combination of individual fibres and the air pockets between them. When solvent is applied, this loose arrangement of fibres may allow easier penetration of the solvent through the yarns, and any matrix produced from fibre dissolution will help to consolidate the fibres, and the yarns will be compacted from the pressure applied during processing. Figure 3-3 suggests that this is the case with the resulting decrease in the relative size of the yarn crosssection across all processed ACCs. It is worth noting that the values for CSA are unlikely to relate strongly to the amount of fibre dissolved. It is more likely to be related to their level of consolidation within the samples and 'flattening' under compaction. The measurements from Table 3-1 suggest that the yarn CSA remains reasonably consistent across all samples, the only exception being with the samples produced using a 3:1 S/C ratio and film, where the CSA decreases. This reduction is likely to be a stronger indication of how much the individual fibres have become more closely packed and the generation of the fibre-matrix interface.

The influence of S/C weight ratio is further emphasised when looking at the calculated densities of the processed ACCs in Table 3-1, as compared to the expected densities of the cellulose materials from literature (outlined in section 2.3.3). The density the ACC sample produced using a 3:1 S/C weight ratio and interleaf film is considerably higher than that across all samples produced using 1:1 and 2:1 S/C weight ratios. This increased density when using a 3:1 S/C weight ratio supports the notion that sufficient matrix can be generated when more solvent is used. This matrix can then distribute effectively within the fibres and fill the available space between the yarns, increasing density to a value that aligns more closely with the density of pure cellulose. With a 2:1 S/C weight ratio, it is suggested that the film dissolves but remains primarily between the layers which would result in an increased thickness as observed. One might expect this to contribute to an increase in peel strength, however, as it remains in between the layers, it means there is a lack of sufficient penetration of matrix material through the fibre assembly, which prevents this from occurring. Whilst the key aim of the interleaf film is to place matrix in-between the textile layers, it is also important to

fill the space between the interwoven yarns to ensure voids can be reduced. The difference in yarn size that can be seen across the three S/C weight ratios in Figure 3-3 (c), Figure 3-3 (g), and Figure 3-3 (k) supports this theory. Less void space can be seen within the yarn cross section and a noticeably smaller yarn size is present when using a 3:1 S/C weight ratio, suggesting a more consolidated yarn from improved solvent penetration. It could be proposed that this sample exhibits an optimum combination of matrix and reinforcement, in addition to excellent consolidation of the components. Using a 3:1 S/C weight ratio allows sufficient dissolution, and any loss of cellulose that occurs through flashing is compensated for, allowing more matrix to remain in the ACC. Voids can still be visibly seen in this sample (Figure 3-3 (1)), however, the relative magnitude of these void regions compared to the other samples is lower, and improved consolidation of the fibres within the yarns is achieved. The combination of the interleaf film and a sufficient S/C weight ratio allows matrix to be produced and crucially, maintained.

There are two types of bonding being supported through this:

- Bonding between the layers (inter-laminar bonding)
- Bonding between the yarns within the textile (intra-laminar bonding).

With more matrix present, there is sufficient material to fill the pockets of space between the yarns as well as provide more consistent interlaminar matrix to enhance the fibre-matrix interface. As discussed in Chapter 1, achieving the proper balance between fibre and matrix is just as crucial as ensuring a strong interface, and the contribution of their unique properties transferred to the composite is driven by their respective volume fractions [56]. The addition of the interleaf film results in two possible effects on the resulting fibre volume fraction of the ACC. On one hand, if the film is dissolving instead of the fibre, then the presence of a higher volume of undissolved fibre will result. It has been reported that dissolution mode depends strongly on the solvent's ability to disrupt the long-range order of cellulose chains [208]. The interleaf film comprises cellulose II which has a comparatively lower degree of polymerisation when compared to native cellulose [20] in the cotton textile. It, therefore, may be expected to have increased mobility in solution and a faster dissolution rate, subsequently dissolving more preferentially than the cotton. In this work, however, the ACCs are processed at high temperatures and so it is suggested that the amount of solvent has a more prominent influence on the overall cellulose dissolution, rather than influencing the different sources individually. Previous work on cellulose dissolution has shown that the dissolution of cotton obeys time-temperature superposition [103]. In this work, dissolution time and temperature are fixed at 10 minutes and 100 °C respectively. By processing at an elevated temperature, it is suggested that as dissolution occurs so rapidly, it is governed more so by the amount of solvent used, rather than time and temperature. As a result, the concentration of dissolved cellulose in the surrounding solution is higher compared to previous work where the yarns were in excess solvent [103]. Solution viscosity will be subsequently higher, which in turn affects the kinetics of the process. Within a duration of 10 minutes, a larger fraction of the film may dissolve compared to the textile due to it being significantly thinner (0.023 mm compared to 0.229 mm respectively) and, therefore, having higher surface area to volume fraction. While the cotton may appear to dissolve more slowly because it is thicker, the total amount dissolved may be similar.

This leads to the second possibility that adding the film places additional matrix component within the composite, which simply increases the overall amount of

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matrix in the ACC. In this scenario, fibre dissolution remains relatively consistent and independent of the presence of the film and how the film dissolves. This would result in the same volume of undissolved fibre that would occur without the film, but also more matrix component, which reduces the fibre volume fraction and its contribution of properties to the composite. This is evidenced in the decrease in tensile strength observed for the samples with the film, when compared to those made without the film, suggesting that the film increases the proportion of matrix component, thus reducing fibre volume fraction. The decrease in tensile strength, however, is relatively small, so a good balance of matrix and fibre can be achieved to allow efficient transfer of fibre properties, without excessively reducing fibre volume fraction. Thus, the process of hot compaction with interleaf cellulose films can improve Youngs modulus and peel strength, without any significant loss of tensile strength.

The percentage gain in mass from adding an interleaf film can be calculated by comparing the mass of one layer of film, with the overall mass of two cloth layers. The mass of one layer of Natureflex film is 0.294 g, and the mass of two layers of cloth textile is 2.94 g, and so the ratio of film mass to textile mass is, therefore, 0.1. This means that a 10 % gain of cellulosic material can be achieved by adding the film during preparation, which effectively 'dilutes' the cellulosic reinforcing fibres by 10 %. With a 3:1 S/C weight ratio, Young's modulus can be doubled, and furthermore, peel strength can be increased dramatically, making this a very effective strategy for getting an excellent balance of mechanical properties.

#### **3.3.2** Influence of Interleaf Film on Crystalline Structure

X-ray diffraction (XRD) was used to investigate the changes in crystal structure of the ACCs using 3:1 S/C weight ratio both with, and without the interleaf film. The crystalline composition of each sample was determined by deconvolution of the XRD diffractograms obtained from specimens taken from each sample and are summarised in Table 3-2.

Table 3-2 Crystalline composition of ACCs as analysed by XRD

	Cellulose I	Cellulose II	Amorphous
	Fraction (%)	Fraction (%)	Fraction (%)
ACC - No Film	$71 \pm 1$	$6.2 \pm 0.2$	$23 \pm 1$
	57 + 1	8 8 + 0 4	34 + 1

The deconvolution curves from both samples are presented in Figure 3-4. A typical diffractogram for each sample is presented in Figure 3-5. It can be seen from Figure 3-4 that on addition of the interleaf film, the relative size of the cellulose I peaks, particularly the main reflection at 22.4°, decreases when compared to the sample prepared without film. The reduction of cellulose I content from  $71 \pm 1$  % to  $57 \pm 1$  % confirms the notion suggested earlier, that a reduced fibre volume fraction (which contributes the cellulose I fraction) arises through the addition of the film, resulting in the observed decreased tensile strength. At the same time, cellulose II peaks begin to appear more prominently, and the broad amorphous peak at  $18.2^{\circ}$  increases. As the matrix fraction is a combination of both cellulose II and amorphous cellulose, this supports the earlier suggestion that the increased matrix production brought about by adding the film subsequently reduces the overall fibre volume fraction.



Figure 3-4 The deconvolution curves of ACCs produced using a 3:1 solvent to cellulose weight ratio, without interleaf film (a), and with interleaf film(b). The experimental measurement is shown in the black dotted line, and the black curve is a summation of the crystalline peaks of cellulose I (shown in blue, orange and brown), and cellulose II (shown in grey and green). The amorphous peak is shown in red.

The increased size of the peaks at  $20.2^{\circ}$  and  $21.8^{\circ}$  (indicative of the presence of cellulose II) are shown in Figure 3-4, highlighting the presence of the film. This is supported by observation of the peaks for the sample prepared without film, particularly the peak at  $21.8^{\circ}$  which has a noticeably smaller shoulder peak.

It is worth noting that in a yarn-based architecture, crystal alignment is predominately along the vertical axis of a yarn. This means that when performing an equatorial diffraction scan of a textile reinforced ACC, a  $2\theta$  scan may result where some peaks are absent. Additionally, textile yarns possess a helical structure which can lead to some peak modification due to a slight variation in twist angle of fibres within the yarn. In this work, however, the peaks generated have been used to simply highlight the relative change in cellulose I, cellulose II and amorphous cellulose as a result of processing with and without the film. Therefore, this is not deemed significant in this analysis as absolute values are not being sought.



Figure 3-5 XRD diffraction patterns of ACCs produced with S/C weight ratios of 3:1, without interleaf film (red line) and with interleaf film (blue line).

Within these constraints, the deconvolution technique can be a useful method to evaluate structural changes and allow the dissolution and fractions of the various phases to be followed and compared to one another. It is also worth noting that although the overall relative fraction of the reinforcing fibres is decreased by the incorporation of the film, Young's modulus increases. This suggests that the properties of an ACC are highly dependent on developing good adhesion between the various phases, a dependence not unlike traditional composite materials as discussed in previous chapters. This method of producing ACCs with the addition of an interleaf film offers an excellent route to achieve a good balance of mechanical properties through increased compatibility within the yarns of the textiles, and between the woven textile layers.

# 3.3.3 Influence of [C2MIM][OAc] % in DMSO

Table 3-3 shows the viscosities of the solvent solutions, measured at  $25^{\circ}$ C and  $100^{\circ}$ C.

% DMSO in [C2MIM][OAc]	Viscosity @ 25°C (mPa.s)	Viscosity @ 100°C (mPa.s)
0 % (Pure [C2MIM][OAc])	$150 \pm 2$	$7.8 \pm 0.9$
20 %	$32 \pm 2$	$4.68\pm0.04$
30 %	$28.2\pm0.2$	$4.3 \pm 0.1$
40 %	$26.6\pm0.1$	$3.4 \pm 1.0$
50 %	$14 \pm 3$	$2.6 \pm 0.4$
60 %	$10.2\pm0.5$	$2.22\pm0.03$
80 %	$2.8\pm0.2$	$0.991 \pm 0.001$
100 % (Pure DMSO)	$1.5\pm0.1$	$0.80 \pm 0.04$

Table 3-3 Viscosity measurements of solvent solutions with various wt%[C2MIM][OAc] in DMSO

The viscosity of the pure IL solution is significantly reduced through the addition of DMSO, for example with the addition of 20 % DMSO at 25°C, a fivefold decrease in viscosity of the IL is observed. There is, however, a notable reduction in viscosity of the pure IL as temperature is increased from 25°C to 100°C, indeed at 100°C, the viscosity of the pure IL is comparable to adding around 60 % DMSO at 25°C. As DMSO wt. % increases, the decrease in viscosity is less apparent at the processing temperature of 100°C. This suggests that the benefit of adding DMSO will be felt predominantly at the preparation stage (at room temperature), rather than during dissolution (at 100°C), as applying solvent to the woven cloth layers will be easier if the solvent viscosity is reduced significantly.

Results from mechanical testing are presented in Figure 3-6 and images of ACC cross-sections are shown in Figure 3-7. Calculated values for ACC thickness, density, and yarn CSA for ACCs prepared using various wt. % of [C2MIM][OAc] in DMSO are presented in Table 3-4.



Figure 3-6 Mechanical properties of ACCs produced with additional interleaf film in-between layers of cotton textile, using a 3:1 solvent to cellulose weight ratio, using various [C2MIM][OAc] % in DMSO. Tensile strength and Young's modulus are shown in (a) and peel strength is presented in (b). C10-CY corresponds to a sample processed for 10 minutes using a solvent solution consisting of Y wt. % ionic liquid.

The importance of achieving a balance of solvent viscosity and sufficient [C2MIM][OAc] is highlighted in Figure 3-6 (a), where it is shown that as more DMSO is added to the solvent, Young's modulus decreases, which provides some insight into the matrix amount that has formed within the composite during processing. As discussed in Chapter 1, sufficient matrix formation supports a strong fibre-matrix interface, which helps optimise the properties through efficient transfer of external loads to the fibres [102]. Young's modulus is at its highest when using pure, or 80 wt.% [C2MIM][OAc], beyond which, an overall decrease can be observed. As Table 3-3 shows, viscosity is decreased as more DMSO is added. A solvent solution of low viscosity would promote excess flashing under compaction, reducing matrix formation that can surround the fibres. The results suggest that whilst it is beneficial to reduce the viscosity of the solvent to aid mass transport, it is also important to avoid reducing viscosity too much that it then promotes excess flashing. Looking at Figure 3-6 (b), a consistently high peel strength is obtained between 50 and 80 wt.% [C2MIM][OAc], and this is notably improved from using 100 % pure [C2MIM][OAc], particularly with 80 % [C2MIM][OAc].

Young's modulus is optimised at [C2MIM][OAc] concentrations between 100 wt.% and 80 wt.%, and as such there is no significant benefit to adding more than 20 wt.% DMSO. It is interesting to note that when using 50-30 wt.% DMSO in [C2MIM][OAc], peel strength values are still in a range comparable to when using 20 wt.% DMSO. This suggests that there is still sufficient matrix formed even when the amount of [C2MIM][OAc] is significantly reduced. Within a specific time window, the increase in DMSO may speed up [C2MIM][OAc] activity, such that it can achieve a comparable dissolution activity to the mixture with 80 wt.% [C2MIM][OAc]. It is nonetheless important to consider the balanced of matrix required to support interlaminar adhesion, and the fibre volume fraction required to provide sufficient tensile properties to the material. The decrease in Young's modulus when adding 50-30 wt.% DMSO indicates that while sufficient interlaminar adhesion is achieved from dissolution, it not sufficient to enable efficient transfer of external load to the fibre reinforcement. It is acknowledged that pure [C2MIM][OAc], and 80 wt.% of [C2MIM][OAc] in DMSO are seen to yield the optimal Young's modulus, however, the potential cost benefits of offsetting some [C2MIM][OAc] with DMSO are worth considering, not to mention the

improved ease at which the solvent can be introduced to the textile stack during preparation.



Figure 3-7 Cross-sections of prepared ACCs at various weight % [C2MIM][OAc] in DMSO. (a) 100 % (b) 80 % (c) 70 % (d) 60 % (e) 50 % (f) 40 % (g) 20 %.

Tensile strength remains relatively constant at all concentrations of [C2MIM][OAc], as shown in Figure 3-6 (a). Given that this property comes primarily from the reinforcing component of the material as discussed earlier, the narrow range of values (42 - 52 MPa) suggest that there is no significant change in the amount of yarn being dissolved. The fibre CSA estimates from image analysis show a wide variation between values  $(0.013 - 0.025 \text{ mm}^2)$ , but as mentioned earlier, the CSA values correlate more to ACC consolidation. There is a visibly thinner appearance of the samples produced using 80 and 60 wt.% [C2MIM][OAc] for example, indicating that the decrease in visible yarn CSA coincides with matrix penetration through the layers, binding the fibres and layers closer together. Conversely, a weaker consolidation is observed when using 20 and 40 wt.% [C2MIM][OAc], coinciding with the drop in properties and density for these samples. Interestingly, the interleaf

film can still be seen when pure [C2MIM][OAc] is used, which reinforces the idea that some addition of DMSO supports faster dissolution times and is beneficial when processing for shorter periods. Adding more than 20 wt.% DMSO, however, results in less consolidation within the ACC due to a combination of increased flashing of a less viscous solvent solution and a reduced capacity to dissolve cellulose. This evidenced in the resulting mechanical properties of the samples prepared with more than 20 wt.% DMSO shown in Figure 3-6 (a).

Table 3-4 Calculated values of thickness (mm), density (g/cc), and yarn CSA (mm2) for ACCs prepared using various weight % of [C2MIM][OAc] in DMSO.

Sample ID	% DMSO	% [C2MIM][OAc]	Thickness (mm)	Density (g/cc)	Yarn CSA (mm <sup>2</sup> )
C10-100	0	100	$0.30\pm0.01$	$0.93\pm0.01$	$0.021 \pm 0.001$
C10-80	20	80	$0.22\pm0.005$	$1.3\pm0.02$	$0.015\pm0.001$
C10-70	30	70	$0.334\pm0.004$	$0.95\pm0.02$	$0.018\pm0.002$
C10-60	40	60	$0.28\pm0.02$	$1.13\pm0.03$	$0.019\pm0.001$
C10-50	50	50	$0.27\pm0.02$	$0.97\pm0.03$	$0.013\pm0.001$
C10-40	60	40	$0.34\pm0.01$	$0.86\pm0.01$	$0.020\pm0.004$
C10-20	80	20	$0.31\pm0.01$	$0.87\pm0.01$	$0.025\pm0.001$

The results of the first two parts of the work suggest that using 80 wt.% [C2MIM][OAc] in DMSO with a 3:1 S/C weight ratio is indeed a good combination, leading to a more consolidated sample with increased density (less internal voidage), coupled with optimised peel strength and modulus. A proposed 'optimised' sample using a 3:1 S/C ratio, and 80 wt.% [C2MIM][OAc] in DMSO solvent solution was identified for further study in the final part of this chapter.

