ABSTRACT

AGATE, SACHIN RAVINDRA. Advances in Biomaterials for Flexible Electronics and Optics. (Under the direction of Dr. Lokendra Pal and Dr. Lucian Lucia).

The flexible electronics sector is a growing market with continuous advances for improvements in performance. The innovative designs of electronics products and single use items have resulted in a need to address issues such as waste recycling and an uninterrupted supply of raw materials. The recollection of unwanted materials and recycling them can be a big task with various limitations. It would be a great advance if most of the materials become bio-based, thus safely degradable and reducing efforts for waste management. Therefore, one can select lignocellulosic biopolymers for their renewable resources and biodegradability.

Cellulosic biopolymers are used in various ways for flexible electronics. A major application is in the form of a substrate on which the electrically functional materials are deposited. Today’s widely acceptable technology uses passive substrates that do not contribute to the ink distribution process. This results in the need of various mechanical systems to ensure the positional accuracy of the ink with respect to the substrate. This work shows how we can create surface patterns on the substrate using photo-induced reactions that contribute to ink distribution. One can think of creating physical patterns as well as chemical modifications of the surface to allow the inks to react differently in different regions. The physical changes in the substrate are possible through swelling and de-swelling of the material, ablation, or both in combination. This swellability, if achieved through water, will be a better processing parameter for making the system highly renewable. Such a system is possible through usage of hydrogels.

Here, in this work, carboxymethyl cellulose, and lignocellulosic material are studied for their application as highly water absorptive substrates/films. Different methods for tuning them
zonally are employed, such as spatial degradation with UV irradiation and surface crosslinking with a UV active crosslinker. In hydrogels, such spatial ablation generates localized weakening of the matrix and swelling differences. The transparent nature of hydrogels made from carboxymethyl cellulose allows formation of optical lenses directly from the film shaped substrate using this technique. Further, the increased oxygen transmission ability of ablated films provide them scope for contact lens application. Using the UV ablation technique for application of flexible electronics is possible where swelling differences in ablated and non-ablated areas create a temporary channel structure. The swollen hydrogel matrix acts as channel walls. This shows the ability to self-distribute the electrically functional material (ink) into the emerging channel structure, resulting in a conductive pattern generation. In another mechanism, the photo-ablation is used for physical channel development by material loss, and the surface crosslinking is used for reducing the hydrophilicity and water absorption into the hydrogel surface. Combined effects are then used for pre-fixing locations of two separate electrically functional elements. This process opens an opportunity to reduce the levels of print registrations. Therefore, it introduces a new way of generating flexible electronic circuits.

The principles of zonal control of water absorption are also applied to the lignocellulosic materials, where UV irradiation results in surface modification of lignin containing material. The crosslinking of lignin and changes in morphology give rise to a non-absorbent surface. This property is used for selective absorption of the material and deposition of electrically functional material for pattern generation. In summary, the water based swellable/absorbent systems can be spatially tuned to create temporary or permanent physical and chemical changes.
Advances in Biomaterials for Flexible Electronics and Optics

by
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DEDICATION

To all those who love GOD and others.
BIOGRAPHY

Sachin Agate is from India. He is a paper and printing professional with 7.5 years for working experience prior to joining PhD at NC state university. Printing and flexible electronics is one of many areas of his interests. Learning new things and applied technology is his passion where one can utilize the knowledge for better and innovative applications.

He started his life journey from Pune and earned bachelor’s degree in Printing Engineering at University of Pune (now known as Savitribai Phule Pune University). Followed by this level of education he wanted to pursue master’s degree and got admitted to Western Michigan University. His ideas were to gain work experience before proceeding for next level of education. After 8 years, he decided to join PhD.

Apart from his dream of developing innovative applications for printing and mass production, in his life he would like to meet various people and grow spiritually. He would like to help others with whatever capacity he has at the time.
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1. INTRODUCTION

Synthetic polymers are well known for their tunabilities and mass production; however, they are generally not ecofriendly. On the other hand, ‘nature’ produces a great number of complex molecules and polymers on a very large scale, which would take great efforts for synthesis by human efforts. Nature is effective at minimizing wastage in the synthesis of desired molecules as they are constructed with high precision at cellular levels. It is of utmost importance to utilize the natural materials such as cellulose and its derivatives in all possible applications from a sustainability point of view.

Natural biomaterials have already shown a great potential for various applications such as electronics,\textsuperscript{[1]} medicine,\textsuperscript{[2-4]} packaging,\textsuperscript{[5, 6]} fuels,\textsuperscript{[4, 7, 8]} and cosmetics.\textsuperscript{[9, 10]} Exciting advancements in the field of flexible hybrid printed electronics have garnered special attention since they offer a low cost alternative to conventional fabrication processes while enabling large-scale manufacturing of electronic devices. However, because of the poor sustainability and much higher costs of the active materials in electronic and biomedical devices, new developments utilizing cellulose and its derivatives are needed for the large-scale construction of flexible devices. According to a review, the estimated electronic waste in 2018 was 50 million tonnes at an annual growth rate of 3-5\%.\textsuperscript{[11]}  

1.1 Motivation

Cellulosic biopolymers have attracted significant attention for their renewable and tunable properties as well as their abundance. For example, their mechanical properties such as stress strain relationships can be as soft as biological tissue or as stiff as steel or carbon fibers. Also, light transmittance properties such as opacity and transparency relationships can be as clear as plastic or as translucent or opaque as metals with proper modifications. The secrets to the functionality of
cellulosic biopolymers are the base materials, the modification process, and the formation of the final product. Scientifically, we envision leveraging and tuning these properties to provide technical and scalable advantages for commercialization of multifunctional materials that can be in the form of films, coatings, and substrates for a multitude of applications with industrial impact in the areas of medical, sensing, and electronics technologies.

1.2 Objectives

Based on current needs, the objective of this research was to better understand and modify cellulosic biopolymers without significantly altering biodegradability, compostability, biocompatibility, and other unique properties. A major task of this work was devoted to the development of a new technology that targets photoinduced spatial resolution of cellulose based hydrogels for controlled swelling, optical activity, and biocompatibility, enabling the creation of highly functional and low-cost films and coatings for optical application and substrates for electronics.

Printed electronics is a growing field, where electrical circuits are printed on flexible substrates and used for low cost applications. The need for environmental protection and sustainability demands the maximized usage of bio-based and biodegradable materials for printed electronics. Cellulose is one of the naturally abundant polymers that can be used for applications in electronics. Later in this Chapter, the background on the cellulosic materials and lignin materials are discussed followed by their proposed usage for printed electronics. Chapter 2 does a comprehensive review of the usage of cellulose based materials for printed electronics. Here, the current studies did not show applications of cellulose based hydrogels as a substrate for electrical circuit generation. Also, lignin containing nanocellulose is not explored to a greater extent for
printed electronics. Therefore, CMC based photo-tunable hydrogel and lignin containing nanofibrillated materials were chosen for printed electronics and are discussed in next chapters.

**Chapter 3** discusses cellulose-based hydrogels and their current applications. Further, it discusses the carboxymethyl cellulose (CMC) based hydrogels, where citric acid is used as a crosslinker and riboflavin (vitamin B₂) as a photo-sensitizer for the production of on demand and on-site reactive oxygen (singlet oxygen). In this chapter, the concept of UV photodegradation of the hydrogels is discussed, which is based on the UV excitation of the molecules and the photolysis of water. These concepts of the photo-degradation are used for micro-structuring of the hydrogels for applications are discussed in the following chapters.

**Chapter 4** mainly focuses on the spatially resolved patterns on the hydrogel films for shape tuning and optical activity. Here, the tuning of the hydrogels based on crosslinking is studied to find the suitable conditions for stable and easily handleable, transparent films. These films are then photo-ablated for weakening the hydrogel matrix. As a result, the water absorption capacity changes spatially. Though, the goal was to seek the films for application of printed electronics, it was evident that the same films can be used to develop biomedical devices such as contact lenses. Specific patterns of photodegradation lead to internal stress development and formation of a lens like curved film surface. The work shows that the lens shapes can magnify the image. Interestingly, the oxygen transmission capacity can be tuned with this process, which is a very important aspect of the contact lenses. Finally, the mechanism involved in the photodegradation have been studied.

Contact lenses are used for correcting eye viewing conditions and as discussed in the Chapter 4, the hydrogel films can be tuned to form contact lenses. However, before continuing further studies, we need to understand market demands from the currently available hydrogel-based contact lenses, their limitations and possible gaps, which can be addressed by new
technologies. Chapter 5 is the report for this study, which was conducted under the iCorps program supported by the National Science Foundation (NSF). More than 30 interviews were conducted to know users, doctors and manufacturer’s point of view in the contact lens market. This chapter also estimates the possible impact of this new process of lens making on the reduced waste generation.

As the CMC based hydrogels are shown to have spatial tunability via a photo-degradation mechanism, a novel way for creating a substrate is studied in Chapter 6. UV photo exposure can cause hydrogel degradation, which leads to more water absorption. If a high molecular weight CMC is chosen for hydrogel preparation, it shows great water absorption capacities and prominent swelling differences based on the matrix strength tuned by photo ablation. This physical change can be used for a new type of electrical circuit creation. In addition, a new type of surface hydrophobization has been studied to create spatial hydrophobic zones on a hydrophilic hydrogel surface. Pyridine was used with UV photo excitation to achieve such zones. This mechanism can assist the deposition of water-based materials, which may not be accepted in the hydrophobized zones. Thus, two functional materials can be deposited by creating photo-ablated channels and hydrophilic zones. This method can be used to reduce the registration related issues by fixing positions of functional materials in advance.

For printed electronics, the surface of the substrate plays an important role in ink acceptance and anchoring. A lignin containing nanocellulose can form a gel like structure and provide reduced hydrophilicity on the coated surface. If such material contains high amounts of lignin that can be zonally crosslinked, then it can assist in photo patterning and selective deposition of aqueous material. In Appendix A, a new method of using lignin containing cellulose micro-, nano- fibrils for UV patterning and polypyrrole deposition is discussed. Appendix B shows a new
method to form such L-CMNF and its characterization. Appendix C has XPS data for polypyrrole formed on the substrates discussed in chapter 6 and appendix A.

1.3 Background

With the advent of technology, electronics are being integrated with our daily usage appliances, making them smarter and easier to use. Space constraints and minimization of electrical energy are demanding the flexible electronic circuits to be accommodated in various shapes. This indeed has caused the invention of printed electronics. In 1944, the first patent for a printed circuit board was approved for Paul Eisler. Following this invention, people have started printing circuits since the 1950s. Using printed electronics, one can achieve flexible and low-cost appliances at a much higher production rate than the previous methods of etching a circuit board and mounting electronic components. Paper is one of the flexible substrates for printed electronics along with polymers like polyethylene terephthalate (PET) and polyimide. Paper is made from ligno-cellulosic biomaterials.

Contact lenses are an example of biomedical devices, which are used for vision correction along with the aesthetic enhancement of each user. Hydrogels are employed to create soft and breathable contact lenses. Oxygen permeability and softness are important factors for the lenses. In the current market, methacrylate and silicone are widely used hydrogel materials, which are processed using lathe cutting and cast molding. Usage of biomaterials will be a great step towards biodegradability of a product at the end of its life.

1.4 Cellulosic Biomaterial

Biomaterials are of vast variety. They can be obtained from plants as well as animal sources. The most abundant biomaterials are wood-based materials, which need relatively lower investment. As the plants and trees are at the bottom of the food chain, they are primary producers
and energy waste is lower as compared to other organisms. One can extract the most abundant polymer of the wood i.e. cellulose for further processing and product development. Cellulose, when hydrated becomes a flexible natural polymer with a very stable chemical structure. The natural degradation of cellulose is possible through bacterial and fungal activities. As compared to lignin and hemicellulose in the wood (other major polymers), it shows interesting physical properties such as flexibility and the ability to form natural crystals in a nanometer range. Lignin and hemicellulose as branched polymers have limitations in having flexibility and no crystallites in lignin. In addition, these nanocrystals of cellulose show high acid resistance and physical strengths.

Cellulose is a polymer of glucose molecules linked through $\beta$-1,4 linkages (Figure 1.1).

The glucose units are highly stable in response to chemical reactions while the attached three-hydroxyl groups are highly reactive. This makes the polymer a strong chain with possible reactive sites. The absence of conjugated bonds makes it highly transparent to the visible light at the molecular level. In bulk, the trapped air, crystals, and light scattering can render it opaque. One can thus think of various applications of cellulosic materials, which need the strength and inertness towards the visible light. We have its day-to-day non-edible application as a ‘paper.’

![Cellulose](image.png)

Figure 1.1: Cellulose.

The attached hydroxyl groups on the cellulose dissociate due to ionic liquids or an alkaline environment. At lower pH, the glycosidic $\beta$-1,4 linkages can get cleaved by acid hydrolysis. It is therefore possible to have side chains and crosslinks on the cellulose at hydroxyl sites or glycosidic linkages that can be degraded to have low molecular weight polymers. Based on end
applications, users can treat the cellulose with a series of mechanical and chemical treatments. The raw plant materials can be mechanically treated and further chemically treated to remove lignin from the natural fibers of cellulose. Extended mechanical treatments can further reduce the cellulose fibers into micro fibrils and nano fibrils. The strong acid treatments dissolve the amorphous regions of cellulose and leave behind the cellulose nanocrystals.\textsuperscript{[19]} Alternatively, strong alkali treatments dissolve the cellulose by dissociating hydroxyl groups and disrupting the hydrogen bonds holding the chains together.\textsuperscript{[20]} The grafting or tempo-mediated oxidation of such dissolved cellulose is easy.

Several modified cellulose products are possible by utilizing different forms of cellulose such as macro fibers, micro- and nano- fibrils, nano crystals and dissolved cellulose. The difference between each of the varieties is the availability of accessible hydroxyl groups i.e. those on the surface. The inaccessible groups remain engaged in hydrogen bonding with other cellulose molecules in the structure. On a further stage, dissolved cellulose can be regenerated\textsuperscript{[25]} into cellulose fibers and be used in textile applications. Instead of purifying cellulose by removing lignin and hemicelluloses, one can also think of retaining them to obtain unique properties such as partial hydrophobicity due to the presence of lignin and the light absorption capacity at lower cost and higher yield. In theory, many composites can be made from such products by taking advantage of reactivity of lignin and flexibility of cellulose fibers.

1.5 Ligno-cellulosic materials

Lignin is another major biopolymer in the plants. It is a large molecule of aromatic rings (Figure 1.2 for pre-cursors of lignin) linked together to form a three-dimensional structure.\textsuperscript{[26]} The purification of plant-based cellulose is done by removal of lignin through the pulping and bleaching process. Based on the extraction process, the lignin can have different applications.\textsuperscript{[27],}
Lignosulfonates are used for production of vanillin, industrial lubricants, cement and concrete mixing, sand stabilizers, sequestering agents, emulsifiers, and adhesives. On the other hand, kraft lignins show applications such as fire-retardant foams and activated charcoal production. Another common usage is to burn the lignin to gain thermal energy. Modern applications are carbon fiber making, bioplastics, and battery making.

Figure 1.2: Pre-cursors of lignin.

A main reason for removal of lignin from the wood pulp is to increase the strength of the cellulose based products such as paper. In native form, the lignin acts as the binder for carbohydrates in the wood. It is hydrophobic and its presence in the cellulose pulp reduces the hydrogen bonding capacity of the fibers. Additionally, it affects the color of the paper. However, in nanometric form, the lignin containing pulp can provide some interesting functionalities. The surface area and density of the nanocellulose can be higher due to the presence of lignin. This increases the mechanical strength of the material and reduces the roughness. The paper made from such cellulose shows higher water contact angle. Lignin can act as a UV blocker and can be added in the CNC films to achieve transparency for visible light at the same time. In the cellulose based composites, the lignin can act as compatibilizer for hydrophobic materials. Researchers
are finding other applications, as in antimicrobial paper with composites of gold and silver nanoparticles.[32]

Lignin-containing nanocellulose can be used as reinforcing materials for hydrogels[33] or provide hydrophobic sites in the hydrogel to hold hydrophobic drugs, which otherwise cannot be held in a hydrophilic matrix.[34] Other hydrophobic materials can be held inside the lignin containing hydrogels.[35] The lignin–resorcinol–formaldehyde aerogels were shown improved strength by inclusion of bacterial cellulose.[36] An additional advantage can be the natural UV protective hydrogel for various applications. Wood based lignin containing nanocellulose can show a higher yield than purified nanocellulose. This can reduce the associated costs.