# **3.3.4** Influence of interleaf film on off-axis properties.

ACC samples were prepared according to the various stacking arrangements outlined in Figure 3-1 following the optimum solvent configuration identified previously (3:1 S/C ratio and 80 wt.% [C2MIM][OAc] in DMSO). Compaction time, temperature and pressure remained fixed at 10 minutes, 100°C and 2 MPa respectively. Samples were tested by applying load in three directions relative to the warp yarn orientation: 0 ° (longitudinal), 90 ° (transverse), and 45 ° (bias) directions illustrated in Figure 3-8.



Figure 3-8 Direction of longitudinal, transverse, and bias tensile testing of ACCs.

It was hypothesised that improved stress transfer from the matrix to the yarns could be obtained through the addition of the film, and this would in turn lead to improved off-axis properties. To test this, samples were subjected to non-axial loading, that is, not aligned to the direction of the yarns. In addition, a sample of unprocessed cotton cloth was tested, and the results are summarised in Figure 3-9 and Figure 3-10.



Figure 3-9 Comparison of longitudinal  $(0^{\circ})$ , transverse  $(90^{\circ})$  and bias  $(45^{\circ})$  mechanical properties of all-cellulose composites prepared with stacking sequences (0,0), (0,90) and (0,90,90,0). Unprocessed cotton cloth (Raw cloth), and the sample made without interleaf film (C0) is also shown for comparison.

The unprocessed (raw) cotton cloth shows the largest variation in tensile properties in the warp (longitudinal) and weft (transverse) directions, and this variation is mirrored in the composite prepared without interleaf film (C0), albeit comparatively larger values. There is a notable increase in Young's modulus in all directions for the ACCs made with the interleaf film, and the longitudinal and transverse properties are considerably closer together. This agrees with the hypothesis that extra matrix formation from the interleaf film helps to stabilise the reinforcement yarns, which subsequently reduces the effect of crimp on load dissipation and allows a more efficient transfer of stress. Although tensile strength reduces through all stacking sequences, this reduction is minimal when compared to the improvement in modulus and peel strength, as seen in Figure 3-10.



Figure 3-10 Comparison of longitudinal peel strength of all-cellulose composites prepared with stacking sequences (0,0), (0,90) and (0,90,90,0). The sample made without interleaf film (C0) is also shown for comparison.

Using a (0,90) stacking sequence not only aligns the properties in the 0° and 90° directions but also enhances the properties in the 45° bias direction, consistent with classical lamination theory (CLT) [209]. This suggests that the mechanical properties of ACCs align with those of traditional composite laminates, offering a promising insight into the potential of this ACC preparation method.

The symmetric sample produced using a (0,90,90,0) stacking sequence yielded interesting results and further insights. This sample exhibited a significantly high peel strength along with minimal variation in Young's modulus across all tested directions. However, the notable reduction in tensile strength, especially in the 45° direction, presents a different picture. The ACCs produced initially had one layer of interleaf film inserted between two textile layers. In the case of a symmetric sample, four textile layers were used, requiring three interleaf film layers to be inserted in between. Considering the ratio of film mass to textile mass, the addition of the film now results in a 15 % increase in cellulosic material, compared to the 10 % increase as was the case in the two-layer samples. This would potentially result in increased

matrix production, as evidenced by the elevated peel strength, but at the cost of a lower fibre volume fraction, and possible shift in failure mode. Previously it was hypothesised that ACCs produced using two textile layers might experience some delamination before ultimate failure at which the fibres then break. At this point it is suggested that the matrix has already fractured, leaving most of the load to be carried by the fibres. In this scenario, whilst there is enough interface to promote load transfer from the fibres to the matrix, the interfacial bond is not so strong as to cause the matrix to crack under applied load. In the symmetric sample, the increased matrix production results in cracks forming in the matrix, which can lead to brittle failure of the composite [210]. This could explain why the off-axis strength of the ACC is lower as the interface becomes compromised as a result of crack propagation. When load is applied in the 45° direction there are no fibres to take the loading, the drop in mechanical properties confirms that the matrix has broken before the fibres.

#### **3.4 Conclusions**

This chapter has studied the benefits of adding an interleaf cellulosic film in between layers of cotton textile, as applied to a partial dissolution process under applied temperature and pressure. This produced ACCs with an excellent balance of mechanical properties, in particular, excellent interlaminar adhesion was obtained through addition of the film, which essentially places extra matrix material where it can have the most effect. The film dissolution led to matrix production between the textile layers, sufficiently bonding them together and allowing the partially dissolved fibres to successfully bond to the interface. A solvent solution comprising 80 % [C2MIM][OAc] in 20 % wt. DMSO, and a 3:1 solvent to cellulose weight ratio was found to provide enough matrix to offset the loss of dissolved cellulose through flashing so that sufficient matrix could not only support bonding between the layers (inter-layer bonding), but also bonding between the yarns within the textile (intra-layer bonding). This combination of solvent parameters and processing with interleaved films was able to obtain a twofold and threefold improvement in Young's modulus and peel strength respectively. The improved adhesion facilitated improved stress transfer of external loads, within a relatively low processing time of 10 minutes, and Young's modulus was significantly improved from  $2.18 \pm 0.20$  GPa to  $4.20 \pm 0.16$  GPa with only minimal losses (from  $57 \pm 2$  MPa to  $47 \pm 1$  MPa) in tensile strength.

Additionally, improvements were observed in the  $45^{\circ}$  direction by orienting the warp yarns of two layers at 0° and 90°. Table 3-5 summaries the process conditions and resulting properties of the optimised ACC identified in this study.

Table 3-5 Process conditions, mechanical and physical properties of the optimumACC sample identified through the body of work in this chapter.

Tensile Strength (MPa)	Young's modulus (GPa)	Peel strength (N/m)	Thickness (mm)	Density (g/cc)	Yarn CSA (mm <sup>2</sup> )
$47 \pm 1$	$4.2\pm0.2$	$917\pm73$	$0.220\pm0.005$	$1.3\pm0.02$	$0.015\pm0.001$

Solvent configuration: 3:1 S/C ratio 80 % [C2MIM][OAc] / 20 % DMSO

It is worth bearing in mind that dissolution temperature, pressure and time were fixed throughout this chapter and to some extent, therefore, a one-factor-at-a-time (OFAT) approach was used to ascertain the ideal solvent configuration. The next chapter will explore the application of statistical design of experiments (DoE) in multi-factor analysis as applied to these dissolution conditions, to investigate its use as a tool to efficient process understanding and optimisation. The interest is whether this multi variable approach can find a further set of optimum conditions with an improved balance of mechanical properties to those shown in Table 3-5 acquired through OFAT.

# Chapter 4.

# Application of design of experiments to optimize all-cellulose composites.

## 4.1 Introduction

In the drive to accelerate the commercialisation of sustainable materials, it is crucial to understand the manufacturing process to ensure functional materials can be produced in a commercially feasible way. The previous chapter presented a study into the benefits of using interleaved films in the production of ACCs and explored how best to configure the solvent solution to obtain the best ACC properties through a one-factor-at-a-time (OFAT) approach.

There has been limited investigation into the interactive relationships of ACC processing parameters. In this chapter, the dissolution conditions of temperature, pressure and time (previously fixed) are now explored through a statistical design of experiments (DoE) approach, introduced in section 1.8, with an aim to assess the robustness of experimental design methods through validation of identified optimum conditions. This, to the best of available knowledge, has not previously been reported for ACC processing. By applying DoE in the context of the ACC preparation method presented in the previous chapter, insights will be gained into its practical applications across all ACC production methods. This approach also serves as a powerful tool for identifying optimal process conditions that may otherwise be overlooked through traditional methods, bringing awareness to the research

community to the tools available to help advance ACC research towards commercialisation.

Initially a full factorial design is employed to explore the effects of processing time, temperature, and pressure, with the goal of identifying any potential synergistic interactions and assessing their impact on the mechanical properties of ACCs. Subsequently, an inscribed central composite (CCI) response surface design is utilized. Here, there are two primary objectives:

- 1. To assess the effectiveness of DoE methodology to a system where some preliminary insight into suitable parameters already exists.
- To determine whether DoE can uncover a new set of optimized processing variables not previously found, thus demonstrating its potential to advance ACC research beyond the development stage and into commercial viability.

The work presented in this chapter led to my second publication entitled "Design of experiments in the optimization of all-cellulose composites" published in Cellulose (Victoria, A., et al., Design of experiments in the optimization of all-cellulose composites. Cellulose, 2023. 30(17): p. 11013-11039).

## 4.2 Experimental Methods

ACCs were made using two layers of cotton textile and a single layer of Natureflex film placed in-between as described in section 2.2. Bleached 100 % cotton with a plain weave was used as the cellulosic textile in this study, details of which are provided in section 2.1 along with details of the Natureflex film.

# 4.2.1 Composite Processing

Details of the procedure for preparing ACCs can be found in section 2.2, however, in this work, the solvent impregnation stage method was refined to ensure consistency in solvent application and to reduce any variation associated with this stage of the processing, for example, any variable wetting across the surface of the textile layers. Instead of using a brush to apply the solvent to the textile layers, the first layer was immersed in solvent, after which the layer of cellulose film was added and smoothed down. The second textile layer was then immersed in the remaining solvent and added to the stack. Prior to immersion, the solvent mixture was divided into the two parts to ensure equal amounts of solvent were introduced to the textile layers. The cotton textile layers were stacked with respect to the warp yarns at  $0^\circ$ , giving a stacking sequence of (0,0) as shown in Figure 4-1.



Figure 4-1. Textile stacking arrangement of 0,0 used in the preparation of ACCs, where the warp yarns of both layers are aligned in the same direction.

The solvent amount was based on a 3:1 S/C ratio to allow sufficient matrix production, and to compensate for flashing as discussed in Chapter 3. Additionally, there is no gain from limiting solvent use at laboratory scale when scaling up would involve the use of a solvent bath, exposing the textile substrate to excess solvent. Additionally, the investigation into % weight of [C2MIM][OAc] in DMSO in Chapter 3 led to a solvent mixture comprising by weight, 80 % [C2MIM][OAc], and 20 % DMSO to allow ease of application by reducing the IL viscosity. The processing factors of temperature, pressure and time during compaction were of primary interest and were varied as part of the experimental design and are described in the subsequent sections of this chapter. After solvent removal by soaking in water overnight, the stack was placed in the heat press once more to be dried as outlined in section 2.2.

# 4.1.1 Mechanical testing and Characterisation

ACC samples were tested and characterised according to the methods described in section 2.3.

# 4.1.2 Experimental design

#### **Full Factorial Design**

A  $2^3$  full factorial design was employed to screen the three factors of dissolution temperature, pressure, and time, and explore their potential effects on the mechanical properties of ACCs. Each of these factors under investigation have two levels representing lower and upper setting limits. The experimental domain within which to conduct experiments was ascertained through a preliminary scoping exercise involving the production of test samples at various test conditions, bearing in mind those used in Chapter 3. Upper and lower limits were determined from operational constraints, whilst also being aware of the importance of maintaining ACC quality. The outcomes of the scoping stage are outlined as follows.

For the compaction temperature, it was found that a temperature of 30 °C could be accurately maintained in the laboratory environment and as such was chosen for the lower temperature limit. An upper limit of 150 °C ensured the evaporation of DMSO could be avoided [211], as well as ensuring a stable temperature range. A lower pressure limit of 1 MPa was chosen to support efficient compaction of the cellulose layers and reduce shape distortion, and an upper limit of 3.6 MPa could be held consistently throughout the duration of the process. To investigate the processing time, several preliminary samples were made at the upper limits for temperature and pressure of 150 °C and 3.6 MPa respectively. This determined that ACC quality could be reasonably maintained without sample breakage when processed for a maximum duration of 180 minutes. Whilst undesirable for an industrial process, it was agreed that 180 minutes would be a suitable upper time limit to explore a wider design space and obtain the best outcomes from the experimental design. The parameters and coded values of factors are shown in Table 4-1.

Symbol	Factors	Levels							
_		Low (-1)	Mid (0)	High (1)					
А	Temperature (°C)	30	90	150					
В	Pressure (MPa)	1	2.3	3.6					
С	Time (mins)	1	90.5	180					

	Table 4	-1.	<b>Parameters</b>	and	coded	values	used in	the	full	factorial	design.
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Actual values used in the experiment are shown. () Coded values are displayed in brackets.

The full factorial design includes 8 factorial runs located at the corner points of the experimental space, and a run located at the centre point of all factor ranges, known as a centre point. The centre point was replicated five times to provide a balanced estimation of error and assessment of repeatability [155, 159], giving a total of six centre points. Coefficient of variance (COV) was used to quantify the level of variation across the centre points, calculated according to Equation 4-1.

#### **Equation 4-1**

 $Coefficient of variation (COV) = \frac{standard deviation}{mean} \times 100$ 

To reduce the risk of systematic errors, the order of the 13 total runs were randomized. The resulting 13 experimental runs along with measured responses are shown in Table 4-2.

Table 4-2. Experimental runs used in full factorial design. Samples are listed in run order with corresponding sample ID's. Centre points are denoted by (CP) next to samples ID.

		Factor settings								
Run No.	ID	Temperature A	Pressure B	Time C						
1	1F (CP)	90	2.3	90.5						
2	<b>2</b> F	30	3.6	180						
3	<b>3</b> F	30	3.6	1						
4	<b>4F</b>	30	1	1						
5	5F (CP)	90	2.3	90.5						
6	<b>6F</b>	30	1	180						
7	7F (CP)	90	2.3	90.5						
8	<b>8</b> F	150	1	1						
9	9F	150	1	180						
10	10F (CP)	90	2.3	90.5						
11	11F	150	3.6	1						
12	<b>12F</b>	150	3.6	180						
13	13F (CP)	90	2.3	90.5						
14	14F (CP)	90	2.3	90.5						
A = B =	Temperature Pressure (M	e (⁰C) Pa)								

C = Time (mins)

ACCs were prepared according to the full factorial design and tested, and the data was then fitted to a linear model (discussed in section 1.8.5.2 and shown in Equation 1-2) including main effects and interactions.

#### **Response Surface Design**

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For the subsequent optimisation stage, an inscribed central composite (CCI) design was established based on the same experimental domain as outlined in Table 4-3.

Symbol	Factors		Levels							
Symbol	r actors	Low $(-\alpha)$	(-1)	Mid (0)	(1)	High (a)				
А	Temperature (°C)	30	53	90	127	150				
В	Pressure (MPa)	1	1.5	2.3	3.1	3.6				
С	Time (mins)	1	36	90.5	145	180				

Table 4-3. Parameters and coded values used in the response surface design.

Actual values used in the experiment are shown. () Coded values displayed in brackets.

The upper and lower limits of the CCI are maintained from the original full factorial, and the axial points fall inside the experimental domain such that each factor has five levels. As mentioned in section 1.8.6, axial points in central composite designs are typically positioned at a distance  $\alpha$  from the centre point which is beyond the original factorial limits, with  $\alpha$  determined from Equation 1-4 for three factors. A CCI design is essentially a scaled-down CCC design to allow the original factorial design limits to be true limits. This leads to a design where in terms of coded values, the factor limits denote the location of the axial points, and a factorial cube is created within those limits, at a distance 1/ $\alpha$  from the centre point. For example, the distance between the CP and the upper/lower limits of temperature is 60 °C. Dividing this by  $\alpha$  results in a value of 37 °C. This is the distance from the CP of the scaled down factorial points as shown in Table 4-3. The response surface model is discussed in section 1.8.6 and shown in Equation 1-3.

Table 4-4 shows the 14 runs determined by the CCI, along with the six centre point replicates from the full factorial design, giving a total of 20 runs.

Dun No	Sample ID	I	Factor settings						
KUII INO.	Sample ID	Α	В	С					
1	1C	30	2.3	90.5					
2	2C	90	2.3	180.0					
3	3C	90	1.0	90.5					
4	4C	90	2.3	1.0					
5	5C	150	2.3	90.5					
6	6C	90	3.6	90.5					
7	7C	53	1.5	35.7					
8	8C	127	3.1	35.7					
9	9C	53	3.1	145.3					
10	10C	127	1.5	145.3					
11	11C	127	3.1	145.3					
12	12C	127	1.5	35.7					
13	13C	53	1.5	145.3					
14	14C	53	3.1	35.7					

 Table 4-4. Experimental runs used in response surface design. Samples are listed in run order with corresponding sample IDs.

 $A = Temperature (^{\circ}C)$  B = Pressure (MPa)C = Time (mins)

C = Time (mins)

# 4.1.3 Statistical Analysis

Minitab was used to generate the full factorial and CCI designs and analyse the experimental data through regression analysis and analysis of variance (ANOVA) outlined in section 2.4.1. A model was generated from backward elimination of insignificant terms, determined using the p values ( $p \ge 0.05$  considered insignificant). Coefficient of determination,  $R^2$ , was calculated to validate how well the experimental data are represented by the independent terms of the model [182, 197, 206]. The adjusted coefficient of determination,  $R^2_{(adj)}$ , was used to validate the strength of the model with respect to the number of model terms [160]. Additionally, the predicted coefficient of determination,  $R^2_{(pred)}$  was used to gauge the predictive power of the resulting model [157].

# 4.1.4 **Response Optimisation and Validation**

Optimum process conditions were determined using Derringers desirability function [196] as outlined in section 2.4.2. ACC samples were processed according to these conditions and tested to determine how well the obtained model was at predicting the properties of additional ACCs.

# 4.2 Results and Discussion

# 4.2.1 Statistical analysis of the full factorial design

The resulting ACCs from the experimental runs were tested and characterised using the methods described in section 2.3. The measured mechanical properties of the ACCs are shown in Table 4-5.