1.6 Printing processes and challenges

A printing process is a method of transferring ink to selective areas on a substrate. Various printing process are available for commercial usage, which are chosen for print production based on the substrate and number of copies to be printed. Gravure, flexography, offset lithography and screen printing are the most commonly used processes.[37] However, these processes have fixed design that is replicated per copy. For small runs or highly specialized applications, digital printing is employed with the ability to vary a print design from copy to copy. Such printers use inkjet and electrophotography methods for commercial purposes. Figure 1.3 shows schematics of printing processes.

Any of the printing processes involve multiple printing units. A single print unit prints a part of an image in one color and transfers the substrate to next units for printing other inks. Combined, these inks form a multicolor image. An important step involved is the matching of the positions of these image parts so that they do not appear to be moved relative to each other. If the
relative positions are off beyond a human’s discerning limits, then the prints appear to be blurry and images become unrecognizable.

![Diagram of printing processes]

Figure 1.3: Printing processes a) gravure b) flexography c) offset lithography d) screen printing e) inkjet printing. S: substrate, I: impression roller, G: gravure cylinder, A: anilox roller, P: plate cylinder, B: blanket cylinder, M: mesh, DB: doctor blade, N: ink nozzle.

For tonal reproduction, printers use the halftoning process, where any image is split into tiny dots of colors. The density of dots gives the appearance of color toning. When a printing process is adopted for electronics printing, one must understand that the halftoning process is no longer required. All the ink dots must be electrically connected to each other so that the printed pattern can conduct the electricity. At the same time, all image areas need to transfer the ink to the substrate. Otherwise, any missing dot or image break will result into disconnected circuits. In other words, the printing should be defect-free.

In the above said printing processes, the substrate is simply a surface that accepts ink, no matter where it is applied on it. Therefore, the role of substrate is passive in the image formation.
If a substrate can take active part in ink acceptance and distribution, then it will be an added advantage for the whole process. Modulating the hydrophilicity of the substrate surface and bulk can lead to the formation of the ink accepting and ink repelling area, which function like the lithographic process. If ink repelling areas are generated on the surface of the substrate, they will help in preventing the print defects such as mis-registration. Such zones can be created by another printing station, such as printing a hydrophobic pattern. However, that limits the image resolution to the print resolution. Another way is to treat the substrate with photographic methods where fine patterns can be created with laser beams, and it is possible to modulate the beam energy to control the reaction rates on the surface and bulk of the material.

1.6.1 Material selection for the study

A detailed review of usage of cellulose based materials for printed electronics is in Chapter 2, where the properties of substrate for printed electronics are discussed. It was noticed that the cellulose-based hydrogels are least utilized for printed electronics. Their water absorbency can be utilized for treating them with photolithographic methods. It was also noted that the lignocellulosic materials need attention for further study in the field of printed electronics. Recently, industrial hemp has been permitted for its production for research. It is a low-cost material and it can be utilized to produce nanocellulose. This lignocellulosic material will be studied for its ability to serve as a substrate in the production of flexible electronics.
2. CELLULOSE AND NANOCELLULOSE-BASED FLEXIBLE-HYBRID PRINTED ELECTRONICS AND CONDUCTIVE COMPOSITES—A REVIEW

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2.1 Abstract

Flexible-hybrid printed electronics (FHPE) is a rapidly growing discipline that may be described as the precise imprinting of electrically functional traces and components onto a substrate (such as paper) to create functional electronic devices. The mass production of low-cost devices and components, such as, environmental sensors, bio-sensors, actuators, lab on chip (LOCs), radio frequency identification (RFID) smart tags, light emitting diodes (LEDs), smart fabrics and labels, wallpaper, solar cells, fuel cells, and batteries are major driving factors for the industry. Using renewable and bio-friendly materials would be advantageous for both manufacturers and consumers with the increased use of (FHPE) electronics in our daily lives. This review article describes recent developments in cellulose and nanocellulose-based materials for FHPE, and the necessary developments required to perpetuate their use in commercial applications. The aim of these developments is to enable the creation of FHPE devices and components made almost entirely of cellulose materials.

2.2 Introduction

Flexible-hybrid printed electronics is a rapidly growing field because it provides high throughput manufacturing of electronics that enables economies of scale resulting in more affordable products. Printing for electronics has been available since the 1950s. Today, different printing processes like gravure, flexography, screen, offset, inkjet, and laser induced forward
Because products printed using these processes are electrically functional, various types of substrates and inks are utilized to get a desired circuit with *a priori* necessary mechanical properties. Paper can be one of those substrates. Environmental concerns and end-of-life disposal challenges are grand challenges for 21st century society that demand an examination of renewable resources such as cellulose and its offspring, nanocellulose for mitigation of these issues. Theoretically, any substrate can be used for the creation of electronics. Some examples of substrates that have been used are: glass, polydimethylsiloxane (PDMS), paper, polyimide, polyethylene terephthalate, polyvinylchloride with fabric, polytetrafluoroethylene, polyethylene, and polyethylene naphthalate.

In the printing industry, cellulose is most commonly used in the form of paper. Apart from being used as a flexible (non-conductive) substrate for printed circuits, cellulose can also be used in the design of conductive substrates in conjunction with various functional inks including dielectric, conductive, semi-conductive, and photo-voltaic. Therefore, it can be used in the development of sensors, lights/displays, solar cells, and membranes in batteries. To improve upon the electrically functional properties of cellulose, researchers have blended it with other materials or grafted functional groups onto its surface. However, such research is still in the early stages and is not yet ready for commercial applications. Currently, simple systems utilizing inorganic materials are favored for use in commercial applications.

Electrically functional components are often made using a single material to provide their performance. This is often the case with conductive inks, which use a single metal element. More complex systems using a combination of materials may also be used to increase performance and functionality. As an example, metallic inks made of silver, gold, and copper may be used. By combining copper and silver, printers are provided the additive
benefits of low oxidation and high conductivity from each of the component parts. Organic based conductive inks made of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), polyaniline (PANI), graphene, carbon nanotubes have also been explored. Implementation of cellulose-based materials can provide the ability to create conductive inks. Cellulose has been used as a matrix for conductive materials, or as a backbone for grafted electrically functional material. In the review, the current state of research pertaining to these cellulose-based materials and their modifications are described as they pertain to the development of substrates and functional inks in the field of flexible and hybrid printed electronics.

2.3 Cellulose-based Substrates in Printed Electronics

Paper, which is made of renewable, recyclable, biodegradable, and non-toxic cellulose materials, is an attractive substrate for printed electronics. It is flexible, (physically) tunable, and can be heated to higher temperatures than PET (polyethylene terephthalate) films, which are the dominantly used substrates for FHPE. Various studies have shown that a paper’s various properties (i.e., chemical composition, surface energy, hydrophilicity, porosity and surface structure) have significant impacts on the performance of printed components.

2.4 Paper properties

2.4.1 Porosity/Roughness

Porosity and surface roughness of a substrate are important properties known to impact print quality. They impact ink penetration and ink-film continuity (as shown in Figure 2.1), which can result in disconnection between conductive particles.
PET films, the dominant substrates used in FHPE, are highly smooth and non-porous compared to paper. The use of paper substrates for FHPE applications requires careful tuning of a given sheet roughness and porosity. A relatively simple way to accomplish the tuning of paper substrate roughness and porosity among other properties is with coatings. Specific details relating to paper coatings research will be further described in a later section. The outcome of this research provides some insight into the current challenges for utilizing paper substrates in the development of FHPE devices and components.