		Fac	tor sett	ings	Responses														
Run No.	ID	A	В	С	1 St (	'ensile rengtl MPa)	h	Y Modu	oung ulus (	's GPa)	Thick	ness	( <b>mm</b> )	De (j	ensity g/cm <sup>3</sup>	, ρ )	Void	l cont (%)	ent
1	1F (CP)	90	2.3	90.5	75	±	4	3.3	±	0.2	0.23	±	0.02	1.39	±	0.01	7.3	±	0.4
2	<b>2</b> F	30	3.6	180	67	±	2	2.5	±	0.2	0.26	±	0.02	1.20	±	0.01	20.2	±	0.3
3	3F	30	3.6	1	62	±	2	1.9	±	0.2	0.33	±	0.02	0.96	±	0.01	35.9	±	0.4
4	4F	30	1	1	47	±	2	1.4	±	0.1	0.34	±	0.02	0.96	±	0.01	35.8	±	0.3
5	(CP)	90	2.3	90.5	76	±	2	3.5	±	0.8	0.22	±	0.01	1.39	±	0.01	7.6	±	0.9
6	6F 7F	30	1	180	59	±	2	2.55	±	0.03	0.28	±	0.02	1.09	±	0.01	27.7	±	0.9
7	(CP)	90	2.3	90.5	74	±	5	3.3	±	0.2	0.23	±	0.02	1.33	±	0.04	12	±	3
8	8F	150	1	1	23	±	1	3.1	±	0.2	0.28	±	0.01	1.13	±	0.04	25	±	3
9	9F 10F	150	1	180	64	±	3	3.9	±	0.1	0.19	±	0.02	1.48	±	0.01	2	±	0.9
10	(CP)	90	2.3	90.5	83	±	2	3.6	±	0.1	0.24	±	0.01	1.32	±	0.03	12	±	2
11	11F	150	3.6	1	47	±	2	3.8	±	0.1	0.25	±	0.01	1.29	±	0.02	14	±	1
12	12F	150	3.6	180	74	±	1	3.8	±	0.1	0.21	±	0.01	1.30	±	0.03	13	±	2
13	(CP)	90	2.3	90.5	67	±	5	3.2	±	0.2	0.22	±	0.01	1.35	±	0.02	10	±	1
14	(CP)	90	2.3	90.5	81	±	1	3.3	±	0.4	0.22	±	0.01	1.33	±	0.03	11	±	2

 Table 4-5 Mechanical property responses from the experimental runs of the full
 factorial design.

A = Temperature (°C)

B = Pressure (MPa)

C = Time (mins)

#### **Tensile Strength**

It was not possible to capture tensile strength and derive a model from the full factorial experimental data. The results from the ANOVA analysis are presented in Table 4-6, but to summarise, all model terms were insignificant (p > 0.05), and the model indicator was also insignificant (p = 0.060). R<sup>2</sup>, R<sup>2</sup><sub>(adj)</sub> and R<sup>2</sup><sub>(pred)</sub> were 0.55, 0 and 0 respectively, further highlighting the inadequacy as a model. Although curvature was suspected (p < 0.05), the lack of other valid fit statistics suggests that a higher order model may not provide a more robust estimation.

	Degrees of	Sum of	Mean		
Source	freedom	squares	square	F-Value	P-Value
Model	7	1807.23	258.18	0.87	0.581
A: Temp (°C)	1	94.3	94.3	0.32	0.596
B: Pressure (MPa)	1	404.02	404.02	1.37	0.295
C: Time (mins)	1	904.91	904.91	3.06	0.14
AB	1	11.73	11.73	0.04	0.85
AC	1	338.47	338.47	1.15	0.333
BC	1	48.42	48.42	0.16	0.702
ABC	1	5.38	5.38	0.02	0.898
Residual	5	1477.07	295.41		
Curvature	1	1320.37	1320.37	33.7	0.004
Pure Error	4	156.7	39.17		
Total	12	3284.3			
$\mathbb{R}^2$	0.5503				
R <sup>2</sup> (adj)	0				
R <sup>2</sup> (pred)	0				

Table 4-6 ANOVA analysis from the full factorial model for tensile strength.

The lack of a model for tensile strength may seem unsatisfactory from a statistical point of view, however, it does support the notion that this parameter remains relatively stable across the range of processing variables, indicating its insensitivity to variations in the process as previously discussed in Chapter 3 (Figure 3-2).

In Chapter 3 it was demonstrated that inserting an interleaf cellulosic film in between textile layers introduces an additional source of cellulose that fully dissolves to form the matrix component. This matrix is sufficient to effectively bond the textile layers together and impregnate the fibre assembly, resulting in a well consolidated ACC with efficient load transfer to the partially dissolved fibres. With a dissolution-driven process under applied pressure, some dissolved cellulose and solvent can be lost through flashing, however, by using a 3:1 S/C ratio, it is possible to retain enough solvent to fully dissolve the film and only partially dissolve the fibres. Although the matrix fraction and ACC consolidation may vary depending on process conditions, the fibre fraction in the ACC is likely to remain relatively stable even at elevated temperatures where the rate of dissolution is increased [103]. This stability could explain the minimal variation in tensile strength, given that this

property is governed primarily by the composite's fibre content [49, 51].

#### Young's modulus

Table 4-7 shows the results of the ANOVA analysis for Young's modulus. A first order linear model was fitted for this parameter with time and temperature as main effects and no interaction terms.

	Degrees of	Sum	of	Mean		
Source	freedom	squares		square	F-value	p-value
Model	2	5.9172		2.95862	21.72	0.00015
A: Temp (°C)	1	5.2155		5.21548	38.3	0.00007
C: Time (mins)	1	0.7018		0.70176	5.15	0.04431
Residual	11	1.4981		0.13619		
Curvature	1	0.9193		0.91935	15.88	0.00258
Lack-of-Fit	5	0.4579		0.09159	3.79	0.08498
Pure Error	5	0.1208		0.02416		
Total	13	7.4153				
$\mathbb{R}^2$	0.798					
R <sup>2</sup> (adj)	0.7612					
R <sup>2</sup> (pred)	0.6494					

Table 4-7 ANOVA analysis from the Full Factorial model for Young's modulus

Recall for each factor and factor combination in the model, a p-value below 0.05 indicates a statistically significant effect within a 95 % confidence interval [182]. Additionally, the p-value for the overall model is significant (p < 0.05), suggesting that the model fits the experimental data well [160, 182, 197]. Other statistical indicators further support the confidence in the derived model, for instance, the F-value of 3.79 and p-value of 0.08 for the lack of fit indicates that the model is statistically insignificant relative to pure error.
The R<sup>2</sup>, adjusted R<sup>2</sup>, and predicted R<sup>2</sup> values were 0.80, 0.76, and 0.65, respectively, with the difference between adjusted and predicted R<sup>2</sup> being less than 0.2, indicating strong agreement between the model and the data [182, 197, 212-214]. Based on these indicators, the model for Young's modulus was considered statistically acceptable. Young's modulus could, therefore, be reliably estimated using a linear model as shown in Equation 4-2 below, where A and C represent temperature (°C) and time (minutes), respectively. The model is presented using uncoded factors, meaning that temperature and time are expressed in their actual units rather than coded units such as -1, 0, or 1, which typically denote factor levels in experimental design [160].

#### **Equation 4-2**

*Young's modulus* (*GPa*) = 1.526 + 0.01346 *A* + 0.00331 *C* 

Figure 4-2 presents the main effects plots for Young's modulus, illustrating how Young's modulus varies with temperature and time according to the model estimation. The plots reveal a clear positive influence of both temperature and time, with temperature having a comparatively larger effect than time. This aligns with the data shown in Table 4-5 which indicates that the lowest and highest Young's modulus values are observed in samples 4F, prepared at the lowest temperature and shortest time, and sample 9F, prepared at the highest temperature and longest time, respectively.



Figure 4-2 Main effects plots for Young's modulus showing its variation with temperature and time according to the model captured through the CCI.

Figure 4-3 shows Young's modulus plotted against ACC thickness and ACC density, highlighting strong correlations between these metrics that emphasize the role of physical properties in influencing Young's modulus [1, 215]. A thinner material will likely result from a reduction of internal void space as air is pushed out under compaction, as well as a loss of excess matrix fraction as dissolved cellulose is expelled. Longer dissolution times provide more time for air to diffuse out of the sample which would make the sample thinner. This produces a material with increased density (less internal voiding), which seems to influence Young's modulus as suggested in Figure 4-3(b). This is likely to be the controlling factor rather than the fractions of fibre or matrix for example, as dissolving power remains constant by fixing S/C ratio. The fibre and matrix fractions would, therefore, be similar for all samples produced via this batch processing route. The results strongly support the notion that density is one of the most important factors to consider in ACC performance [1, 215].



Figure 4-3 Young's modulus of prepared ACCs plotted against (a) thickness and (b) density.

The variation in thickness is evident in the ACC cross-sections obtained through optical microscopy as shown in Figure 4-4. Notably, samples 4F and 9F shown in Figure 4-4(a) and Figure 4-4(f), exhibit the lowest and highest Young's modulus, respectively. These samples were prepared at the minimum and maximum settings for temperature and time, offering some insight into the positive influence the two process factors may have. The cross-section of sample 9F, processed at the highest temperature (150°C) and time (180 minutes), shows a noticeably thinner and more consolidated ACC compared to sample 4F, which was prepared at the lowest temperature (30°C) and shortest time (1 minute). Sample 9F has a density of 1.48 g/cm<sup>3</sup>, significantly higher than sample 4F.



Figure 4-4 Optical microscopy cross-section images of ACCs prepared for the full factorial design including corer points (a-h) and centre points (i-n). Sample IDs are in the form 'ID(X)(Y)\_Z' which represents an ACC prepared at a temperature of X  $^{\circ}$ C, a pressure of Y MPa, and a time of Z minutes, prefixed with sample ID. CP denotes the samples prepared at the centre points. Scale bar represents 100 µm.

Figure 4-5 provides a comparison of these properties and illustrates their positioning within the two-dimensional space of the sample parameters. The increased density of sample 9F indicates a lower void content, and recalling the observations made in Figure 4-3(b), modulus is improved in the absence of internal voids. The external dimensions used to calculate modulus would be larger than they should be for a sample containing more internal voids. In addition, the reduction in voids may enhance the fibre-matrix interface and improve bonding between layers, leading to efficient load transfer. This is evidenced in the improvement of Young's modulus

from  $1.40 \pm 0.05$  GPa for samples 4F to  $3.9 \pm 0.1$  GPa for sample 9F. Figure 4-4(ad) also highlights the influence of temperature in promoting dissolution as evidenced by the visibility of the interleaf film between textile layers. As previously noted, complete dissolution of the film is desirable to ensure that the matrix can fully penetrate the fibre assembly and minimise void content. This is supported by the lower range of density values for all samples prepared at 30 °C, which range from 0.96 to 1.20 g/cm<sup>3</sup>.



# Figure 4-5 Images and comparison of properties of samples prepared at the lowest and highest temperature and time settings in the full factorial design.

Whilst there is strong evidence to support the influence of dissolution time and temperature in ultimately driving Young's modulus, Table 4-7 highlights that there may be curvature (p < 0.05), suggesting the optimized region may be located within the experimental domain, and not necessarily towards the boundaries. Recall centre point (CP) samples were produced as part of this design which, in addition to

providing assurance on reproducibility, can also help to detect local curvature [159] as detected in this case. Reproducibility was quantified through calculation of coefficient of variance (COV) across the centre points. A COV under 10 % indicates good process reproducibility, confirmed for both Young's modulus and tensile strength whose COV values were 5 % and 7 %, respectively.

It is worth taking a closer look at the range of values for the ACC mechanical properties to gain further insight into the trends captured and the significance of the CPs. Figure 4-6 presents a plot of Young's modulus and tensile strength for all prepared ACC samples, arranged in order of ascending Young's modulus. One would expect to observe a direct correlation between Young's modulus and tensile strength as is seen here; as Young's modulus increases, tensile strength appears to follow an upward trend. The exceptions to the trend are samples 8F and 11F, both of which were processed at 150 °C for 1 minute. These samples exhibit lower tensile strength values than the suggested curve would suggest, particularly sample 8F which has a notably reduced value of  $23 \pm 1$  MPa. Whilst this sample could be an outlier, it is possible that the combination of maximum temperature  $(150^{\circ}C)$  and a very short processing time leads to rapid cellulose dissolution and an accumulation of matrix material that cannot be adequately expelled as flash. Although this results in more matrix fraction, the reduced pressure prevents this from being utilized effectively, hindering its penetration through the fibre assembly. This results in poor consolidation which would lead to the observed decrease in tensile strength. The ANOVA does not highlight this, even though one might expect the range of values for tensile strength (from 23 MPa to 83 MP) to be wide enough to allow this property to be captured. What is seen from Figure 4-6 is that Young's modulus and tensile strength are not always correlated at the extreme points, suggesting that

tensile strength may be more sensitive to extreme conditions, leading to the process behaviour being more difficult to capture.



Figure 4-6 Young's modulus and tensile strength of ACC samples prepared for the full factorial design, in order of ascending Young's modulus. Sample 4F was prepared at the lowest temperature and shortest time, and sample 9F was prepared at the highest temperature and the longest time. (CP) denotes runs prepared at the centre points.

Interestingly, the CPs show promise among all the prepared samples, supporting the curvature detected in the ANOVA analysis for Young's modulus. There are only three samples that exceed the values for Young's modulus obtained at the CPs; samples 11F, 12F, and 9F, all prepared at the maximum temperature setting of 150 °C, with two of them prepared at the maximum time setting of 180 minutes. The Young's modulus values obtained at the CPs are, however, only slightly lower that these samples. Additionally, tensile strength peaks for the sample produced at the CPs, indicating that overall, the best balance of properties among all factor combinations are obtained at the CPs. Looking back at Figure 4-4, the CP samples

indeed exhibit good consolidation, suggesting that the most substantial overall improvement may occur near the centre of the experimental space, potentially reducing the need for higher temperatures and prolonged dissolution times.

#### 4.2.2 **Process and quality considerations.**

Product quality is a crucial aspect to be aware of when looking to optimise a process. Photographs of each prepared ACC after processing are shown in Figure 4-7, highlighting discolouration in the samples prepared at the highest time settings, in addition to some loss of quality and consistency of the surface. Optimizing mechanical properties is essential, but maintaining product quality and visual appeal is equally important. Therefore, such desirability attributes must be considered to ensure a good balance of properties can be obtained without sacrificing quality.



Figure 4-7 Images of ACC samples produced for the full factorial design including the six CPs.

A dissolution time of 180 minutes would typically not be favourable for a commercial process, given the aim is to produce materials in the most time-efficient way [48, 216]. Additionally, the importance of sustainable manufacture must not be overlooked, and as such, it is of interest to explore the energy requirements associated with processing conditions. From the temperature and time settings of each experimental run, a value representing the heat energy used in production can

be calculated, as shown in Equation 4-3, where room temperature in the lab is taken as  $20 \text{ C}^{\circ}$ .

#### **Equation 4-3**

Heat energy used in production(C°. hr)

= (Temperature(C°) – Room temperature(C°)) x Time(hr)

This then provides a metric to allow for a comparison of the energy used in producing each sample. Additionally, the mechanical absorbed energy (toughness) during tensile testing can be determined by calculating the area under the stressstrain plots, to indicate how much energy the material absorbs under tensile loads. Figure 4-8 shows both the heat energy used in production, and mechanical absorbed energy for each sample from the full factorial design, plotted in the same order as shown in Figure 4-6, in order of ascending Young's modulus.



Figure 4-8 Mechanical absorbed energy (yellow line) and heat energy used in production (red line) plotted for each ACC sample in order of ascending Young's modulus.

Looking at Figure 4-6 and Figure 4-8, the energy required to produce sample 9F (which has the highest modulus) at maximum temperature and time is significantly higher than that required to produce the CPs, which absorb the most energy. This observation further reinforces the idea that the optimal region may be located closer to the centre of the experimental domain, balancing reduced energy requirements with favourable property performance.

The next phase of this chapter involves extending the work to a response surface design to investigate possible curvature and identify the optimum region, as well as estimate potential higher order quadratic effects [213].

# 4.2.3 Statistical analysis of the CCI design

The experimental conditions assigned to the CCI design, along with measured responses are shown in Table 4-8.

Table 4-8 Experimental runs used in the CCI design, with responses. Samples are listed in run order, and sample IDs are given as XC where X represents run order. The CPs from the full factorial design are included for completeness.