As an example, Trnovec et al. compared coated paper to PET film. They found that the paper had a higher resistivity compared to PET. They concluded this was the result of the paper’s increased porosity.\textsuperscript{[55]} They found that for a roughness \(\sim150\) times higher than PET, resistivity increased by 50-1000 times. The effect of porosity or pore volume becomes less significant as ink volume increases due to the likelihood of excessive pore filling.\textsuperscript{[56]} The adverse effects of porosity can be reduced by increasing the amount of ink (i.e., thicker ink film). Similarly, it has been found that the impact of surface roughness becomes less significant with an increase in the width of the printed features.\textsuperscript{[57]} To reduce surface roughness, nanoscale cellulose in the form of cellulose nanocrystals (CNC) can be used as shown by Hoeng et al.\textsuperscript{[58]} A cardboard surface with a roughness of 66 nm, showed a reduction in roughness to 3.6 nm, after it was coated with TEMPO (2,2,6,6-
Tetramethylpiperidine 1-oxyl) oxidized CNC. Though higher roughness reduces conductivity, it can also increase ink anchoring. Dogome et al. observed that silica coated photo quality paper had less ink anchoring compared to matte quality paper where the surface roughness increased from 1.47 µm to 4.31 µm.\textsuperscript{[52]}

Researchers are continuing to develop new and innovative ways to circumvent issues from the high levels of porosity and roughness innate to paper substrates to enable their use in FHPE applications. This research is providing a new understanding of material interactions between paper and electrically functional materials and furthers the ability to implement such materials in the development of FHPE. Two of the key areas that are undergoing further research and development with regards to material interactions between these materials, are surface energetics and absorption capacity.

2.4.2 **Surface Energy/Absorption Capacity**

Surface energy and absorption capacity are important substrate properties for any printing technique and all types of printing methods. They impact ink penetration, ink film thickness, and image resolution (Figure 2.2), which subsequently impact the performance of functional prints.
When selecting a substrate for a given application, it is critical to consider the surface energy and absorption capacity. As an example, it has been shown that reduced surface energies with treatment by fluorinated polymer and capillary absorption are an effective way to enable the achievement of finer prints (about 60 µm with inkjet printing ink) by preventing lateral ink spreading.\textsuperscript{[52]} Although the use of fluorinated polymers provides an effective method for the reduction of absorption, it is not an ideal material due to environmental and health concerns. The research conducted by Dogome et al, 2013 does show that by reducing capillary absorption, lateral ink spreading can be prevented and finer features can be printed. Other methods to reduce ink spreading would provide more meaningful and useful possibilities for the development of FHPE. Because it is known that reduced porosity also plays a role in reduced absorption of ink,\textsuperscript{[58]} research has been conducted to adjust the surface energy of substrate and its porosity.
Localized pretreatment with a UV curable polymer can be used.\cite{59} As shown in their work, the authors observed an approximate 3-fold increase of conductivity due to these treatments on most of the selected papers. With the importance of substrates’ properties being evident on printability and subsequent functional capabilities, the need for a broader knowledge and tool set for the manipulation of such properties is of the utmost importance for the further development of FHPE utilizing paper substrates. Therefore, this review has considered and reviewed a few possible methods to enhance (paper) substrate properties and some of the resulting materials being developed for use in FHPE applications are described.

2.5 Methods to Enhance Substrate Properties for Printability

2.5.1 Chemical

The chemical composition of paper is an important factor affecting the performance of electrically functional inks. Increasing the internal sizing of paper is one way to modify the chemical and subsequent physical properties of a paper substrate. Increasing paper sizing will decrease surface energy, prevent ink penetration, and subsequently, result in higher functional performance of conductive materials.\cite{60} Sometimes, chemical compatibility of paper with ink is of concern. Inks can interact with chemicals within paper and result in adverse effects such as the agglomeration of ink and non-uniform distribution of the ink.\cite{60} The use of an ink fixation agent, poly(diallyldimethylammoniumchloride) (P-DADMAC) has been shown to decrease the conductivity of PEDOT:PSS inks due to its cationic nature. Similarly, Trnovec et al. found that PEDOT:PSS inks can lose performance by increased pH due to coatings.\cite{55} One application where chemical interactions are of great importance are those pertaining to microfluidics. Here, the achievement of selective ink penetration or ink wicking into paper is used for the creation of various functional devices, such as (bio) sensors. Jenkins et al. have demonstrated such a
possibility using nitrocellulose substrate. The selective hydrophobicity required for microfluidic channels was achieved using PDMS traces and silane treatment. Other than chemical modifications, there are physical modification techniques that exist to tailor these properties for application specific purposes.

2.5.2 Physical

Calendering is a well-established physical modification method, which has been shown to decrease surface roughness. Hrehorova et al. observed that a decrease in surface roughness due to calendering resulted in decreased conductivity of printed traces. However, Ihalainen et al. observed that resistivity is lower for surfaces with reduced roughnesses at shorter correlation lengths. The effect of “roughness scales” on conductivity is worthy of more attention in future research. The roughness after calendering also depends on the components making up the paper. It was observed that the filler structure and fibers around them have an impact on this property. Rosette shaped PCC (precipitated calcium carbonate) bound in MFC (micro fibrillated cellulose) have lower surface roughness compared to platy kaolin in MFC after calendaring. The physical modifications that calendering produces will impact the substrate absorption capacity of paper. Substrate absorption capacity is another critical property that should be considered for the optimization of printing media. Certain applications will have higher levels of substrate absorption, and hence, calendering will not be a beneficial modification technique to increase the printability of functional components. When physical (calendering) and chemical treatment techniques are not feasible, other modification methods must be implemented.

2.5.3 Coatings

The use of coatings often provides an easy and (often) inexpensive way to enhance the properties of paper substrates. Coated paper can provide enhanced features by reducing porosity,
roughness, and improving moisture barrier properties (Figure 2.3). If a barrier coating layer is applied, the cellulose substrate becomes resistant to humidity changes and dimensional stability increases. Dimensional changes, due to humidity, will decrease conductivity in the case of conductive traces.\cite{41,57} This decrease in conductivity can be due to the increase in roughness i.e., surface unevenness due to a humid environment.\cite{57} Bollstrom et al. observed that this effect of humidity is prominent on very fine printed lines (line widths ranging in average of 75-685 µm).\cite{57} Thus, humidity can be detrimental to the performance of printed electronics devices. The longer the moisture barrier layer remains functional, the higher the resistance to device failure due to humidity. Currently, the most widely implemented moisture barriers are synthetic or petroleum-based products. It has long been desired to discover and use natural replacements for these products. Although the discovery of a material to completely replace such conventional products is difficult, it is possible to utilize natural products in parallel with synthetics to enhance properties and reduce negative environmental and health impacts caused by petroleum-based products.
One such product could be micro-fibrillated cellulose (MFC),\textsuperscript{[64, 65]} which is a material that consists of long and thin fibers, which form a three-dimensional network. These fibers have both crystalline and amorphous regions. MFC fibers have high viscosity and yield stress, in part, due to the fiber lengths and the three-dimensional nature of their structures. They also display shear thinning behavior\textsuperscript{[66]} and have high water holding capacity, making them good candidates as rheology modifiers in numerous applications, such as paper coatings. MFC fibers can come in a variety of sizes with differing lengths and diameters from the nano- to macro-scale. However, these fibers are interconnected. Therefore, the use of a singular size is not currently available. The ability to separate and utilize the fibers of any given size would be highly beneficial for the tailoring of application specific uses including coatings pertaining to the paper and electronics industries.
There is still much room for improvement in surface modification methods, techniques, and the understanding of the impact of such of various material interactions. The further development of knowledge pertaining to these areas will provide the ability to further implement paper into the electronics industries. Some current innovative ways in which paper and cellulose are being used in the electronics industry are in applications of transparent substrates, dielectric materials, electrolytes, and/or conductive materials.