	Samula	Fa	ctor sett	ings			Respo	onses		
	Sample	٨	D	C	Young's Modulus		<b>Tensile Strength</b>		ngth	
	ID	A	D	C	(	(GPa)		(MPa)		
1	1C	30	2.3	90.5	2.3	±	0.1	56.1	±	2.4
2	2C	90	2.3	180.0	2.9	$\pm$	0.1	79.6	$\pm$	1.1
3	3C	90	1.0	90.5	3.1	$\pm$	0.0	63.2	$\pm$	1.2
4	4C	90	2.3	1.0	2.3	$\pm$	0.1	68.0	$\pm$	2.0
5	5C	150	2.3	90.5	3.0	$\pm$	0.0	78.5	$\pm$	2.2
6	6C	90	3.6	90.5	3.0	$\pm$	0.1	69.8	$\pm$	1.8
7	7C	53	1.5	35.7	2.9	$\pm$	0.1	73.1	$\pm$	1.7
8	8C	127	3.1	35.7	2.9	$\pm$	0.2	70.1	$\pm$	1.7
9	9C	53	3.1	145.3	2.7	$\pm$	0.1	71.3	$\pm$	1.3
10	10C	127	1.5	145.3	3.2	$\pm$	0.1	73.7	$\pm$	1.9
11	11C	127	3.1	145.3	2.8	$\pm$	0.1	88.9	$\pm$	5.1
12	12C	127	1.5	35.7	2.9	$\pm$	0.2	48.9	$\pm$	1.2
13	13C	53	1.5	145.3	2.5	$\pm$	0.1	62.2	$\pm$	1.5
14	14C	53	3.1	35.7	2.7	$\pm$	0.1	65.5	$\pm$	0.7
				Centre Poi	nts					
	1F (CP)	90	2.3	90.5	3.3	$\pm$	0.2	75.4	$\pm$	3.5
	7F (CP)	90	2.3	90.5	3.3	$\pm$	0.3	73.8	$\pm$	4.6
	10F (CP)	90	2.3	90.5	3.6	$\pm$	0.1	83.1	$\pm$	1.7
	13F (CP)	90	2.3	90.5	3.2	$\pm$	0.2	67.4	$\pm$	4.8
	14F (CP)	90	2.3	90.5	3.3	$\pm$	0.2	81.2	$\pm$	1.4
	5F (CP)	90	2.3	90.5	3.52	±	0.08	75.4	±	2.1

 $A = Temperature (^{o}C)$ 

B = Pressure (MPa)

C = Time (mins)

It was not possible to obtain a response surface model for tensile strength as no significant terms (p > 0.05) were found for this property. With five levels for each factor instead of three, most of the factor combinations in the CCI design are located

at the interior points of the experimental domain. Unlike the full factorial design, the CCI design does not include runs that are combinations of all extreme factor settings. Half of the 14 experimental runs are combinations of factor levels all within the experimental space, with no upper/lower limits involved. The other half comprise just one factor set at its upper or lower limit. The cross-sectional images of the ACCs samples prepared for the CCI design are presented in Figure 4-9 and all samples show a narrower range of variability in thickness and consolidation. This contrasts with the samples obtained in the full factorial design, where consolidation and thickness varied more widely. This is reflected in the model's limited ability to capture differences within the relatively narrow range of tensile strength values, and further indicates the overall stability of this property within the chosen experimental domain.



Figure 4-9 Optical microscopy cross-section images of ACCs prepared for the response surface CCI design. Sample IDs are in the form 'ID(X)(Y)\_Z' representing an ACC prepared at a temperature of X °C, a pressure of Y MPa, and a time of Z minutes, prefixed with sample ID. Scale bar represents 100  $\mu$ m.

#### Young's modulus

It was possible to fit a second order quadratic model to the experimental data for Young's modulus as shown in Equation 4-4 in the form of uncoded factors, where A, B and C represent temperature in °C, pressure in MPa, and time in minutes, respectively.

#### **Equation 4-4**

Young's modulus (GPa)

 $= 0.696 + 0.03653A + 0.01583C - 0.000180A^2 - 0.000082C^2$ 

The ANOVA results are presented in Table 4-9. For this model, the R<sup>2</sup>, adjusted R<sup>2</sup>, and predicted R<sup>2</sup> values were 0.75, 0.68, and 0.49, respectively, with the difference between adjusted and predicted R<sup>2</sup> being less than 0.2. Additionally, the model is statistically insignificant (p > 0.05) relative to lack of fit, as demonstrated by a p-value of 0.22 and corresponding F-value of 2.06. All coefficients in the model are significant (p < 0.05) except for time as a main linear effect. However, given the significance of the quadratic effect, this term must remain in the model to maintain hierarchy [155, 188]. The significance of temperature and time as main effects, initially identified in the full factorial design, is further indicated in the response surface model. This suggests that their significance is more attributable to quadratic effects than to linear terms. As noted in the initial full factorial design, pressure is found to be insignificant (p > 0.05), which is interesting given is role in reducing void content and improving consolidation under compaction [9, 113]. The pressure range selected in this work, however, may be sufficient to achieve the desired consolidation.

Source	Degrees of freedom	Sum of squares	Mean square	F-Value	P-Value
Model	4	1.8398	0.45995	11.17	0
A: Temp (°C)	1	0.31424	0.31424	7.63	0.015
C: Time (mins) 1		0.04292	0.04292	1.04	0.323
A <sup>2</sup> : Temp <sup>2</sup>	1	0.78151	0.78151	18.98	0.001
C <sup>2</sup> : Time <sup>2</sup>	1	0.79998	0.79998	19.43	0.001
Residual	15	0.61749	0.04117		
Lack-of-Fit	Lack-of-Fit 10		0.04967	2.06	0.221
Pure Error	5	0.12081	0.02416		
Total	19	2.45729			
$R^2$	0.7487				
R <sup>2</sup> (adj)	0.6817				
R <sup>2</sup> (pred)	0.4864				

 Table 4-9 Analysis of Variance (ANOVA) from the response surface model for

 Young's modulus.

#### Influence of temperature and time on Young's modulus

The main effects plots in Figure 4-10 display the quadratic effects of both temperature and time on Young's modulus based on the derived model, reflecting the curvature suspected in the full factorial design. An increase in modulus is achieved with increased temperature and time up to a point, after which the property begins to drop. This is also represented through the two-dimensional contour plot in Figure 4-11, where the region of optimized modulus lies around the mid-points of temperature and time within the design space.



Figure 4-10 Main effects plots for Young's modulus as a factor of processing factors temperature and time.

Achieving a sufficient balance of matrix and fibre reinforcement is crucial for the functionality of ACCs. The volume of matrix formed afterwards, depends on the extent of cellulose dissolution and its retention during compaction. In Chapter 3 it was hypothesised that a combination of sufficient solvent and high temperature would lead to complete film dissolution, and partial fibre dissolution. This would preserve fibre reinforcement whilst generating enough matrix to bond the textile layers together and penetrate the fibre assembly. Sufficient matrix contributes to strong interfacial bonding, allowing efficient load transfer from the matrix to the reinforcing fibres, resulting in good mechanical performance. Extending the temperature range beyond 100°C in this chapter provides the opportunity to study what happens at lower and indeed, higher temperatures.



Figure 4-11 2D contour plot of Young's modulus as a function of temperature and time, generated from the statistical model.

The reduced Young's modulus observed at low temperatures (30–50 °C) suggests that while some dissolution occurs, it is insufficient to fully dissolve the film and allow adequate matrix dispersion throughout the fibre assembly. This was evident in the full factorial phase, where samples produced at the lowest temperature and shortest time settings of 30 °C and 1 minute (Figure 4-9(a) and (c)) showed signs of poor consolidation and incomplete film dissolution. Although there was slight improvement with an extended processing time of 180 minutes, (Figure 4-4(b) and (d)), it remained minimal. In samples prepared at 30 °C and 53 °C, as shown in Figure 4-9(a-d), the film is still visible, although increased processing time did lead to some improvement in consolidation. Over time there is more opportunity for matrix penetration to occur, resulting in a small improvement of properties as suggested in Figure 4-11.

Improvements in Young's modulus through increased temperature or time align with previous research on the time-temperature superposition of cellulose dissolution

[217], particularly at the lower settings of both factors. The optimised region highlights the beneficial effects of increasing temperature and time within the first 100 minutes and below 100 °C. Here, the increased temperature accelerates dissolution, which, with extended processing time, results in longer compaction and more consolidation. Beyond this range, further increases in one or both factors appear to reverse the trend, leading to a decrease in Young's modulus not captured in the original full factorial design. This reversal might be due to increased dissolution of the fibre, leading to a lower fibre volume fraction in the ACC which would contribute to reduced properties. Although more matrix material may result from increased fibre dissolution, it is likely to be expelled over time, leading to an uneven composition of fibre and matrix. For instance, Figure 4-9(m) shows a sample prepared at a high combination of temperature and time that appears thinner and more uneven than the rest, and there is a noticeable lack of sufficient matrix surrounding the fibres. Limiting fibre dissolution is crucial for achieving a good balance of mechanical properties, and the cellulosic film provides additional matrix material to facilitate this balance. The primary objective is to ensure the processing conditions are sufficient to simply 'wet' the fibres so that a strong fibre-matrix interface is created. The region for maximising Young's modulus is where overall, the amount of dissolved cellulose from both precursors is minimal. In this scenario, the film fully dissolves due to it being physically thinner, and the fibres within the yarns only partially dissolve their outer fibre layer, leaving the inner core of highly orientated cellulose [20, 87] intact to provide strength.

It is important to recognise that the trends provided in Figure 4-10 and Figure 4-11 are based on a best fit model obtained through analysis of the measured data. As with any experimental work, there will inevitably be variations between the data and

the model, particularly when working with natural materials that possess inherent variability. Since the full factorial and CCI designs were analysed independently, there may be some variation in each model estimation due to them being based largely on different data sets. For example, the decline in properties at higher temperature and time estimated from the CCI model is less evident in the full factorial runs, as sample 9F prepared at the maximum temperature and time exhibits a high modulus, rather than a reduced one. Nevertheless, it is important to remember the observations from Figure 4-7, and the discolouration of the samples prepared at the highest time settings. Avoiding a loss in quality and consistency is an important consideration in addition to mechanical properties.

In the CCI design, samples 10C and 11C, prepared at higher temperature and time settings, exhibit Young's modulus values similar to those obtained at the centre points. This suggests that the properties are levelling off rather than decreasing. The discrepancy between the model and the data arises from the best fit based on the majority of available data, bearing in mind that the CCI model benefits from more runs and thus more data that the full factorial. Overall, the estimations for Young's modulus are reasonably consistent with the full factorial design in relation to significant factors, allowing the response surface model derived from the CCI design to offer insights into optimizing the ACCs. The ability to accurately predict properties based on these optimized conditions will be explored next.

## 4.2.4 **Optimisation and Validation**

Derringer's desirability function was used to obtain the optimum combination of process conditions to maximize Young's modulus, based on the obtained CCI

response surface model with a standard deviation of 0.2. Optimal settings of 101.41  $^{\circ}$ C for temperature and 96.83 minutes for time were identified to produce an ACC with an average Young's modulus of  $3.3 \pm 0.1$  GPa. Temperature was rounded to the nearest  $^{\circ}$ C as this is the precision of the heat press equipment. Time was set to the nearest minute to reflect the accuracy that can actually be achieved when taking into account the time taken in loading and unloading samples. Therefore, a temperature and time of 101  $^{\circ}$ C and 97 minutes respectively is quoted and used in this work.

The predicted Young's modulus of  $3.3 \pm 0.1$  GPa aligns with the observed Young's modulus values from the CCI runs, as the samples with the highest modulus values were those prepared at the centre points, prepared at conditions close to the desirability prediction. This reinforces the earlier hypothesis that the most favourable combination of properties is likely to be found within the mid-range of the processing factors. As pressure was not found to be significant in the final model, the midpoint of the pressure range was selected for sample preparation. Five replicates were produced, and five specimens were tested for each replicate. The mean and coefficient of variance were then calculated across all replicates.

Measured properties of the in-lab test samples, along with COV and standard deviation across replicates are presented in Table 4-10. Figure 4-12 shows images of the test samples. From the five experimental samples, a Young's modulus of  $3.4 \pm 0.1$  GPa was obtained, with a COV of 6.2 % and standard deviation of 0.2. There is a good agreement between model and experimental values indicated by a COV of 0.85 %, meaning that the model is capable of successfully predicting the properties of the ACCs and optimizing Young's modulus. An independent two-sample t-test (p

concluding that there was no significant difference between them [180, 197].

Table 4-10 Properties of experimental samples prepared at the identified conditions for optimising Young's modulus, along with predicted Young's modulus.

Processing conditions				Young's modulus (GPa)		
Temperature (°C)	erature Pressure Time (C) (MPa) (mins)		n	Average	S.D	
Experimental san	nples					
101	2.3	97	5	3.4	0.2	
101	1	07		2.4	0.1	
101	1	97	2	3.4	0.1	
101	3.6	97	2	3.37	0.03	
Model prediction						
101	-	97	20	3.3	0.2	

Additional samples were produced at pressure settings of 1 and 3.6 MPa to verify the insignificance of pressure in the final model, and to investigate whether pressure influences the physical characteristics of the ACCs. For each pressure setting, two replicates were made and tested. The COV between the model and the experimental samples was 1.7 % for the sample made at a pressure of 1 MPa, and 1.1 % for the sample made at a pressure of 3.6 MPa, indicating that there is little difference between the variance of the experimental samples and model. The COV between all experimental samples was 0.6 %, further confirming that pressure is not an influential factor. However, it should be noted that the pressure range used in this study was relatively narrow compared to previous works that have explored this parameter [105, 116]. It is possible that this pressure range was too narrow to cause any substantial change in properties.



Figure 4-12 Images of ACC samples produced at the identified optimum conditions of 101 °C, and 97 minutes at 2.3 MPa. Additional samples prepared at 1 MPa and 2 MPa are additionally shown.

# 4.2.5 Characterisation of the optimized ACCs

Table 4-11 shows additional properties for the samples prepared at the optimum conditions, with fixed pressure of 2.3 MPa. Cross-sections from three of these samples are presented in Figure 4-13.

Although tensile strength could not be accurately modelled, the optimised samples exhibited a tensile strength of  $72 \pm 2$  MPa, and an average peel strength of  $811 \pm 160$  N/m, indicating excellent interlaminar strength. Furthermore, the ACCs produced had a density of  $1.42 \pm 0.03$  g/cm<sup>3</sup>, surpassing all but one of the densities obtained in the original full factorial samples. The only exception was sample 9F, prepared at maximum temperature and time settings, which had a marginally higher density of  $1.48 \pm 0.01$  g/cm<sup>3</sup>, however, as noted previously this sample showed signs of compromised quality. A density of  $1.42 \pm 0.03$  g/cm<sup>3</sup> is notably higher than previously reported densities of ACCs prepared from cellulosic fibres such as lyocell [97, 218] and flax [97]. Whilst density measurements are not frequently reported in ACCs prepared using textile reinforcement, this value suggests that the density achieved here is comparable to, or higher than that of ACCs made using lyocell fabric [116], and post-consumer cotton [219]. High density in ACCs indicates a low void content [3, 215] and the void content for these samples can be estimated as  $5 \pm 2$  %.

Table 4-11 Measured properties of optimised ACCs prepared at temperature, pressure, and time of 101 °C, 2.3 MPa, and 97 minutes respectively.

Processing conditions						
Temperature (°C)	101					
Pressure (MPa)	2.3					
Time (mins)	97					
Properties						
Young's modulus, E (GPa)	3.4	±	0.2			
Tensile Strength, τ (MPa)	72	±	2			
Failure strain (%)	6.4	±	0.2			
Peel strength (N/mm)	811	±	160			
Thickness (mm)	0.22	±	0.01			
Density, $\rho$ (g/cm <sup>3</sup> )	1.42	±	0.03			
Estimated void content (%)	5	±	2			

The excellent consolidation observed in the optimised ACCs is obtained without compromising the balance of matrix and fibre and is reflected in the properties obtained. The results emphasize the importance of density as a powerful factor in driving the mechanical performance of ACCs [215].



Figure 4-13 Optical microscopy cross-section images of ACC samples prepared at the identified optimum conditions. Sample ID are in the form 'ID(X)(Y)\_Z' representing an ACC prepared at a temperature of X  $^{\circ}$ C, a pressure of Y MPa, and a time of Z minutes, prefixed with the sample ID.

Young's modulus and heat energy used in production for each of the CCI samples is presented in Figure 4-14 in order of ascending heat energy. The plot also features the average Young's modulus and heat energy of the optimized samples (labelled 'Optimized'), demonstrating a good agreement with the CP samples produced under similar processing conditions. Within the scope of this response surface design, the optimized samples and CPs exhibit the highest modulus and require comparatively less energy than other samples with similar modulus values.

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Sample ID

Figure 4-14 Young's modulus and heat energy used in production for each of the samples in the CCI design, plotted in order of ascending heat energy.

Sample 10C is the only sample with a Young's modulus close to that obtained from the CPs, however the temperature and time settings (127 °C and 145.3 minutes respectively) used to produce this sample, require significantly more energy. In addition to a favourable tensile strength and density, the optimized samples possess desirable properties across a range of parameters.

It is worth bearing in mind that the inherent variability of natural fibres such as cellulose could influence the outcomes of ACCs produced using different commercially sources textiles such as cottons. Whilst the in-lab validation aligned closely with the model prediction for Young's modulus, it is possible that different batches of textiles might yield varying results. The estimation of error calculated from replicate CPs, however, does offer insight into the range of acceptable values for experimental samples that should match theoretical predictions. Applying DoE methodology to ACC processing using a variety of cellulose sources could be

beneficial in exploring a broader range of variability and identifying whether processing behaviour differs across sources.

#### 4.1 Conclusions

The use of statistical DoE is demonstrated in this chapter as a viable approach to understanding ACC preparation in an efficient way. Additionally, the use of DoE in optimising ACC mechanical properties is highlighted. With respect to the preparation of ACCs using cotton textiles and interleaved films as introduced in Chapter 3, it was possible to model Young's modulus through an inscribed central composite (CCI) design, as well as identify a desirable set of processing conditions to maximize this property. This was then validated with in-lab samples that exhibited an average Young's modulus of  $3.4 \pm 0.1$  GPa, when processed at the identified optimum dissolution conditions of 101 °C and 97 minutes, agreeing well with the model prediction of 3.3 GPa. In addition to Young's modulus being modelled successfully, the optimised ACCs exhibited excellent additional properties with a tensile strength of  $72 \pm 2$  MPa and peel strength of  $811 \pm 160$  N/m. Density, an important physical property, was found to be  $1.42 \pm 0.03$  g/cc, higher than the majority of experimental runs and close to the density of cellulose previously discussed as 1.5 g/cc. Achieving optimal mechanical properties appears to be driven by the elimination of internal voids. This an extremely valuable finding, offering promising insights into the effectiveness of statistical DoE to optimise ACC production.

The insignificance of pressure in determining Young's modulus was validated by fixing temperature and time at the optimum settings and preparing ACCs at varied

pressure settings. The results showed that pressure settings of 1 MPa and 3.6 MPa will yield ACCs with a Young's modulus of  $3.4 \pm 0.1$  GPa and  $3.37 \pm 0.03$  GPa respectively, both in excellent agreement with the model prediction. Table 4-12 summaries the process conditions and resulting properties of the optimised ACCs identified in this study.

Table 4-12 Process conditions, mechanical and physical properties of the optimised ACC samples identified through the body of work in this chapter.

Tensile Strength (MPa)	Young's modulus (GPa)	Peel strength (N/m)	Thickness (mm)	Density (g/cc)	Void content (%)		
$72 \pm 2$	$3.4 \pm 0.2$	$811 \pm 160$	$0.22\pm0.01$	$1.42\pm0.03$	$5\pm 2$		
Process conditions:							

101°C 2.3 MPa 97 minutes

This work provides insight into obtaining improved process understanding more efficiently than traditional OFAT methods as utilized in Chapter 3, in the development of ACCs. The work has also demonstrated process reproducibility which supports the future commercialization of ACCs. This is an important step in the field of ACCs and the potential applications of statistical modelling. The next chapter looks at the production of ACCs using regenerated cellulose fibres (Tencel), applying DoE methodology to explore whether similar optimized properties can be achieved.

# Chapter 5.

Design of experiments investigation into the production of all cellulose composites using regenerated cellulosic textiles.

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# 5.1 Introduction

The previous two chapters have focused on the production of ACCs using native cellulose in the form of cotton textiles. The following chapter now aims to explore ACC production using textiles made from regenerated cellulosic fibres, utilizing the DoE methodology developed in the previous chapter. In addition to applying DoE to investigate process-property relationships as done in Chapter 4, this chapter also evaluates the benefits of using the interleaved cellulosic film, which was previously examined using only OFAT methods in Chapter 3. Understanding how best to use regenerated cellulosic fibres to produce ACCs has particular significance for widening the potential applications for waste-derived regenerated fibres.

A  $2^3$  full factorial design was applied initially to determine the effects of processing parameters on ACC mechanical properties. Using the insights gained from the previous chapters, three parameters were chosen for investigation as follows: The significance of temperature and time (as revealed in Chapter 4 on the cotton-based ACCs) led to their inclusion in this chapter. Pressure was also explored in Chapter 4 and was found to have no significant effect on the resulting ACC properties. It was, therefore, not included in this work. Recall from Chapter 3 the OFAT exploration of percentage [C2MIM][OAc] in DMSO with the cotton-based ACCs, which revealed a potential relationship between ACC properties and this parameter. With future scale-up considerations in mind, it was decided that the inclusion of [C2MIM][OAc] in DMSO as a factor to explore with the Tencel-based ACCs would be beneficial, particularly to support future visions for a continuous process. In summary, the factors of dissolution temperature and time and the percentage [C2MIM][OAc] in DMSO were explored.

The full factorial design was subsequently expanded to a face-centred central composite (CCF) response surface design to optimise the response variables of mechanical properties. The primary objectives of this work were as follows:

- To increase understanding of different DoE methods when applied to ACC processing. The CCI design from Chapter 4 was successful in capturing the data, however, it is of interest to see if a comparable quality of information can be gained more efficiently through a CCF.
- 2. To assess the effects of adding the interleaved film during processing. With a predominantly cellulose II system, limiting fibre dissolution preserves more cellulose II rather than cellulose I as in the cotton system. It is, therefore, of interest to assess its use in addition to processing behaviour.

The content of this chapter led to my third publication entitled "Design of experiments investigation into the production of all cellulose composites using regenerated cellulosic textiles" published in Composites Part A: Applied Science and Manufacturing (Victoria, A., et al., Design of experiments investigation into the production of all cellulose composites using regenerated cellulosic textiles. Composites Part A: Applied Science and Manufacturing, 2024: p. 108510).

#### **5.2 Experimental Methods**

ACCs were produced using regenerated cellulose (Tencel), the details of which are provided in section 2.1.

# 5.2.1 Composite processing

Details of the processing method are provided in section 2.2. For the work presented in this chapter, however, the benefits of the interleaved film were investigated, in addition to the processing conditions of temperature and time. ACCs were produced via two systems: one with an interleaved cellulosic film between the layers as previous, and one without the film. A schematic of these systems is provided in Figure 5-1. These systems are referred to as F0 and F1 for ACCs prepared without interleaf film, and for ACCs prepared with an interleaf film, respectively.

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Figure 5-1: Schematic of the stages involved in the preparation and manufacture of the ACCs.

Dissolution temperature and time were investigated as part of this work and as such, were varied according to the experimental design. In addition, the percentage of [C2MIM][OAc] in DMSO (referred to as IL % for this work ) was included as a third continuous factor. In Chapter 3, the IL % was explored through the OFAT approach, where it was established that adding 20 % DMSO (80 % IL) supports the production of a well consolidated ACC and allows for ease of application to the textile stack by lowering the viscosity of [C2MIM][OAc] [35]. This was adopted in Chapter 4 where IL % was fixed at 80 % for the DoE investigation into cotton-based ACCs. As the cellulosic textile precursor is Tencel for this work, it is of interest to explore this parameter to see if there is a more optimum ratio for these ACCs that differs from the cotton-based ACCs. Here, the IL % was varied from 30 % to 100 % to explore its influence further. A solvent to cellulose (S/C) weight ratio of 3:1 was used, as in Chapter 4.

Washing and drying conditions were fixed as previous, and a fixed processing pressure of 2.3 MPa was used for all the experiments. Whilst deemed insignificant

in driving ACC properties, a setting of 2.3 MPa does allow the textile stack to maintain shape during processing.

# 5.2.2 Mechanical testing and characterisation

Tensile strength, Young's modulus and strain-to-failure of ACC samples were tested using the methods described in section 2.3. ACC samples were characterised using the methods described in section 2.3.

# 5.2.3 Experimental design

A 2<sup>3</sup> full factorial design was used for preliminary exploration of compaction temperature, process time, and IL %, and their influence on ACC properties. Here, the three continuous, independent factors each have 2 levels, representing the minimum and maximum settings. Figure 5-2 outlines the experimental domain within which the experiments would be performed, which were determined and refined through preliminary screening experiments and insights from the previous chapters. It was important to ensure the range over which to collect data was wide enough to capture the data effectively, yet suitably constrained to avoid ACC damage and discoloration at extreme conditions of temperature and time. The final minimum and maximum settings were, therefore, established with these considerations in mind. Six centre point (CP) runs were included, comprising a combination of the mid-points of all factor settings.

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Figure 5-2 Geometry of the full factorial (a) and central composite face centred (CCF) (b) design spaces with three factors (A,B,C) with associated experimental runs. The factorial/corner points are shown as blue dots, axial points are shown as red dots, and centre points (CPs) are shown as yellow dots.

Table 5-1 outlines the continuous factors and their coded values. Runs were conducted for both F0 and F1 systems, and so the use of the interleaf film is included as a categorical factor. The full factorial design domain is represented in Figure 5-2(a).

Table 5-1 Factors used in the full factorial design. Actual values used in the experiment are shown, and coded values are displayed in brackets.

Continuous Factors	Lower (-1)	Centre Point (0)	Upper (1)
A: Temp (°C)	30	75	120
B: IL%	30	65	100
C: Time (mins)	10 95		180
Categorical Factor			
Film	No (F0)		Yes (F1)

A lower limit of 30 °C for compaction temperature was chosen to ensure it could be maintained accurately in the laboratory environment. Recall from the previous chapter that discoloration was observed for ACCs processed at dissolution temperatures beyond 120 °C. Whilst Tencel is a new cellulose source (man-made as

opposed to natural cotton), the textile is still cellulosic, and as such it was deemed appropriate to define an upper limit of 120 °C from the previous study. To determine a time range to be explored, several preliminary samples were made at 120 °C, and it was found that damage to the Tencel based ACCs could be avoided if they were processed for less than 180 minutes.

Table 5-2 Experimental runs used in the study and listed in the run order. IDs for ACCs made without film, and with film are prefixed with 'F0' and 'F1' respectively. The first 14 lines represent the full factorial design and the last six lines (in bold) represent the additional CCF runs.

ID (No Eilm)	ID (Eilm)	Factor settings				
ID (NO FIIM)	ID (FIIM)	Α	В	С		
F0_1(CP)	F1_1(CP)	75	65	95		
F0_2	F1_2	30	30	10		
F0_3(CP)	F1_3(CP)	75	65	95		
F0_4	F1_4	120	30	180		
F0_5	F1_5	30	30	180		
F0_6	F1_6	120	100	10		
F0_7(CP)	F1_7(CP)	75	65	95		
F0_8	F1_8	30	100	180		
F0_9	F1_9	120	30	10		
F0_10	F1_10	120	100	180		
F0_11(CP)	F1_11(CP)	75	65	95		
F0_12	F1_12	30	100	10		
F0_13(CP)	F1_13(CP)	75	65	95		
F0_14(CP)	F1_14(CP)	75	65	95		
F0_15	F1_15	30	65	95		
F0_16	F1_16	120	65	95		
F0_17	F1_17	75	30	95		
F0_18	F1_18	75	100	95		
F0_19	F1_19	75	65	10		
F0_20	F1_20	75	65	180		

A = Temperature ( $^{\circ}$ C), B = IL %, C = Time (mins) Centre point IDs are suffixed by (CP).

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Table 5-2 shows the experimental runs used in this chapter. The first 14 runs refer to the full factorial design and include 8 factorial runs (corner points) and an additional

centre point (CP) sample repeated six times. The order of runs to be conducted was randomized to reduce the risk of systematic or biased errors. The data collected as part of the full factorial design was fitted to a linear model discussed in section 1.8.5.2 and shown in Equation 1-2, to include main effects and interactions.

### 5.2.4 Response surface design

For optimisation, a face-centred central composite (CCF) response surface design was used. Recall from section 1.8.6 that a CCF design can be established by expanding on a full factorial design with an extra six axial points located on the face of the experimental design cube, as shown in Figure 5-2(b). This contrasts with the 14 extra runs required in the CCI design used in the previous chapter. Each factor maintains the three levels outlined in Table 5-1, but the additional combinations provide more data to analyse. The response surface model is discussed in section 1.8.6 and shown in Equation 1-3. The extra six samples required to expand the full factorial design are shown in Table 5-2, making a total of 20 runs for the CCF design.

#### 5.2.5 Statistical analysis

The full factorial and CCF designs were generated using Minitab, which was also used to perform ANOVA analysis of the experimental data. Analysis was conducted separately for both systems (F0: ACCs without film and F1: ACCs with film) to allow comparison of these two systems. Factor analysis was focused on the continuous factors of temperature, IL %, and time. Insignificant terms were removed
through backward elimination (by way of the p-value), allowing a model to be generated that linked the response variable to the process factors.

## 5.2.6 Optimisation and validation

Optimum process conditions to produce the most desirable response value were identified using Derringers desirability function [196] (discussed in 1.8.7 and outlined in 2.4.2). Samples were produced in the lab using these identified conditions and tested. The resulting properties were compared to those predicted, to assess how well the obtained model could predict ACC properties.

## 5.3 Results and Discussion

## 5.3.1 Analysis of the full factorial data

Tensile strength, Young's modulus and strain-to-failure were collected for the ACC samples produced for the full factorial design and are shown in Table 5-3. Both systems F0(no film) and F1(with film) are shown, with the average of each run taken from five test specimens. An average value from six centre points (CPs) was calculated.

Table 5-3: Measured responses from the experimental runs of the full factorial design. F0\_CPs and F1\_CPs represent the average values over 6 CPs for F0 and F1 systems, respectively.

	Fact	tor Sett	ings		Responses										
ID	A	В	С	Ye me	oung odul GPa	g's lus l)	Stra failu	ain-1 1re (	to- %)	Te Str (N	ensil eng /IPa	e th )	Den	sity (	(g/cc)
F0_2	30	30	10	1.8	±	0.2	10.8	±	1.0	46.5	±	2.1	0.98	±	0.02
F0_4	120	30	180	3.4	$\pm$	0.1	5.8	$\pm$	0.6	46.4	$\pm$	1.6	1.07	±	0.01
F0_5	30	30	180	4.7	$\pm$	0.2	7.4	$\pm$	0.1	60.9	$\pm$	1.7	1.19	±	0.03
F0_6	120	100	10	5.6	$\pm$	0.1	2.3	$\pm$	0.2	67.6	$\pm$	1.1	1.21	$\pm$	0.03
F0_8	30	100	180	5.1	$\pm$	0.3	3.0	$\pm$	0.0	59.1	$\pm$	1.4	1.23	±	0.02
F0_9	120	30	10	3.0	$\pm$	0.2	6.3	$\pm$	0.1	44.7	$\pm$	1.4	1.03	$\pm$	0.03
F0_10	120	100	180	5.3	$\pm$	0.2	2.1	$\pm$	0.1	64.8	$\pm$	1.6	1.25	±	0.01
F0_12	30	100	10	3.9	$\pm$	0.1	5.1	$\pm$	0.0	53.7	$\pm$	2.2	1.13	±	0.02
F0_CPs	75	65	95	5.5	±	0.2	1.6	±	0.2	58.4	±	2.5	1.22	±	0.03
F1_2	30	30	10	1.7	$\pm$	0.0	15.4	$\pm$	0.3	56.7	$\pm$	1.3	0.97	±	0.03
F1_4	120	30	180	2.5	$\pm$	0.2	10.0	$\pm$	0.4	51.4	$\pm$	4.9	1.03	±	0.02
F1_5	30	30	180	2.6	±	0.0	12.9	$\pm$	0.7	59.1	±	2.0	1.01	$\pm$	0.01
F1_6	120	100	10	3.9	$\pm$	0.3	3.0	$\pm$	0.2	63.1	$\pm$	2.7	1.29	±	0.02
F1_8	30	100	180	3.2	$\pm$	0.3	5.9	$\pm$	0.5	56.9	$\pm$	3.9	1.21	±	0.01
F1_9	120	30	10	3.6	$\pm$	0.1	7.4	$\pm$	0.6	56.7	$\pm$	1.9	1.21	±	0.01
F1_10	120	100	180	3.5	±	0.8	2.5	$\pm$	0.4	58.3	±	3.6	1.32	$\pm$	0.01
F1_12	30	100	10	3.5	±	0.1	7.3	$\pm$	0.8	50.7	±	2.1	1.16	±	0.02
F1_CPs	75	65	95	4.6	±	0.4	2.2	±	1.1	59.6	±	3.3	1.27	$\pm$	0.02

A = Temperature ( $^{\circ}$ C), B = IL %, C = Time (mins)

Figure 5-3 shows tensile strength, Young's modulus and strain-to-failure plotted for each sample, in order of ascending Young's modulus with respect to the ACCs made with the film (F1). Optical microscopy images of all prepared samples are shown in Figure 5-4 and Figure 5-5 for the F0 and F1 systems, respectively.

On comparison of systems F0 and F1, minimal differences in tensile strength are seen, suggesting that the film has little benefit on this property. In Chapter 3 it was found there to be a small reduction (~ 5-10 MPa) in tensile strength when using the film at the fixed processing conditions used. Here, it is found that this property remains relatively unaffected with respect to using the film.



Figure 5-3 Measured values for Young's modulus, YM (a), ultimate tensile strength, UTS (b) and strain to failure, STF (c) across all full factorial runs for ACCs made with film (solid dot) and No Film (cross-box).

There is more variation in values across Young's modulus and strain-to-failure, however. Young's modulus values are higher when the film is not used, with an average increase of 1-2 GPa for majority of samples. F0 and F1 systems are seen to follow similar trends, however, this is particularly strong for strain-to-failure as shown in Figure 5-3 (c). The data from both systems displays consistent patterns with the same high-to-low order observed in both, suggesting that the film does not affect how the process conditions influence this property.



Figure 5-4 Optical micrographs of the full factorial corner points (a-h) and centre points (i-n) for the F0 system.

The sample produced at the lowest factor settings for both systems (F0\_2 and F1\_2) exhibits the highest strain-to-failure. This is indicative of under processing or reduced dissolution of the yarns, which would allow them to untwist and stretch out under applied load, resulting in a high strain-to-failure. This sample also exhibits the lowest Young's modulus, with or without the interleaf film, making it the least desirable ACC of those produced. This does not definitively suggest that these lower settings are insufficient to produce ACCs, but the combination of all three factors at low settings is unlikely to be optimal. Here, a thicker cross-section and less consolidation occurs, as shown in Figure 5-4(a) and Figure 5-5 (a).



Figure 5-5 Optical micrographs of the full factorial corner points (a-h) and centre points (i-n) for the F1 system.