2.6 Cellulose-based Transparent, Dielectric, Electrolyte, and/or Conductive material

2.6.1 Transparent substrate

For optoelectronics, the transparency of the substrate plays an important role. Material that can let light pass through can be used for displays and solar cells. Nanofibrillated cellulose (NFC)\textsuperscript{[67, 68]} is one such material that is being studied for high frequency optoelectronics,\textsuperscript{[69]} Unlike MFC, nano-fibrillated cellulose (NFC) is composed of only nano-sized structures. These fibrils have high aspect ratios, with widths as small as 20-40 nm with a wide range of lengths that can be as high as several microns.\textsuperscript{[70]} They can be produced using various processes involving chemical treatment. Using TEMPO-oxidized NFC, an optical transparency of up to 90\% can be achieved. The importance of TEMPO oxidation can be seen in a study by Torvinen et al.\textsuperscript{[71]} TEMPO NFC is stronger and more transparent than mechanically produced NFC. They observed a significant difference in transmittance. TEMPO NFC has a transmittance of 74 vs. 26 for mechanical NFC. However, the flexural modulus of NFC based papers are not comparable to PET. This can be tuned by using epoxy coatings\textsuperscript{[72]} and acrylic resin matrix.\textsuperscript{[68]}

Similar to cellulose, NFC can be used in a derivatized form such as carboxymethyl NFC. Such a substrate has a large forward light scattering ability and high optical transparency.\textsuperscript{[73]} These
properties decrease glare. Here, materials such as PEDOT:PSS, carbon nanotubes (CNT), tin-doped indium oxide (ITO) and silver nanowires (AgNWs) can be used for the development of transparent electrodes. Additionally, mechanical properties of NFC fiber-based materials are of vital importance as has been adequately shown by Meng et al.\cite{74} In this work carbon nano-tubes (CNT’s) were used to develop carbon nano-tube films with tailorable electrical properties. They found that the inclusion of NFC into CNT containing films increased tensile properties while still enabling promising electrical properties. In addition to the transparent and conductive applications, cellulosic materials can be implemented for dielectric and insulator applications.

2.6.2 Insulator and Dielectric

Oil-impregnated cellulose has long been used as an insulator for transformers and cables. Wood components such as lignin and hemicellulose, along with other native organic contaminants govern the dielectric properties of cellulose.\cite{75} Cellulose has a dielectric constant of about 6.12. Luca et al. determined this value by using a capacitor filled with a cellulose and liquid mixture of benzene and ethylene chloride.\cite{76} When cellulosic material conducts the current, it is suspected that the adsorbed water is responsible for movement of ions (Figure 2.4).\cite{77} These ions can be impurities, specific groups on the cellulose or the dissociated water molecules.

![Figure 2.4: Possible mechanism for ion conduction in moist cellulose.](image-url)
When papers made from algae (*Cladophora*)-based nanocellulose and NFC were compared, it was observed\cite{75} that humidity played an important role in conductivity levels for low frequency currents. However, for higher frequencies, conductivity was less dependent on moisture. This could be due to decreased mobility of ions at high frequency currents. The dielectric loss factor becomes a function of frequency and humidity. In general, the higher frequencies in the range of $10^5$-$10^6$ Hz show a loss factor below 0.5. At lower frequencies below 1 kHz, this loss factor can reach between 2-8. The amount of water absorbed is related to porosity and crystallinity of the material. The more the pores, the higher the absorbed water. The higher the crystallinity, the lower the water content. An important factor noted in this study was the state of absorbed water. If water is in bulk of the cellulose rather than on the surface, the conductivity is less, observed for NFC.\cite{75} The surface water must contain a free path for conductive ions relative to the water absorbed in the bulk that reduces accessibility to conductive ions. The effect of relative humidity (RH) has shown to increase water content, and thus the conductivity of cellulose samples. The amount of water determines how tightly or loosely bound the water molecules are.\cite{77} This condition can slow the mobility of ions. Conductivity increased from well below $10^{-11}$ S cm$^{-1}$ to above the $10^{-8}$ S cm$^{-1}$ by increasing RH from 11% to above 94%.\cite{75}

Similar to native cellulose, there are studies on cellulose derivatives, which show dependence of dielectric properties on the polar nature of the polymer. Reddy et al. studied solution grown cellulose acetate butyrate (CAB) films for their dielectric properties.\cite{78} The degree of substitution was 2.1 for acetate groups and 0.7 for butyrate groups. The dielectric constant continues to reduce with increases in temperature and frequency. The dielectric loss reduces from 100 Hz to 3 kHz, and then shows a peak near $10^5$ Hz, which diminishes again. In all cases, the loss does not go above 0.13. The dielectric constant remains below 5 and above 3.8. The conductivity
of such films was below $10^{-6}$ S cm$^{-1}$. As a general trend, the decrease in dielectric constant with temperature and frequency is suspected to be due to weak polar nature of carboxylic groups in side chains. The sudden increase in dielectric loss at higher frequencies occurs due to side group relaxation that corresponds to the glass transition temperature.

El-Sayed et al. studied blends of PVA and CMC.\textsuperscript{[79]} They saw the temperature and frequency dependence of the dielectric constant and dielectric loss tangent. The increased temperature and frequency caused increases in dielectric constant, loss and conductivity. Similar to CAB films, the material shows peaks near glass transition regions. Presence of water molecules increases dielectric properties. Though these properties are condition dependent, the dielectric constant of CMC was observed in the range of 2-10, the dielectric loss tangent was below 1 and the conductivity was in the range of $10^{-9}$ to $10^{-6}$ S cm$^{-1}$. It was seen that the blends with PVA can cause a spike in the dielectric constant up to 1000 due to chain relaxation near glass transition regions.

Another nano form of cellulose known as Cellulose nano crystals (CNC’s) are under review for their usability in designing electrical circuits. CNCs are made by treating cellulose with sulfuric acid, which hydrolyzes the amorphous regions resulting in a highly crystalline cellulose material. CNC can be created from different origin (sources) and extraction methods, as shown in Table 2.1.
Table 2.1: CNC dimensions from various starting materials and methods.

<table>
<thead>
<tr>
<th>Cellulose source</th>
<th>Hydrolysis method</th>
<th>CNC dimension</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rice husk fibers</td>
<td>60 wt% H₂SO₄ solution for 30 min</td>
<td>Average diameter: 12.4 ± 4.6 nm</td>
<td>[80]</td>
</tr>
<tr>
<td>Pandanis tectorius</td>
<td>60 wt% H₂SO₄ solution at 45 °C for 45 min</td>
<td>Length: 50-400 nm (average 200 nm)</td>
<td>[81]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Average diameter: 5-25 nm</td>
<td></td>
</tr>
<tr>
<td>Kenaf bast fibers</td>
<td>65 wt% H₂SO₄ solution for 120 min</td>
<td>Average length: 124.3 ± 45.3 nm</td>
<td>[82]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Average diameter: 11.3 ± 2.6 nm</td>
<td></td>
</tr>
<tr>
<td>Banana psedostems fibers (Musa sp.)</td>
<td>50 ml of 64 wt% H₂SO₄ solution at 45 °C for 70 min stirring</td>
<td>Average length: 135 ± 12 nm</td>
<td>[83]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Average diameter: 7.2 ± 1.9 nm</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Average aspect ratio: 21.2 ± 2.8</td>
<td></td>
</tr>
<tr>
<td>Raw cotton linter</td>
<td>60 wt% H₂SO₄ solution with Teflon© bar dispersing element at 45 °C for 60 min</td>
<td>Length: 161-193 nm (average: 177 nm)</td>
<td>[84]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Width: 10-13 nm (average: 12 nm)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Aspect ratio: 20-24 (average: 19)</td>
<td></td>
</tr>
<tr>
<td>Ushar (Calotropis procera) seed fiber</td>
<td>64 wt% H₂SO₄ solution (fiber to acid ratio of 1:20) at 50 °C for 75 min under strong agitation</td>
<td>Length: 140-260 nm</td>
<td>[85]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Diameter: 14-24 nm</td>
<td></td>
</tr>
</tbody>
</table>