Interestingly, the most desirable combination of properties is seen from the CPs which possess the highest Young's modulus and lowest strain-to-failure. Additionally, Figure 5-4 and Figure 5-5 show that for both systems, the most consolidated cross-sections are achieved at the CPs, consistent with the improved properties when compared to the factorial points. This initial analysis suggests that the region around the CPs may be most optimum for ACCs, made with the regenerated Tencel fibres, irrespective of whether the film is used or not. Indeed, the samples with strain-to-failure values in the region of 4 % show improved consolidation than those exhibiting higher values, as seen in samples F0\_6, F0\_8 and F0\_10 (Figure 5-4 (d, g, h)) and samples F1\_6 and F1\_10 (Figure 5-5(g,h)), coinciding with the increased Young's modulus values. It is suggested that higher

strain-to-failure values are attributed to poor bonding within the composite structure, and an unprocessed fibre in the ACC could, therefore, stretch more under applied strain, giving a higher strain-to-failure of the overall ACC. Additionally, whilst the strain-to-failure of lyocell fibres is in the region of 20 % [87, 116], a matrix produced from lyocell fibres is in the region of 4 % [87], which supports the above observations. This suggests that a strain-to-failure in the region of 4 % can be used as a guide for this work, to achieve good consolidation between the fibre and matrix phases indicative of sufficient processing in the ACCs.

#### **5.3.2 Presence of the film**

Another crucial observation emerging from Figure 5-5 is that the film layer can still be seen clearly. This was not the case in Chapter 3 with the cotton-based ACCs where it was found that when the film fully dissolved, the matrix component provided by the film could penetrate the fibre assembly as well as sit between the textile layers. This led to the intralayer and interlayer bonding within the material being reinforced, contributing to improved mechanical properties when compared to a scenario where the film only partially dissolved. It is possible that the process conditions obtained through the full factorial design are not sufficient to achieve full dissolution of the film. It is observed that many samples are under processed with large strain-to-failure values and, therefore, it may be expected that the film would not fully dissolve. However, the film is visible across all full factorial samples, including the six CPs, which possess the best balance of properties. It is entirely possible that there is an optimal region not captured yet from the full factorial design, something to bear in mind when conducting the ANOVA analysis in the next stage.

ANOVA analysis was conducted using the data obtained through the full factorial design for both F0 and F1 systems separately. Table 5-4 and Table 5-5 show the results of the ANOVA for strain-to-failure for the F0 and F1 systems respectively.

	Degrees of	Sum of			
Source	freedom	squares	Mean square	F-Value	P-Value
Model	1	40.040	40.040	7.010	0.021
B: IL (%)	1	40.040	40.040	7.010	0.021
Residual	12	68.572	5.714		
Curvature	1	47.253	47.2531	24.38	0
Lack-of-Fit	6	21.154	3.526	106.570	0.000
Pure Error	5	0.165	0.033		
Total	13	108.612			
$\mathbb{R}^2$	0.3687				
R <sup>2</sup> (adj)	0.316				
R <sup>2</sup> (pred)	0.1195				

Table 5-4 Analysis of Variance (ANOVA) from the full factorial data for failurestrain for ACCs prepared without film (F0).

To summarize, it was possible to capture strain-to-failure in some capacity for both systems, however, the fit of the model to the data was not strong as indicated by low coefficient of determination ( $\mathbb{R}^2$ ) values of 37 % and 50 % for the F0 and F1 systems respectively.

	Degrees of	Sum of	Mean		
Source	freedom	squares	square	F-Value	P-Value
Model	2	133.490	66.745	5.640	0.021
A: Temp (°C)	1	42.937	42.937	3.630	0.083
B: IL (%)	1	90.553	90.553	7.650	0.018
Residual	11	130.227	11.839		
Curvature	1	115.28	115.28	77.13	0
Lack-of-Fit	5	8.712	1.742	1.400	0.361
Pure Error	5	6.235	1.247		
Total	13	263.717			
R <sup>2</sup>	0.5062				
R <sup>2</sup> (adj)	0.4164				
R <sup>2</sup> (pred)	0.2043				

 Table 5-5 Analysis of Variance (ANOVA) from the full factorial data for failure

 strain for ACCs prepared with film (F1).

The results of the ANOVA for Young's modulus are presented in Table 5-6. Young's modulus was captured only for the F0 system, however, again, the model was not a good fit to the data, as evidenced through a low  $R^2$  value of 30 %.

As discussed in section 1.8.5, a key limitation of a full factorial design is its inability to estimate quadratic effects. A full factorial study can capture only linear relationships with interactions, as there is not enough data to estimate quadratic effects. If there is minimal variation between extreme factorial points, the design will inevitably fail to detect any intermediate changes.

	Degrees of	Sum of	Mean		
Source	freedom	squares	square	F-Value	P-Value
Model	1	6.045	6.045	5.190	0.042
B: IL (%)	1	6.045	6.045	5.190	0.042
Residual	12	13.978	1.165		
Curvature	1	6.848	6.849	10.570	0.008
Lack-of-Fit	6	6.042	1.007	4.630	0.057
Pure Error	5	1.088	0.218		
Total	13	20.024			
$\mathbb{R}^2$	0.3019				
R <sup>2</sup> (adj)	0.2437				
R <sup>2</sup> (pred)	0.016				

Table 5-6 Analysis of Variance (ANOVA) from the full factorial data for Young's modulus for ACCs prepared without film (F0).

Centre points (CPs) are valuable additions to experimental designs such as full factorial designs. As mentioned previously, they help to indicate the reproducibility of a process, as well as provide an estimation of error [155, 159]. The presence of CPs can also offer insight into possible quadratic effects of factors that the full factorial alone cannot capture. In this case, the CPs did indeed provide some information to indicate possible curvature, which is indicated by a significant p-value (p < 0.05) shown in Table 5-6.

The results of the ANOVA for strain-to-failure for F0 and F1 systems are presented in Table 5-7 and Table 5-8, respectively, and the low  $R^2$  values for both systems again indicate that the models are not a good fit to the data sets. Significant curvature is also suspected, consistent with the lack of fit of the captured linear models.

	Degrees of	Sum of	Mean		
Source	freedom	squares	square	F-Value	P-Value
Model	1	40.040	40.040	7.010	0.021
B: IL (%)	1	40.040	40.040	7.010	0.021
Residual	12	68.572	5.714		
Curvature	1	47.253	47.2531	24.38	0.000
Lack-of-Fit	6	21.154	3.526	106.570	0.000
Pure Error	5	0.165	0.033		
Total	13	108.612			
$\mathbb{R}^2$	0.3687				
R <sup>2</sup> (adj)	0.316				
R <sup>2</sup> (pred)	0.1195				

 Table 5-7 Analysis of Variance (ANOVA) from the full factorial data for failure

 strain for ACCs prepared without film (F0).

Whilst inconclusive, the results of the ANOVA at this stage are unsurprising given the best balance of Young's modulus and strain-to-failure is observed at the CPs. Based on this, an expansion to a response surface design is a worthwhile next step, and the next stage involves the expansion of the full factorial design to a CCF design. Here, the design space can be explored further across both F0 and F1 systems.

Degrees of	Sum of	Mean		
freedom	squares	square	F-Value	P-Value
2	133.490	66.745	5.640	0.021
1	42.937	42.937	3.630	0.083
1	90.553	90.553	7.650	0.018
11	130.227	11.839		
1	115.28	115.28	77.13	0.000
5	8.712	1.742	1.400	0.361
5	6.235	1.247		
13	263.717			
0.5062				
0.4164				
0.2043				
	Degrees of freedom 2 1 1 1 1 1 5 5 5 13 0.5062 0.4164 0.2043	Degrees of         Sum of           freedom         squares           2         133.490           1         42.937           1         90.553           11         130.227           1         115.28           5         8.712           5         6.235           13         263.717           0.5062         0.4164           0.2043	Degrees of freedomSum of squaresMean square2133.49066.745142.93742.937190.55390.55311130.22711.8391115.28115.2858.7121.74256.2351.24713263.7170.50620.41640.20431	Degrees of freedomSum of squaresMean2133.49066.7455.640142.93742.9373.630190.55390.5537.65011130.22711.83911115.28115.2877.1358.7121.7421.40056.2351.247113263.7170.506210.41640.20431

 Table 5-8 Analysis of Variance (ANOVA) from the full factorial data for failure

 strain for ACCs prepared with film (F1).

It is of interest to assess the effectiveness of a DoE study, the methods chosen, and initial observations prior to moving to the next stage of investigation. It is not immediately apparent from the full factorial data, what the impact of the film on ACC mechanical properties truly is. Irrespective of whether the film is used or not, the centre points appear to yield the best balance of properties thus far, suggesting an optimized process region may involve the mid points of process factors, rather than the extremes as might be expected. After the CPs, samples F\_6 and F\_10 across both systems have the best balance of properties, both produced at the highest temperature and IL% settings. The difference between these samples is time, suggesting that this may not be a significant factor, however, it is not advisable to make this assumption from a full factorial design. The strength of the CPs is a reminder of the limitations of the full factorial approach in estimating beyond first-

order effects. Acquiring more data through an expansion of the design will allow second-order effects to be estimated.

## 5.3.4 Analysis of the CCF design.

As illustrated in Figure 5-2 (b), the experimental runs of the CCF comprise those of the original full factorial design, plus an additional six runs. The results from these six additional runs are presented in Table 5-9.

Table 5-9 Measured responses from the six additional experimental runs produced to form the CCF.

	Fact	tor Sett	ings	Responses											
ID	Α	В	С	Y m	oun odu (GP	ng's Ilus 'a)	St: fail	rain lure	1-to- (%)	Te Str (N	ensil eng <u>/IPa</u>	e th )	Dens	ity	( <b>g/cc</b> )
F0_15	30	65	95	5.5	±	0.3	1.8	±	0.1	53.5	±	2.6	1.18	±	0.02
F0_16	120	65	95	6.1	±	0.2	1.6	±	0.02	64.8	±	3.5	1.18	±	0.02
F0_17	75	30	95	6.2	±	0.1	3.0	±	0.2	59.4	±	0.6	1.27	±	0.02
F0_18	75	100	95	5.9	±	0.2	1.7	±	0.2	62.9	±	3.0	1.25	±	0.02
F0_19	75	65	10	5.5	±	0.4	1.5	±	0.01	57.6	±	2.8	1.26	±	0.00
F0_20	75	65	180	6.3	±	0.1	1.4	±	0.2	68.0	±	4.8	1.27	±	0.01
F1_15	30	65	95	6.0	±	0.2	2.1	±	0.3	57.8	±	1.6	1.31	±	0.01
F1_16	120	65	95	6.0	±	0.3	1.4	±	0.1	63.3	±	0.9	1.25	±	0.00
F1_17	75	30	95	3.4	±	0.1	8.8	±	0.8	56.4	±	3.1	1.10	±	0.02
F1_18	75	100	95	5.6	±	0.1	1.7	±	0.2	60.1	±	2.5	1.33	±	0.01
F1_19	75	65	10	5.5	±	0.1	1.5	±	0.1	59.5	±	3.2	1.25	±	0.02
F1_20	75	65	180	6.7	±	0.03	1.2	±	0.02	62.4	±	1.1	1.32	±	0.02

A = Temperature ( $^{\circ}$ C), B = IL %, C = Time (mins)

Density and strain to failure are plotted against Young's modulus for the ACCs prepared without film (system F0) and presented in Figure 5-6. Here, all the results from the full factorial, CCF and CPs fall on the same straight line. The CPs are located within a more desirable region (higher Young's modulus, lower strain-to-

failure, higher density) than the corner points of the full factorial design, and the six centre face points (axial runs) from the CCF (red points) overall show improved Young's modulus values (5-6 GPa) when compared to the CPs (average 4.6 GPa), revealing a new optimal region where the Young's modulus is the highest. This region was not revealed previously in the original full factorial design runs (blue), nor was it occupied by the centre points (yellow).



Figure 5-6 Density (a) and strain to failure (b) are plotted against Young's modulus for all runs in the CCF design for ACCs made without film (F0). Corner points from the full factorial design are shown in blue, The average CP value is shown in yellow, and the additional CCF axial runs are shown in red.

Whilst arguably unsurprising, the advantage of expanding a full factorial design to a response surface design is highlighted here, where additional samples can start to narrow down the region of optimisation from the initial experimental domain. Prior to statistical analysis of the data, it could be suggested that the optimized region bears similarities to the processing conditions of the CPs, i.e., the mid-points. Perhaps a combination of mid-point factor settings leads to more desirable ACCs, suggested by the CCF, which offers more precision.

Optical micrographs of the six experimental runs for the F0 system are presented in Figure 5-7. When compared to the eight corner points of the full factorial (Figure 5-4), these additional samples exhibit improved consolidation.





Similar observations are seen with the F1 system as shown in Figure 5-8, however, the CCF runs are not in line with the trend observed from the full factorial design data. Instead, they have their own correlation, evidencing the curvature in the data that was not picked up from the full factorial points alone. The CCF expansion has captured a region of processing conditions where, for the F1 system, Young's modulus is more sensitive to changes in density. This is highlighted through the decreased gradient of the trendline captured for the CCF data.



Figure 5-8 Density (a) and strain to failure (b) are plotted against Young's modulus for all runs in the CCF design for ACCs made with film (F1). Corner points from the full factorial design are shown in blue, The average CP value is shown in yellow, and the additional CCF runs are shown in red.

The additional CCF samples made with film (F1) are presented in Figure 5-9. For both systems, the highest Young's modulus is achieved with samples F0\_20 and F1\_20, with values of 6.3 GPa and 6.7 GPa respectively. Here, both temperature and IL % are at the mid-points, however, the increased time to 180 minutes helps to increase Young's modulus beyond that achieved at the CPs. It could be that more time is needed to push the internal air out from the sample, an observation made in the previous two chapters when using cotton. F0\_20 (Figure 5-7(f)) appears noticeably flatter than F1\_20 (Figure 5-9 (f)). Sample F1\_20, however, is comparable in in thickness to the rest of the samples. It is also worth noting that the film can be seen in between the layers of the extra CCF samples, the same observation that was made previously with the full factorial samples.



Figure 5-9 Optical micrographs of six additional samples (F1 system) prepared for the CCF.

It was postulated earlier that the film may only be partially dissolving at the process conditions assigned by the full factorial design, and by exploring the design space further, a more optimum region where the film fully dissolves could be found, forming a more consolidated ACC with improved mechanical properties. The extra samples do exhibit Young's modulus values of up to 6.6 GPa, which is higher than the samples produced in the full factorial design, however, the film is still visible, leading to a rethink of the film behaviour in the context of the textile, or more specifically, the Tencel fibre structure.

It is possible that the layer seen is in fact, dissolved cellulose that has remained in between the textile layers, and on coagulation, has formed a layer of matrix component. This hypothesis can be supported by the work of Chapter 3 and the samples made at comparable process conditions to those made in this chapter. For example, Figure 5-10 shows optical microscopy images of the ACCs made in Chapter 3, prepared using cotton textile and interleaved films at 100°C, 2MPa for 10 minutes, using 60 and 70 % IL in DMSO. Here, it is noted that full dissolution of the film occurred.



Figure 5-10 Optical microscopy images of ACCs from Chapter 3, prepared using cotton textile and interleaved films at 100 °C using 70 % (a) and 60 % (b) IL in DMSO.

Sample F1\_16 (shown in Figure 5-9(b)) was prepared using 65 % IL at 120 °C for 95 minutes. The 65 % IL concentration sits between those used in the previous chapter (70 % ad 60 %), and the higher temperature and time settings would support more, rather than less, dissolution of the film. Given the film dissolved fully in the cotton samples, there is a strong likelihood that it would dissolve here with the Tencel samples. What is interesting here, is that a distinct region between the textile layers can still be seen, suggesting that whilst the film dissolved, it had nowhere to go, subsequently coagulating to form matrix exactly where it was placed during preparation.

The work presented in Chapter 3 led to the discovery that the film significantly improved interlaminar bonding in ACCs. To do so, however, it had to dissolve partially at least, to support a strong interface and avoid delamination. It didn't

necessarily need to penetrate through the textile to improve bonding, however, its mere presence provided the composite with enough matrix to bond the layers together. This then resulted in a significant increase in peel strength. The use of a 3:1 S/C ratio resulted in an ACC with the optimum Young's modulus as well as interlaminar bonding. This was associated with the film penetrating through the fibre assembly, supporting consolidation within the material, contributing to fibre-matrix bonding, and thus enhanced mechanical properties. The 3:1 S/C ratio has been used in the subsequent chapters of this thesis. Of the 20 samples prepared for the F0 and F1 systems, 18 comparative samples exhibited the same failure upon tensile testing, suggesting that overall, inter layer and intra layer bonding wasn't significantly influenced using the film. Four samples delaminated upon testing for both F0 and F1 systems, and these samples were all processed at 30 % IL, the minimum setting for this parameter.

The presence of the dissolved film offers insight into the structure of Tencel, as discussed in section 1.2.2. Recall that Tencel fibres are bundles of multiple filaments that have a smooth and spherical cross-section meaning they can pack more closely together. This makes it more difficult for the solvent to access the inner regions of the fibre during dissolution. Cotton fibres, on the other hand, are irregularly shaped so when bundled to form a yarn, there is more space available for the solvent to access the inner regions. The reduced accessibility of the filament bundles possibly explains why the film is still seen in the ACCs, rather than dissolving and penetrating through the fibres as seen in cotton-based ACCs. In the case of the Tencel, the film dissolves but is unable to move as easily. On coagulation, it remains in between the textile layers.

## 5.3.5 ANOVA analysis of the CCF design

Minitab was used to analyse the CCF data, and each system (F0, F1) was analysed separately. The extra CCF runs did not help to capture tensile strength, however, this was unsurprising given the limited range of values across all 20 runs. This outcome was consistent across both systems, which indicates that tensile strength is insensitive to the processing conditions or the presence of the film.

Table 5-10 and Table 5-11 display the ANOVA results for the F0 system for strainto-failure and Young's modulus, respectively.