No matter the chemical treatment method or source of the cellulose, the resulting materials are rod-like and highly stiff, having a narrow size distribution which are drastically shorter than MFC. CNC’s have a typical diameter in the range of 2-20 nm with length distributions between 100-600 nm.[86] As compared to MFC they have much lower viscosity and yield strength. The water holding capacity of these materials are very poor in comparison to MFC as well. However,
they do show self-assembly and birefringence and have outstanding mechanical properties such as a high Young’s modulus (~150 GPa). CNC, being a crystalline cellulose can act as a dielectric layer due to less water absorption. This ability of CNC to act as dielectric materials was tested for development of organic field effect transistors (OFET).[87] The on-off ratio, ON current vs. leakage current for gate, was observed to be $10^4$. For 140 nm thick CNC film the stable bias voltage can be below 10 V and have a leakage current below 15 V with $2 \times 10^{-9}$ A.[87] Another method for developing dielectric cellulose materials can be accomplished using derivative methods absent of doping. As an example, a cellulose derivative ‘trimethylsilyl cellulose (TMSC) was tested in conjunction with other functional materials to develop low-voltage complementary organic circuits. TMSC is a hydrophobic material with insulating properties. Such an insulator has very low electron trap density, thus, the I(V) hysteresis is almost absent.[88]

2.7 Conductive paper

Going one step further, the dielectric nature of cellulose can be made conductive with the help of suitable doping. The film of ethyl cellulose (EC), doped with iodine, was used to study the electrical properties of the composite.[89] The dopant concentration, when changed from 0.5 through 5%, increased conductivity by about 10 times. The increased temperature caused thermal ionization of the dopant and resulted in increased conductivity by ~ 8 times. It was seen that the excitation voltage showed two different slopes for current. At voltages below 1.95, the slope was $1-1.18$, which later changed to $1.9-2.4$. These changes in conductivity are a result of the reduction in barrier gaps for the iodine dope. The source of excited electrons in this case was metal electrodes across the film. The conduction mechanism was the Richardson-Schottky mechanism, which is field dependent on the thermionic injection mechanism. Therefore, as the electrodes change, the
conductivity changes. Al-Sn combination of electrodes showed highest conductivity when compared to Al-Al, Al-Ag, and Al-Au.

Another doping material is ammonium-based proton donors. Cellulose films doped with ammonium carbonate (NH₄CO₃) were studied for creating solid-state electrolytes. Carboxymethyl cellulose (CMC) and 7% ammonium carbonate film gave the highest conductivity value of 7.71 x 10⁻⁶ S m⁻¹.[90] CMC film doped with ammonium fluoride (NH₄F) showed the highest conductivity, namely, 2.68 x 10⁻⁷ S cm⁻¹ at 9% doping.[91] It should be noted that the above-mentioned doped films showed Arrhenius behavior. As the temperature increases, the conductivity increases. The dielectric constant of such films drops from 13, when starting below 100 Hz and to near 0, when above 10k Hz. Similar to the above doping materials, the doping of CMC derived from Kenaf bast fiber with ammonium acetate (CH₃COONH₄) (Figure 2.5)[92] has shown conductivity (protons hopped from NH₄ group to carbonyl oxygen of CMC).

![Proton hopping](image)

Figure 2.5: Proton donor and conductivity through proton hopping in the CMC based ink.

The highest value was 5.77 × 10⁻⁴ S cm⁻¹ at 20% doping. The purpose of this study was to develop an electrolyte film that can be used for proton battery and solar cells. This film showed electrochemical stability up to 2.5 V. It was noted that more than 20% doping reduced conductivity by forming neutral ion pairs. The neutral ion pair caused the protons to be associated back to the
ammonium groups. A similar observation was reported in earlier studies by Samsudin et al. where they used NH₄Br as a proton donor.⁹³ The 25% dopant gave the highest conductivity of 1.12 x 10⁻⁴ S cm⁻¹. Instead of conductive salts such as ammonium salts shown above, conductive polymers can be bound to cellulose. Luong et al. used aniline polymerized on the NFC (obtained by enzymatic hydrolysis) to create a PANI/NFC composite.⁹⁴ PANI/NFC composite was found to form a stable suspension in wide pH range from 1 to 7. This was a greater range than the simple PANI suspension that requires pH between 2 and 3. It was noted that 5 wt% of PANI on NFC shows conductivity of 2.6 x 10⁻⁵ S cm⁻¹. The strength of this composite paper (~178 MPa) was found to be close to neat NFC paper (~173 MPa). As the level of PANI increased, the conductivity increased, and the strength decreased. Here the NFC provides stability to PANI and thick layers can be cast on the glass at higher concentrations. Authors have achieved a conductivity of 1.8 S cm⁻¹ at 80 wt% of PANI. However, the strength reduced to 37 MPa due to complete covering of NFC, thereby affecting its ability to form hydrogen bonds with neighboring NFC. The percolation threshold of PANI was calculated to be 4.57 vol%.

Conductive properties need not be controlled for paper during formation. Paper properties can be modified by external coatings or absorption of conductive materials such as Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) or ionic liquids such as 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim]BF₄).⁹⁵ When papers made from microcrystalline cellulose (MCC) were tested, MCC without residual hemicellulose showed better adsorption of the PEDOT:PSS. Two ratios of PEDOT:PSS were chosen as 1:2.5 and 1:6. It was seen that the lower the PSS levels, the better the adsorption on MCC. Overall adsorption is governed by the repulsive forces between MCC and the doping material. PEDOT:PSS complex is anionic. Hence, its adsorption on cellulose surface increases by reduction of repulsive forces between cellulose and
PEDOT:PSS. This can be achieved by reducing pH. Similarly, increasing salt, can affect the adsorption by screening the charges or shrinking the polyelectrolyte, which helps in adsorption or penetration in pores. The salt concentration showed a peak near 0.03% concentration suggesting that after a point, increasing salt has a negative effect on adsorption. It was seen that PEDOT:PSS adsorptions could improve conductivity from $10^{-12}$ S cm$^{-1}$ to $10^{-2}$ S cm$^{-1}$. The study shows that too high refining of paper fibers reduces the pores and thus, the polymer adsorption. High pressure calendering has been beneficial in polymer packing and improved conductivity. The addition of N-methyl-2-pyrrolidone (NMP), dimethylsulfoxide (DMSO) enhances the conductivity of PEDOT:PSS by plasticizing the complex, washing out the PSS$^{-}$ ions and causing the conformational changes in PEDOT. It can be further increased by small amounts of multiwall carbon nanotubes (MWCNT) as the MWCNT have good electrical properties. For the ionic paper made from [bmim]BF$_4$, it was noted that the voltage change did not affect ion conductivity. One advantage for such external coating is to have selective areas of paper treated, providing the required conductive properties.

Researchers are also investigating the use of composite paper to provide improved physical, mechanical, and conductive properties. Incorporation of graphene,$^{[96]}$ graphene oxide (GO),$^{[96-99]}$ and reduced graphene oxide (RGO)$^{[96, 97]}$ can tune paper properties, providing improved mechanical properties and making paper ‘conductive.’ Cellulose nanocrystals (CNC),$^{[98]}$ amine-functionalized nanofibrillated cellulose (A-NFC)$^{[96]}$ and NFC$^{[97, 99]}$ are examples of these composite papers, which have been used in various studies. In one such study a composite paper was made with CNC/GO and was observed to be conductive above 25 V. In contrast to this, it is claimed that the composite paper made with NFC/GO is non-conductive. In addition to the electrical performance imparted by the addition of NFC/GO, it has also been observed that loading
of GO by 1% increased tensile strength by 17% and increased the thermal stability of the paper. In another study, an A-NFC and RGO composite was produced with a conductivity of 71.8 S m⁻¹, with the addition of 10% RGO. In comparison, a non-functionalized NFC/RGO composite had a conductivity of 15.4 S m⁻¹. Which shows that doping using amine functionalization can greatly improve the conductivity of cellulosic materials. Additionally, 1% RGO in NFC increased tensile strength by 12%. Depending on the process, an RGO concentration above 5% may not improve mechanical properties. Addition of RGO in NFC based paper will enable the creation of a conductive substrate, which improves tensile strength and mechanical properties, even in the presence of high humidity’s. 