Source	Degrees of freedom	Sum of squares	Mean square	F-Value	P-Value
Model	4	103.915	25.979	17.810	0.000
A: Temp (°C)	1	10.219	10.219	7.010	0.018
B: IL (%)	1	36.700	36.700	25.160	0.000
A <sup>2</sup> : Temp <sup>2</sup>	1	7.578	7.578	5.190	0.038
$B^2$ : $IL^2$	1	15.777	15.778	10.820	0.005
Residual	15	21.881	1.459		
Lack-of-Fit	10	21.718	2.172	66.610	0.000
Pure Error	5	0.163	0.033		
Total	19	125.796			
$\mathbb{R}^2$	0.8261				
R <sup>2</sup> (adj)	0.7797				
R <sup>2</sup> (pred)	0.5838				

Table 5-10 Analysis of Variance (ANOVA) from the CCF data for failure strainfor ACCs prepared without film (F0).

The poor fit statistics indicate that the system was not captured well across both properties. To summarize, a quadratic relationship was found linking IL % and dissolution temperature to strain-to-failure, however as seen in Table 5-10, the

model had a significant lack of fit as evidenced by the F-value (F-value < 0.05). Looking at Table 5-11, Young's modulus was also captured in a quadratic model involving IL % and dissolution time; however, this was associated with a low predicted coefficient of variance ( $R^2_{(pred)}$ ) of 21 %. The poor fit statistics put into question the predictive ability of the models captured.

	Degrees of	Sum of	Mean		
Source	freedom	squares	square	F-Value	P-Value
Model	3	14.375	4.792	6.282	0.005
B: IL (%)	1	4.443	4.443	5.824	0.028
C: Time (mins)	1	2.665	2.665	3.494	0.080
C <sup>2</sup> : Time <sup>2</sup>	1	7.267	7.267	9.527	0.007
Residual	16	12.206	0.763		
Lack-of-Fit	11	11.067	1.006	4.418	0.057
Pure Error	5	1.139	0.228		
Total	19	26.581			
$\mathbb{R}^2$	0.5408				
$R^2$ (adj)	0.4547				
$R^2$ (pred)	0.2094				

Table 5-11 Analysis of Variance (ANOVA) from the CCF data for Young's modulus for ACCs prepared without film (F0).

### 5.3.6 Young's modulus (F1 system)

For the F1 system (where interleaf film was used), however, the additional runs did allow the data to be captured across both Young's modulus and strain-to-failure.

Young's modulus was fitted to a second order quadratic model as shown in Equation 5-1. The equation is shown in the form of uncoded factors where B represents IL %, the only significant factor identified for this property. This suggests that the film may reduce the sensitivity of mechanical properties to the processing parameters.

#### **Equation 5-1**

*Young's modulus* (*GPa*) =  $-2.33 + 0.2152 B + 0.001526 B^2$ 

Table 5-12 presents the results of the ANOVA analysis for the F1 system. The model fits the experimental data well, which is indicated by the p-value (p < 0.05) for the model indicator [160, 182, 197]. As explained in Chapter 1, a p-value less than 0.05 indicates a significant effect of the associated factor. Furthermore, there is no significant lack of fit, as highlighted by the associated p-value (p > 0.05), and F-value (> 1) which indicates confidence in the models [157, 197]. The difference between the  $R^2_{(adj)}$ , and  $R^2_{(pred)}$  values is less than 0.2, indicating that the derived model agrees well with the experimental data obtained. This was not the case for the F0 system.

Table 5-12 Analysis of Variance (ANOVA) from the CCF model for Young'smodulus. ACCs made with film (system F1).

	Degrees				
	of	Sum of	Mean		
Source	freedom	squares	square	F-Value	P-Value
Model	2	20.910	10.455	11.772	0.001
B: IL (%)	1	3.428	3.428	3.860	0.066
$B^2$ : $IL^2$	1	17.482	17.482	19.685	0.000
Residual	17	15.098	0.888		
Lack-of-Fit	12	11.543	0.962	1.353	0.391
Pure Error	5	3.555	0.711		
Total	19	36.008			
$\mathbb{R}^2$	0.581				
$R^2$ (adj)	0.5314				
$R^2$ (pred)	0.4273				

The proposed effect of IL% on Young's modulus is displayed in the main effects plot in Figure 5-11, suggesting that the optimum IL% for maximizing this property is 70 %. Interestingly, this value is similar to the concentration used in the previous chapters, which was 80 %. A sufficient amount of ionic liquid must be used to process the ACCs and achieve good bonding between the fibres and the matrix, however, the addition of DMSO is beneficial to allow ease of application of solvent solution to the ACC stack through lowering its viscosity.



Figure 5-11 Main effects plot for Young's modulus as a function of IL % (F1 system).

## 5.3.7 Strain-to-failure (F1 system)

It was possible to capture strain-to-failure for the F1 system, and the results of the ANOVA analysis for this property are shown in Table 5-13.

Source	Degrees of freedom	Sum of squares	Mean square	F-Value	P-Value
Model	3	305.457	101.819	45.860	0.000
A: Temp (°C)	1	37.006	37.006	16.670	0.001
B: IL (%)	1	115.931	115.931	52.220	0.000
$B^2$ : $IL^2$	1	152.520	152.520	68.700	0.000
Residual	16	35.523	2.220		
Lack-of-Fit	11	29.142	2.649	2.080	0.217
Pure Error	5	6.381	1.276		
Total	19	340.980			
$\mathbb{R}^2$	0.8958				
$R^2$ (adj)	0.8763				
R <sup>2</sup> (pred)	0.827				

Table 5-13 Analysis of Variance (ANOVA) from the CCF model for strain-tofailure. ACCs made with film (system F1).

Equation 5-2 represents the second order quadratic models for the F1 system, shown in the form of uncoded factors where A and B represent temperature in °C, and IL %, respectively. The model indicates that strain-to-failure has a temperature dependence, but again as with Young's modulus, time was not identified as a significant factor. The difference between the  $R^2_{(adj)}$ , and  $R^2_{(pred)}$  values is less than 0.2 and the model shows a good fit to the experimental data (p < 0.05).

#### **Equation 5-2**

*Strain-to-failure* (%)(F1) = 30.54 - 0.0427 A - 0.6834 B + 0.004509 B<sup>2</sup>

In summary, the CCF data has helped further identify the significant terms across the properties of Young's modulus and strain-to-failure for the F1 system, an improvement from the original full factorial design where no terms were found. The information obtained from the CCF suggests that IL % plays a key role in driving Young's modulus. Recall that the factors of dissolution temperature and IL% which were identified in the full factorial design, are again identified through the CCF. Here, and the additional quadratic effect of IL% has improved the strength of the relationship, highlighted in the increase of R<sup>2</sup> from 54 % to 90 %. Interestingly, time has not been identified as significant in driving ACC properties. This contrasts to the cotton-based ACCs in previous chapter where it was found that whilst dissolution of the film layer was not specifically time-dependent, Young's modulus did improve with increased time, up to a point, after which it decreased. It was suggested that over time, internal air is pushed out which increases the density of the resultant ACC. The properties decreased as time was increased further, and it was suggested that this was due to increased fibre dissolution combined with excess matrix being pushed out. In the Tencel-based ACCs, film dissolution is achieved in all ACC samples, with little influence of time.

Given the data for Young's modulus and strain-to-failure was captured more strongly for the F1 system, it was decided that a multi-response optimisation would be performed across this system on the derived models for Young's modulus and strain-to-failure, using Derringer's Desirability function.

#### 5.3.8 Optimisation

Derringer's desirability function was used to obtain a combination of significant process factors to yield the best balance of Young's modulus and strain-to-failure for ACCs made with film. The aim here was to maximise Young's modulus and maintain strain-to-failure in the region of 4 % to avoid under processing as seen in values for Young's modulus and strain-to-failure.

Table	5-14	Optimu	ım pro	ocessing	conditions	obtained	through	the	response
surfac	e mod	lels for	Young	's modu	lus and stra	in-to-failu	re, for A	CCs	prepared
with ir	nterlea	af film.							

Processing conditions	With Film system
A: Temperature (°C)	30
B: IL (%)	70
C: Time (mins)	10*
Predicted responses	
Young's modulus (GPa)	5.3
Strain-to-failure (%)	3.5 %
Desirability	0.76

\* denotes arbitrary setting for insignificant factors

It is interesting to note that time was deemed insignificant in driving both Young's modulus and strain-to-failure for the F1 system, which was suggested earlier on analysis of the full factorial data. The majority of the extra six samples have indeed higher Young's modulus values and strain-to-failures below 4 % and were produced at three different time settings. This supports a possible conclusion that time is insignificant, however, there is a difference of 1.2 GPa between samples F1\_19 and F1\_20, processed at the same temperature and IL%, but for 10 and 180 minutes respectively. Furthermore, the predicted response for Young's modulus is 5.25 GPa, a value lower than all but one of the extra 6 samples produced for the CCF. Multi-response optimisation can result in a compromise between responses to get the best overall desirability, however, in this case Young's modulus is driven by only IL%. Both responses rely on IL % to drive them, and optimize at 70 % , however, the inclusion of temperature originates from the model for strain-to-failure only.

Therefore, the model irrespective of strain-to-failure would predict an optimum Young's modulus of 5.25 GPa. Nevertheless, analysis of the data has led to the derived models and predicted responses based on the full data set. Validation of the predictions will indeed support confidence in them. Given time was deemed insignificant for the F1 system, a processing time of 10 minutes was chosen for preparing the validation samples. Four replicates were prepared with four specimens tested from each replicate. The mean, and coefficient of variance across all replicates was then calculated.

#### 5.3.9 In-lab validation

Table 5-15 displays the measured properties of the four in-lab test samples, along with coefficient of variance (COV) and standard deviation across the four replicates prepared with film.

Table	5-15	Young's	modulus	and	strain-to-fai	lure o	of F1	experimental	samples
prepa	red at	t the iden	tified opti	imum	n conditions,	with	mode	l predictions.	

Young's modulus (GPa)				Strain-to-failure (%)					
Predict	ion	Measured			Predict	ion	Measured		
Average	S.D	Average	S.D	COV	Average	S.D	Average	S.D	COV
5.3	0.9	4.9	0.3	5.3 %	3.5	1.5	3.3	0.5	13.6 %

An independent two-sample t-test (p = 0.05) was performed to compare the means of the model predictions and experimental samples. The test concluded that there was no significant difference between the mean values for both Young's modulus and strain-to-failure, supporting the validity of the relationships found between process conditions and these mechanical properties. The use of interleaf films appears to enable a process that can be modelled sufficiently to predict mechanical properties such as Young's modulus and strain-to-failure.

Table 5-16 provides a comparison of the mechanical and physical properties of the optimised ACCs produced in this chapter, versus those optimised in the previous chapter. Although a direct comparison is not possible due to the differences in design and factor selection between the two studies, it is interesting to note that a higher Young's modulus can be achieved with Tencel-based ACCs at a reduced temperature. The Tencel-based ACCs also exhibit a lower density (and thus a higher estimated void content), and this may be due to the reduced dissolution time chosen for validation. Notably, time was not identified as a significant factor for Young's modulus in the Tencel study.

Table 5-16 Properties of opti	mised ACCs	produced using	cotton and	l Tencel
textiles with interleaved films.				

	Cotton-based ACCs			Tencel-based ACCs		
Optimized process conditions:						
Temperature (°C)		101			30	
IL (%)		80			70	
Time (mins)		97			10	
Pressure (MPa)	2.3			2.3		
Measured properties:						
Young's modulus (GPa)	3.4	±	0.2	4.9	±	0.2
Strain-to-failure (%)	6.4	±	0.2	3.3	±	0.3
Tensile strength (MPa)	72	±	2	59	±	2
Peel strength (N/m)	811	±	160	963	±	89
Thickness (mm)	0.22	±	0.01	0.276	±	0.004
Density (g/cm <sup>3</sup> )	1.42	±	0.03	1.26	±	0.01
Estimated void content (%)	5	±	2	16.2	±	0.5

The adequacy of the model derived from the CCF has been validated through comparison to in-lab samples, however, it is important to consider the possibility that there may be a more optimal region in the experimental space for mechanical properties, that the CCF has not identified. This is due to the notably higher measured values of the experimental runs that expanded the full factorial design into the CCF. While the CCF was able to capture Young's modulus where than the full factorial design could not, the predicted Young's modulus of 5.3 GPa is lower than the measured values of many of the extra samples.

The CCF approach reduces the number of experimental runs by building on an existing design, making it an efficient route to response surface exploration. Additionally, it enables the mid-points of factors to be explored in combination with more extreme values. Central composite designs such as a central composite circumscribed (CCC) design typically offer this capability, however as described in section 1.8.5, this often requires expanding the design space beyond the original limits. This is not always appropriate as in the case here, where expanding beyond the original boundary limits would result in negative factor settings. The CCF approach keeps axial points within the space, as well as making use of an existing full factorial design. Given that some factorial points of the full factorial exhibited similar favourable properties to the CPs, it was a reasonable strategy to opt for the CCF approach to explore whether an optimized region lay directly near the CPs, or in some combination of factor mid-points. It is also important to acknowledge the limitations of lab-scale experimental work, and whilst every effort is taken to ensure samples are produced consistently (as demonstrated through replicates of CPs and validation samples), there may be specific disturbances (noise factors) that have

yielded lower than expected experimental results, which would limit optimization. It is possible that noise may be too large due to the inherent capabilities of the experimental set up, meaning that predictions cannot be made within a narrow uncertainty range. Nevertheless, the statistics have allowed for an exploration of the design space and different combinations of factors.

As discussed in the literature review of Chapter 1, the CCF explores a more limited space than a CCC does, or indeed the CCI used in the previous chapter, which required more runs. As a consequence, it is possible that regions where the response could be higher, have been overlooked. Nonetheless, the CCF has successfully captured trends for both Young's modulus and strain-to-failure, from which predictions were made and validated. A key finding here is the ability of the F1 system to be modelled, in contrast to the F0 system which was less successful. It is suggested that the film may help to maintain consistent dissolution conditions during sample processing and, therefore, manage uncontrolled variability that arises through flashing. In essence, the film plays a role in reducing noise, thus allowing the ACCs to respond solely to the process factors under investigation.

The film remains between the textile layers suggesting that the structure of Tencel offers little space for it to migrate. This means that any dissolved cellulose from the fibres or film is likely to remain at the filament surface or in between the layers, rather than impregnating the filament bundles. Indeed, it may be that the fibre dissolution occurs only at the filament surface which is more accessible for the solvent. Consequently, dissolved cellulose available for the matrix is positioned such that it can more easily escape the stack through flash, as opposed to if it were impregnating the filament bundles. Flashing may also vary with different process

conditions and introduce noise to the system. If this varies at different process conditions, this could in effect, impact matrix formation unpredictably. By incorporating the film, an attempt is made to counteract this effect, by providing an extra source of cellulose that dissolves along with the textile filaments, thereby making it easier to control flashing. In the previous chapters (cotton-based ACCs) it was shown that using enough solvent could offset flashing and provide enough matrix for consolidation. With the Tencel textile, it may be that by offsetting the flash supports more consistent matrix formation.

## 5.5 Conclusion

The production of ACCs using interleaved films has been demonstrated with a manmade regenerated cellulosic textile. This revealed that the addition of the interleaved film allowed the process to be captured across the mechanical properties of Young's modulus and strain-to-failure, and a relationship between process conditions and mechanical properties was found. Validation samples were made at a temperature of 30 °C with 70 % IL as identified through multi-response optimisation, which exhibited an average Young's modulus of  $4.9 \pm 0.2$  GPa, and strain-to-failure of  $3.3 \pm 0.3$  %. With model predictions of 5.3 GPa and 3.5 % respectively, the predictive ability of the relationship was confirmed, however, several samples in the CCF design were seen to exhibit higher Young's modulus values, leading to the question of whether the 'true' optimum is yet to be found. Table 5-17 summaries the process conditions and resulting properties of the optimised ACCs identified in this study.

Tensile Strength (MPa)	Young's modulus (GPa)	Strain-to- failure (%)	Peel strength (N/m)	Thickness (mm)	Density (g/cc)	Void content (%)
$59 \pm 2$	$4.9\pm0.2$	$3.3 \pm 0.3$	$963\pm89$	$0.276 \pm 0.004$	$1.26\pm0.01$	$16.2\pm0.5$
Process cond	itions:					
30°C						
2.3 MPa						

Table 5-17 Process conditions, mechanical and physical properties of the optimised ACC samples identified through the body of work in this chapter.

10 minutes 70 % IL

The most significant discovery, however, relates to the behaviour of the interleaf film and its role when applied to Tencel, offering insight into how the structure of Tencel influences the resulting ACC in contrast to the native cotton explored in the previous chapters. In the Tencel textile-based ACCs, the film dissolves during the process and forms a coagulated matrix region in between the textile layers, rather than penetrating the fibre assembly as observed with the native cotton textile. Whilst this additional matrix was not seen to improve or reduce ACC mechanical properties, the film provides an immediate supply of dissolved cellulose to the ACC that helps to offset flashing and contribute to more consistent ACC formation, that can be modelled across multiple factors.

# Chapter 6. Conclusions and Outlook

#### **6.1. Overall Findings**

The aim of this thesis was to explore how the properties of All Cellulose Composites (ACCs) can be optimized and enhanced using cellulose-based textiles and interleaf cellulose films. A partial dissolution process using the ionic liquid [C2MIM][OAc], mixed with a co-solvent of dimethyl sulfoxide (DMSO), under hot compaction was employed for the production of the ACCs, with work focusing initially on ascertaining the benefits of using interleaved films. Statistical DoE was then investigated as a route to optimizing ACC properties, applied to native (cotton) and man-made (Tencel) cellulosic fibres. A summary of the main finding of each chapter is provided below.