2.8 Conductive gels and inks

Instead of making the whole substrate a conductive material, it is also possible to create selective areas of paper with conductivity. This can be done by using printed catalyst inks, which convert cellulose to graphitic carbon. One such attempt has been made by printing with aqueous iron nitrate solution and then carbonizing the printed sheets in N₂ gas flow by a single heating step at 10 K min⁻¹ to 800 °C. During this process, the paper is converted into graphitic carbon and ink is converted to Fe₃C. Here, liquid eutectic of iron and carbon is formed in elevated temperature conditions. Due to this eutectic mixture, the printed line width can be increased by a few hundred nanometers in the unprinted area. Such processes gave higher conductivity in the printed areas (18 S cm⁻¹). The paper showed shrinkage to 60%. The unprinted cellulose converted to amorphous cellulose with a conductivity of 0.6 S cm⁻¹.

Another method for creating a gel with conductive properties can also be developed. Such cellulose-based conductive gels may be used for batteries and transistors. An example of the use of such a gel was shown by the grafting of ethyl cellulose (EC) to the lithium salt of 2-acrylamido-
2-methylpropane sulphonic acid (LiAMPS).\textsuperscript{[101]} This grafted polymer was then embedded in polymethyl methacrylate (PMMA) gel. Here, the conductivity achieved was 1.33 mS cm\(^{-1}\). Authors have compared this conductivity with the study of poly(LiAMPS) in MMA and tetraethyleneglycol diacrylate gels.\textsuperscript{[102]} They found an 80\% increase in conductivity. The charge carrying mechanism is most likely the hopping of Li\(^+\) ions. Such grafting resulted in a low glass transition temperature for the grafted EC compared to non-grafted EC. This should ease the chain movement and conformational changes for grafted EC. It showed that the MMA concentration played an important role in rigidity and conductivity. This effect could be due to the presence of a stronger matrix. Increasing the concentration of EC above the threshold can impart steric hindrance to the ion hopping process.

Another example was shown using an electrolytic hydrogel, created when MCC was mixed with LiOH/urea.\textsuperscript{[103]} This mixture was tested as a possible electrolyte-gated transistor where the electrolyte acted as a gate for the transistor. The ionic mobility/conductivity was found to be in the range of 10\(^{-7}\) S cm\(^{-1}\). The charge holding capacity of the gel was found to be related to concentration of MCC. For 4\% MCC, the capacity was 12.1 \(\mu\text{F cm}^{-1}\), while at 8\% MCC it reduced to 2.6 \(\mu\text{F cm}^{-1}\). The concentration also affected the on-off ratio of the transistor, which moved from a range of 10\(^5\) to 10\(^3\).

Cellulose-based ion gels may assist the development of capacitors and gates for field effect transistors.\textsuperscript{[104]} With microcellulose, the ionic liquid made of 1-ethyl-3-methylimidazolium [EMIM] as the cation and bis(trifluoromethylsulfonyl)imide [TFSI] as the anion was analyzed. In addition, different methylphosphonates were added as anions during the study. The cellulose to ionic liquid mass ratio was 3:70. The capacitance of the ion gel was found to be in a high range (10 \(\mu\text{f cm}^{-2}\)), up to 10 kHz frequency. Flexible transistors on paper have been made with these
gates. The semiconducting ZnO was used in nanorod format for flexibility. The gates are sensitive to environmental humidity.

Cellulose-Based Electrically Functional Inks, Fibers, and Electrodes Inks are the colloidal suspensions which dry on the surface of a substrate. It is of great importance to have uniform film formation of the applied ink. If the ink formulation and drying are not compatible with the process, a well-known pinning effect or coffee ring effect is observed, where the particles tend to aggregate at the edges of the drop (Figure 2.6).

![Figure 2.6: Usage of cellulose nano fibers as a matrix for conductive inks and advantage in reduction of coffee ring effect.](image)

To reduce such effects, CNF (cellulose nano fibers) can be used [105]. The addition of 0.1% wt. CNF of 20 nm diameter and 1 µm length has demonstrated remarkable suppression of the coffee ring effect. The prolate shape of CNF causes anisotropic Brownian motion of particles and shows a capillary effect. The motion of particles to the periphery of the droplet is restricted and water transportation is hindered due to the hydrophilicity of CNF. As a result, the droplet starts drying from edge to inside. It is interesting to note that this property is not seen in CNC. CNCs tend to show a strong coffee ring effect. These studies can be used for improved printing of electrically functional inks.

Electrically functional inks and conductive fibers may be developed using cellulose as a supporting matrix or as the base material. Also, grafting the functional chains to a cellulose surface
can provide inks with electrical properties. Barras et al. used CMC as a binder for screen-printed conductive inks. Carbon fibers (CF) and multi-walled carbon nanotubes (MWCNTs) were used as electrically functional materials. These materials are hydrophobic and CMC helps in forming a hydrophilic matrix to hold them in water based ink. The authors also used ethyl cellulose (EC) as a stabilizing and dispersing agent. The concentration of CMC and EC is important to maintain viscosity, and thus, the flow of the screen printing ink. It was observed that EC concentration below 4% was not suitable. Similarly, a CMC concentration below 3% was not viscous enough to provide good printing by screen printing process. Authors also noted a CF concentration below 5% wt. was not enough for good conductivity and more CF was required. The print resolution reduced with an increased CMC amount. Sheet resistivity was found to be 3.1 x 10² Ω/sq. at 25 °C and 15% RH. However, the resistivity was found to be dependent on humidity. Thus, the composite can be used for humidity and temperature sensing.

Cellulose in the form of NFC was also tested for the development of conductive carbon nanofibers. GO was used in the process of carbonization of NFC fibers. The function of GO was to provide a template that helped in the formation of sheets of NFC (Figure 2.7a and Figure 2.7b).

![Figure 2.7: a) Carbonized NFC (do not form carbon nano fibers) b) Carbonized NFC+GO (form conductive nano nano fibers).](image)

The authors were able to achieve a conductivity of 649 ± 60 S cm⁻¹. Such fibers may be utilized for various conductive materials. TEMPO (2,2,6,6-Tetramethylpiperidine 1-oxyl) oxidized CNC (cellulose nanocrystals) has shown the ability to stabilize nano-silver suspensions.
of conductive inkjet inks.\textsuperscript{[58]} Highly charged CNC, due to carboxylate groups, allowed the suspension stability and control over nano-silver synthesis. Cationic surfactants help in stability and synthesis. Ink formulation with 1.2 % wt. of CNC and 2.9 % wt. silver showed conductivity as well as stability. Sheet resistance decreased from 50 $\Omega$/sq to 1 $\Omega$/sq when the sintering temperature changed from 180 °C to 250 °C (cellulose degradation temperature). Dioctyl sulfosuccinate (DSS) as a surfactant was found to be useful at 0.15% concentration.

A few efforts on the utilization of cellulose to develop sensors for humidity and pressure have surfaced. Shukla has shown that grafting the cellulose with polypyrrole\textsuperscript{[109]} or polyaniline\textsuperscript{[110]} can create a moisture sensitive conductive film. Such a film varies the current as a response to changes in humidity. Grafting was observed to be highly advantageous in having electrical properties and hygroscopic properties as compared to individual cellulose and polypyrrole\textsuperscript{[109]} (Figure 2.8). This may be related to the density and surface structure of functional chains. Similarly, grafted polyaniline had promising results.
Another interesting property of cellulose-based materials is the piezoelectric effect due to the natural asymmetric arrangement of molecules in the cellulose crystals. For pressure sensors, work has been done on piezoelectric properties of CNC films. Here, the piezoelectric response of such films was observed to be in relation with CNC alignment and film thickness. Shear piezoelectric constant of crystals was determined to be 2.1 Å/V. In a paper by Rajala et al., a film of CNF (cellulose nano fibrers) showed a piezoelectric sensitivity of 4.7-6.4 pC/N. Work by Zheng et al. on CNF/PDMS aerogel shows that nano generators based on the piezoelectric property of cellulose can be made. It was noted that the voltage generated by CNF/PDMS aerogel based nano generators is ~ 4 times the voltage generated by pure CNF aerogel. This was due to enhanced Si radicals in the structure. CNF plays an important role in providing high surface area and compressibility. Dipole moments cannot be seen in pure PDMS.
Researchers have also considered the application of cellulose-based materials for batteries and supercapacitors. Polymerized polypyrrole (PPy) on poly(N-vinylpyrrolidone) (PVP) coated cellulose nanocrystals (CNCs) was created for usage in high cycling capacity supercapacitors.\cite{114} For batteries, studies were done on cellulose materials.\cite{115} CNC has been studied for developing electrodes for such batteries and thus replacing the polyvinyliden-di-fluoride (PVdF).\cite{116} 4-5% of CNC as a binder for synthetic graphite and carbon-coated LiFePO4 mixed with conductive carbon was used to prepare the electrodes for the battery. The authors claimed to have achieved good capacity and cycling performance for these electrodes compared with the electrodes having a conventional binder. In another study\cite{117} on electrode development for Li-S batteries, NFC/RGO matrix (powder) was used to deposit Sulphur on this powder. This composite material was cast to form electrodes. The laminar pore structure in the matrix enabled 50% wt. sulphur impregnation. The NFC to RGO ratio 1:1 provided better performance. Okubo et al.\cite{118} have shown the usage of CMC (11.1%) as a binder for Li-Si alloy based electrodes. A consolidated table of various methods to create conductive elements using at least one cellulose-based component is shown in the Table 2.2.