*Chapter 3: The use of interleaved films to enhance ACC processing and properties.* In this first experimental chapter, the method of producing ACCs using interleaved films was introduced with a view to addressing the benefits of using the film in conjunction with cellulosic textiles. ACCs were formed from layers of cotton textile with an interleaved cellulose film placed between. A one factor at a time (OFAT) approach was employed to explore the influence of three factors on the mechanical properties of the resultant ACCs. These were dissolution temperature, time, and pressure. The use of the film, and the appropriate amount of solvent in which to immerse the textile stack (S/C weight ratio) were looked at initially, followed by a study into the optimum concentration of [C2MIM][OAc] in the co-solvent DMSO (wt % [C2MIM][OAc]).

ACCs were initially produced at three S/C ratios (that is the ratio of the solvent to the cellulose sample); 1:1, 2:1 and 3:1. A solvent solution comprising a fixed wt % [C2MIM][OAc] of 80 % and therefore 20 % DMSO was used. Two sets of samples were produced, one with the interleaf film, and one without the film. The preparation stage provided some insight into the effects of the S/C weight ratio, highlighting the difficulty in distributing the solvent solution when a 1:1 S/C weight ratio was applied. This was apparent for both sets of samples, and consequently, there was minimal difference in mechanical properties between them. Solvent was observed to be rapidly absorbed into the pockets of space within the yarn structure and with a low solvent volume, this caused inconsistent distribution of solvent. The resulting Young's modulus was low for both sets, associated with high errors due to variation in properties across the ACC and this was visibly apparent in the optical micrographs of the ACCs showing an inconsistent appearance across the ACC cross-section. Interestingly, the film was still visible with a post-process thickness indicating that over 50 % of it had dissolved. Nevertheless, this amount of solvent had not produced sufficient matrix to distribute through the ACC to achieve good mechanical properties.

The most insight on the benefits of the film and optimal S/C weight ratio was gathered from the samples produced using 2:1 and 3:1 S/C weight ratios, particularly for the samples made with the film. The samples produced without the film showed only marginal improvements in properties with increased solvent, however, the samples made with film exhibited noticeably improved Young's modulus over the samples made without film. This suggested that more solvent allowed the film to dissolve completely and supplement matrix production, coating the partially dissolved fibres and providing a strong fibre-matrix interface to support effective load transfer to the reinforcing fibres. Whilst mechanical properties such as Young's modulus are key to assessing the performance of composites, it was peel strength that revealed the ability of the film to prevent delamination between the layers on the ACC. This is because peel strength is very sensitive to the amount of matrix between the layers. Peel strength was improved with the addition of the film for the samples produced at a 2:1 S/C weight ratio, however the ability of the solvent amount to maximise the benefits of the film was highlighted in the sample made with a 3:1 S/C ratio, where an increase in peel strength from  $62 \pm 10$  N/m to  $917 \pm$ 73 N/m was observed when compared to the sample made without the film. The preference of using 3:1 S/C weight ratio over 2:1 S/C weight ratio was attributed to its role in offsetting the inevitable expulsion of dissolved cellulose and solvent during the compaction process, known as 'flashing'. The excess solvent provided by a 3:1 S/C ratio compensates somewhat, for the loss of cellulose and solvent through flashing, allowing sufficient dissolution and matrix production. The matrix remains in the stack and penetrates through fibre assembly, surrounding the fibres and forming a well consolidated ACC observed in the optical micrographs. With an S/C ratio of 3:1 there is always excess solvent, and any that is not required is expelled under pressure during processing.

It was hypothesised that the film could reduce the overall fibre volume fraction by diluting the fibres (adding extra matrix), and this was qualified by the results of the XRD scans that were used to study the changes in crystal structure for samples with a 3:1 S/C weight ratio. The scans revealed a decrease in the cellulose I content

(which would come from the fibre) and an increase in cellulose II and amorphous cellulose when using the film. Despite the reduced fibre fraction, this was offset by the increase in modulus due to improved fibre-matrix adhesion between the phases and layers (improved intra and inter laminar adhesion).

Samples were then made with the interleaf film using the preferred 3:1 S/C weight ratio for the next phase of study, where the concentration of ionic liquid was evaluated. Here, the wt. % of [C2MIM][OAc] in the [C2MIM][OAc]/DMSO solvent solution was varied from 20 % to 100 % (100 % being the pure IL). The measurements revealed that using 80 wt. % of [C2MIM][OAc] in the [C2MIM][OAc]/DMSO solvent solution (as used in the first set of experiments), yielded an optimal balance of Young's modulus and peel strength. It provided a reduction in solvent viscosity to allow for ease of solvent application to the stack during preparation, without reducing the ionic liquid wt. % too significantly (and, therefore, dissolving power) which could be detrimental when processing. It was concluded from this study that the 'optimum' ACCs were produced with the addition of the interleaved film, using a 3:1 S/C weight ratio and an 80 % / 20 % [C2MIM][OAc]/DMSO ratio.

Finally, ACC samples were prepared using various stacking arrangements based on this optimal solvent configuration, while maintaining consistent compaction conditions of 10 minutes at 100 °C and 2 MPa. The samples were tested by applying load in three directions relative to the warp yarn orientation: 0° (longitudinal), 90° (transverse), and 45° (bias). It was found that when prepared using a (0,90) stacking sequence, ACC properties in both the 0°/90° directions and the 45° bias direction were improved.

#### *Chapter 4: Applying DoE to optimize all-cellulose composites.*

In this chapter, a statistical DoE approach was adopted to see if the processing conditions could be further optimized from the experiments carried out in Chapter 3 to achieve desirable ACC mechanical and physical properties. Whilst the dissolution conditions of temperature, pressure and time were fixed in the previous chapter, these were now varied and explored through a full factorial screening design, followed by a response surface central composite inscribed (CCI) design.

The significance of ACC physical properties in driving Young's modulus was highlighted on initial analysis of the raw data, revealing the strong correlation between Young's modulus and the physical properties of density and thickness. The reduction of internal space as air is pushed out during compaction leads to a thinner, denser material. The centre point combinations contained within the full factorial yielded ACCs with a favorable balance of mechanical properties, leading to the possibility of quadratic effects that could not be captured in the full factorial alone. Further samples were produced for the response surface stage according to the CCI design, which was able to capture Young's modulus as a function of dissolution time and temperature. This relationship offered insight into the quadratic effects of these factors, where it was suggested that an increase in dissolution time and temperature was beneficial only to a point, after which properties would start to decline. Increasing time and temperature allows internal air to escape, producing a well consolidated ACC. It could, however, lead to increased fibre dissolution and matrix loss, in addition to a reduction in ACC quality, at longer times and temperature. This reiterated the importance of achieving a good balance of fiber and matrix. The
amount of matrix produced through processing is influenced by the amount of solvent used (S/C ratio) and subsequent dissolution of cellulosic material, but the length of compaction time that the ACC is subjected to, drives the removal of internal air. A prediction was made for the process conditions required to optimize Young's modulus, which was successfully validated in the lab, supporting the use of DoE in ACC processing and optimization. Optimised ACC samples exhibited an average Young's modulus, tensile strength and peel strength of  $3.4 \pm 0.1$  GPa,  $72 \pm 2$  MPa, and  $811 \pm 160$  N/m, respectively.

# Chapter 5: DoE investigation into the production of all cellulose composites using regenerated cellulosic textiles.

This final chapter sought to combine the elements of the previous two chapters, i.e. the role of the film, and the application of DoE, and apply them to study regenerated cellulose-based textiles (Tencel) as opposed to native cellulose (cotton). Consideration of Chapter 3 and Chapter 4 and their respective learnings helped shape the formation of this chapter. Whilst the benefits of the film were clear when applied to native cotton-based ACCs, it was unclear how these might translate to a man-made textile such as Tencel. It was, therefore, decided that the film would be explored as a categorical factor. The continuous factors of dissolution time and temperature were preserved from Chapter 4 given their significance as revealed through the CCI design. The results from Chapters 3 and 4 strongly suggested that the role of pressure had no significant influence on the processing of the ACCs of the resulting mechanical properties within the ranges chosen, and was, therefore, omitted as a factor. The wt. % [C2MIM][OAc] in DMSO was chosen as a third continuous factor (denoted as IL %).

Experimental runs according to a full factorial design were applied to two systems referred to as F0 and F1 representing ACCs made without the film and with the film, respectively. This resulted in two sample sets to analyse. Whilst the full factorial did not capture the data strongly for either system, the most promising balance of mechanical properties was obtained at the mid-point combinations (the CPs), suggesting that an optimum region may lie near the centre of the design space, or as a combination of mid-point factor settings. This confirmed that the design space was correctly chosen based on the results of Chapters 3 and 4.

With six additional experimental runs, the full factorial data set was expanded to a face-centred central composite (CCF) design, allowing the two systems to be explored for non-linear (quadratic) effects. On analysis, only the F1 system (with film) was captured, relating Young's modulus and strain-to-failure to process conditions and providing models for both. Multi-response optimisation was conducted by combining the two models to identify an optimum set of process conditions to maximise Young's modulus and ensure adequate processing by maintaining strain-to-failure at around 4 %. This was subsequently validated in lab, demonstrating the effectiveness of the CCF design to capture the process.

The key discovery from this work related to the behaviour of the film and how it played a role in allowing the F1 system to be captured with a more robust model than the F0 system. It was found that the film was visible between the textile layers after processing, suggesting that the structure of Tencel fibres limits its ability to migrate elsewhere. Dissolved cellulose from the film likely remains between the layers, rather than penetrating the filament bundles, and this is what is seen in the ACC cross-section. The same principle applies to the Tencel fibre itself, as any dissolution occurring on the filament may have limited movement, remaining at the fibre surface. This makes it easier for it to be removed through flashing, leaving little, or inconsistent matrix formation. Incorporating the film adds a source of cellulose that offsets the flashing, stabilising the matrix formation and improving its predictability. Optimised samples exhibited an average Young's modulus, tensile strength, strain-to-failure, and peel strength of  $4.9 \pm 0.2$  GPa,  $59 \pm 2$  MPa,  $3.3 \pm 0.3$ % and  $963 \pm 89$  N/m respectively.

There are standard models used in material science that can be used to predict the properties of composite materials. For example, for a composite under uniaxial tension, the Young' modulus,  $E_{composite}$ , can be estimated using the parallel rule of mixtures as shown in Equation 6-1, where  $E_{fibre}$  and  $E_{matrix}$  represent the moduli of the fibre and matrix phases, and  $V_{fibre}$  and  $V_{matrix}$  are the fibre and matrix volume fractions, respectively.

## **Equation 6-1**

 $E_{composite} = E_{fibre}V_{fibre} + E_{matrix}V_{matrix}$ 

To estimate the Young's modulus of an ACC with a (0,90) stacking of the textile layers, the parallel rule of mixtures can be expressed as shown in Equation 6-2, which accounts for the alignment of the transverse yarns [47].

## **Equation 6-2**

 $E_{composite} = E_{fibre} \frac{V_{fibre}}{2} + E_{matrix} \left(1 - \frac{V_{fibre}}{2}\right)$ 

An estimated fibre volume fraction of 0.8 can be obtained using the results of the XRD analysis from Chapter 3. Looking at Table 3-2, the cellulose I fraction is estimated to be 57% in the processed ACC. The amorphous fraction will be a combination of both matrix and undissolved fibre. Cotton fibres typically comprise 71 % cellulose I and 29 % amorphous material [103]. Assuming that after dissolution, the proportion of cellulose I and amorphous material remains unchanged, this means the fibre fraction can be estimated to be 0.80 (71 % / 57 %). A single cotton yarn was found to have a Young's modulus of 7.6  $\pm$  0.1 GPa, and cellulose film has been found to have a Young's modulus of 1.5 GPa [40], which can be used as an estimate for the matrix. Using these values in Equation 6-2 results in a predicted upper limit for Young's modulus, in the absence of crimp, of 3.9 GPa. This is an estimate of how well these ACCs could perform with the cotton yarns used, assuming perfect bonding between fibre and matrix, and no fibre crimp. With this in mind, the Young's modulus achieved in Chapter 4 of 3.4  $\pm$  0.1 GPa for the cotton-based ACCs is in good agreement with this prediction.

# 6.2. Synthesis of Research Outcomes

This thesis presents an investigation into the production of ACCs formed from cellulosic textiles and interleaved cellulosic films across three experimental chapters summarized above. It is now important to synthesize the outcomes of the research to articulate its relevance and wider impact on the field of ACCs.

Chapter 3 laid the groundwork for producing ACCs from a combination of cellulosic textiles and an interleaved film layer, demonstrating how this combination produces ACCs with exceptional interlayer and intralayer bonding, supporting an excellent balance of mechanical properties.

Process efficiency and optimisation was then addressed through the work of Chapter 4, where statistical DoE was introduced as a route to understanding process-property relationships in a resource efficient way. This work demonstrated DoE as a viable methodology for ACC process exploration, enabling scale-up production to be considered in the context of lab-scale experimental work. The use of DoE to accelerate ACC process understanding is crucial for future commercialization, and the insights gained from this work are important for the cellulose community and indeed, those working in natural or renewable fibre composites. The knowledge gained from attempting different DoE approaches offers further understanding on how best to achieve high performance renewable materials, as well as have confidence to choose the best approach.

With the results of these two chapters in place and the potential for ACCs to be produced, and optimised, it was inevitable that a new question would emerge: Where do ACCs fit in a circular economy, and can they address additional challenges in addition to reducing the use of fossil-derived polymers?

Chapter 5 began to consider this question regarding the wider applications of ACCs, their place as sustainable alternatives to traditional composites, and their value in the context of circularity and sustainable textiles research. The focus shifted from native cotton to man-made cellulosic fibres (MMCFs) in the production and optimization of ACCs, highlighting an application area for sustainable materials produced from end-of-life textiles.

As cellulosic textiles are used extensively in the fashion industry, it follows that ACCs could offer a way to utilize post-consumer textile waste. This could lead to significant improvements in the amount of waste textiles recycled, which is currently a disappointing 12 % from the 53 million tonnes of fibres used in textile manufacturing [220]. However, there are some things to consider in realising the commercial potential of producing ACCs from waste textiles. Crucially, there needs to be a consistent feedstock available to use, which a collection of waste clothing would not provide without some level of pre-sorting. Factors such as fibre composition, use-phase, and laundering history for example, could result in inconsistent feedstocks and difficulties in maintaining consistent composite quality, not to mention the deconstruction needed to turn a three-dimensional clothing item into flat sheets. The utilization of textile waste to produce cellulosic fibres is an active area of research [20, 27, 28, 34], and its potential to overcome these barriers is clear, producing a homogenous fibre that can be woven into a textile preform for use in ACCs. Additionally, this creates a fully circular system whereby the ACC can be re-dissolved after use, re-spun into fibres to be woven into textile, and the process started again. To realise the potential of such technology, further process understanding is required to obtain the best properties from regenerated cellulosebased ACCs. The work of this final experimental chapter led to gaining this very understanding, demonstrating that regenerated textiles could be used as feedstocks for ACC production. This complements research on waste-derived cellulosic fibres providing a more consistent feedstock for ACC production than the use of mixed textiles. ACCs could indeed fit in a circular model for end-of-life cellulosic materials.

# **6.3. Future Directions**

ACCs offer a sustainable alternative to fossil-fuel derived materials and could be well-placed for a variety of applications across the automotive, construction and consumer goods industries. There is great potential to advance this work and this final section outlines some suggestions to guide the development of future projects.

#### Development of DoE

The application of DoE to explore ACC processing has been demonstrated with promising results, however this is a vast subject with designs that span further than those discussed in this thesis. It would be of interest to look at other designs to see if these could capture systems with greater precision, particularly as noted in Chapter 5, where a more optimised region in the design space may exist that wasn't identified by the CCF design. It would be worthwhile to explore alternative designs to more finely pinpoint the optimal space and identify how best to achieve the most desirable ACCs using Tencel, and indeed other cellulosic sources.

Additionally, DoE offers a route to multi-factor analysis as we have seen in this thesis, where process conditions were explored and captured. However, it does not have to end there. The process of production ACCs contains a wider range of factors, particularly when it comes to the textile itself. Textile characteristics such as weave structure could be explored, not to mention the source of cellulose itself. The work in this thesis has focused on two cellulosic sources; native cotton, and man-made Tencel, and whilst some insight can be gained on how the two sources compare, it would be of interest to take a more systematic look at the textile across a range of sources such as flax, hemp, viscose, and indeed waste-derived regenerated fibres. Beyond ACCs, the knowledge and applications of DoE translate into the

wider remit of natural fibre textile composites and how matrix and reinforcement components can be tailored to a desired specification.

#### Data-driven approaches to tailor ACCs

Further DoE exploration could help generate large, robust datasets, and this offers an opportunity to leverage machine learning (ML) approaches to further expand our understanding of ACC processing, leading to the possibility to tailor ACCs fit-forpurpose. With a well develop dataset supported by DoE, ML offers a data-driven approach to optimisation that can lead to enhanced predictability over DoE. Crucially, ML algorithms continue to learn as more data is added and can find correlations in non-linear behaviour. The ACC process could be characterised across a wide range of system factors, incorporating cellulose source, textile characteristics and processing conditions. ML algorithms could then be used to analyse ACCs across a wide range of industry-specific performance metrics. This could then lead to the development of an advanced material informatics system that streamlines the material design and manufacturing process, enabling the creation of tailored materials with specific properties efficiently and effectively. This lays the groundwork for future work into the commercialization of ACCs, where identified process conditions for desired performance can be used as a starting point for process modelling and scale-up. This will allow environmental impacts and economic feasibility of ACC process scenarios to be assessed using life cycle analysis (LCA) and techno-economic analysis (TEA).

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