### 2.9 Conclusions

Interest in paper-based substrates for printed electronics is accelerating rapidly but still early in the product development life-cycle. As evident from the review, a variety of promising strategies have been demonstrated. Different electrical and optical components demand different environment and performance from the cellulose based elements. Therefore, a single cellulose-based system may not be applicable to create a device inclusive of all necessary components. Usage of nanocellulose to control the surface, drying of inks and holding functional materials can improve the performance of printed devices while remaining ecofriendly. Important properties of
cellulose that govern the end results are the source and purity of cellulose, crystallinity, molecular weight or degree of polymerization and treatment given. For example, improvement in transparency of paper by TEMPO oxidation may affect the printability and energy consumption of the devices. Cellulose based substrates and conductive/dielectric materials can be produced with more research. More research on substrate development is required that will permit back-to-back printing with the capability of producing vertical interconnect access. A functional material that is coated, embedded or grafted to cellulose can increase output performance up to a certain level of concentration. Excessive concentration of a functional material may reduce performance. The performance of such materials may not be as good as pure inorganic counterparts. However, its advantage will be in the cost and renewability of materials for products with short life spans.
Table 2.2: Various methods to create conductive elements where at least one component of the system is cellulose.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Ink</th>
<th>Resistivity/ Conductivity</th>
<th>Thickness</th>
<th>Calculated Conductivity</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>MFC and Kaolin (calendered)</td>
<td>Ag nano particle inkjet</td>
<td>0.08-0.23 Ω/sq</td>
<td>~ 3 µm</td>
<td>1.44 x 10^4 - 4 x 10^4 S cm^-1</td>
<td>[62]</td>
</tr>
<tr>
<td>20.1% CNT in CNC</td>
<td>-</td>
<td>10^2 Ω/sq</td>
<td>100 µm</td>
<td>10^-4 S cm^-1</td>
<td>[74]</td>
</tr>
<tr>
<td>5% PANI on NFC</td>
<td>-</td>
<td>2.6 x 10^-5 S cm^-1</td>
<td>-</td>
<td>-</td>
<td>[94]</td>
</tr>
<tr>
<td>80% PANI on NFC</td>
<td>-</td>
<td>1.8 S cm^-1</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>CMC with 7% NH_4CO_3</td>
<td>-</td>
<td>7.71 x 10^-6 S cm^-1 (at 303 K)</td>
<td>-</td>
<td>-</td>
<td>[90]</td>
</tr>
<tr>
<td>CMC with 25% NH_4Br</td>
<td>-</td>
<td>1.12 x 10^-4S cm^-1 (at room temp)</td>
<td>-</td>
<td>-</td>
<td>[93]</td>
</tr>
<tr>
<td>Humid MCC (3% moisture)</td>
<td>-</td>
<td>10^-14 S cm^-1</td>
<td>-</td>
<td>-</td>
<td>[77]</td>
</tr>
<tr>
<td>CNC coated card board</td>
<td>Inkjet ink 1.2% CNC and 3% Ag nano particles</td>
<td>1 Ω/sq (annealed at 250 °C)</td>
<td>-</td>
<td>-</td>
<td>[58]</td>
</tr>
<tr>
<td>Photo paper type 3</td>
<td>Screen ink with 3% CMC and 10% carbon fibers</td>
<td>3.1 x 10^2 Ω/sq (at 25 °C and 15% RH, 10 layers of ink)</td>
<td>-</td>
<td>-</td>
<td>[107]</td>
</tr>
</tbody>
</table>
Table 2.2: continued

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Ink</th>
<th>Resistivity/ Conductivity</th>
<th>Thickness</th>
<th>Calculated Conductivity</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paper</td>
<td>70% silver ink with vinyl chloride copolymer</td>
<td>~0.039 Ω/sq</td>
<td>12 µm</td>
<td>2.14 x 10^4 S cm^{-1}</td>
<td>[1]</td>
</tr>
<tr>
<td></td>
<td>60-65 % silver with polyester resin</td>
<td>~0.042 Ω/sq</td>
<td>30 µm</td>
<td>0.79 x 10^4 S cm^{-1}</td>
<td></td>
</tr>
<tr>
<td>Silver ink</td>
<td>Electrodag® PD-056</td>
<td>0.28 Ω/sq (12 BCM anilox)</td>
<td>2.11 µm</td>
<td>1.69 x 10^4 S cm^{-1}</td>
<td></td>
</tr>
<tr>
<td>Papers with roughness between 0.99 and 1.84 μm (porosities between 1.03 to 2.32 ml/min)</td>
<td>Flexo Silver inks Acheson PM-500 and Electrodag® PD-056</td>
<td>0.21 Ω/sq to 0.37 Ω/sq</td>
<td>1.57 – 4.54 µm</td>
<td>0.7 x 10^4 – 3.03 x 10^4 S cm^{-1}</td>
<td>[40]</td>
</tr>
<tr>
<td>Photo IJ paper (20-30 nm Silica coated, roughness 1.47 µm)</td>
<td>Silver nano particle inkjet ink (1-5 layers)</td>
<td>&lt;5 Ω/cm (before and after treatment of paper by methyl-nonafluorobutylether and methylnonafluoroisobutylether (C₄F₉OCH₃))</td>
<td>-</td>
<td>-</td>
<td>[52]</td>
</tr>
<tr>
<td>Substrate</td>
<td>Ink</td>
<td>Resistivity/ Conductivity</td>
<td>Thickness</td>
<td>Calculated Conductivity</td>
<td>Source</td>
</tr>
<tr>
<td>-----------</td>
<td>-----</td>
<td>--------------------------</td>
<td>-----------</td>
<td>-------------------------</td>
<td>--------</td>
</tr>
<tr>
<td>Matt IJ paper (10-20 µm Silica coated, roughness 4.31 µm)</td>
<td>Silver nano particle inkjet ink (1-5 layers)</td>
<td>10-40 Ω/cm and 10-30 Ω/cm (before and after treatment of paper by methylnonafluorobutylether and methylnonafluoroisobutylether (C₄F₉OCH₃))</td>
<td>-</td>
<td>-</td>
<td>[52]</td>
</tr>
<tr>
<td>Coated offset paper (Kaolin and CaCO₃ coated, roughness 3.04 µm)</td>
<td></td>
<td>~15 Ω/cm and 10-20 Ω/cm (before and after treatment of paper by methylnonafluorobutylether and methylnonafluoroisobutylether (C₄F₉OCH₃))</td>
<td>-</td>
<td>-</td>
<td>[52]</td>
</tr>
</tbody>
</table>
Table 2.2: continued

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Ink</th>
<th>Resistivity/ Conductivity</th>
<th>Thickness</th>
<th>Calculated Conductivity</th>
<th>Source</th>
</tr>
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<td>Laboratory paper</td>
<td></td>
<td>&gt;5 x 10^6 Ω/cm and 25-160 Ω/cm</td>
<td>-</td>
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<td>[52]</td>
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<td>(roughness 3.28 µm)</td>
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<td>(before and after treatment of paper by methylnonafluorobutylether and methylnonafluoroisobutylether (C₄F₉OCH₃))</td>
<td>-</td>
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<tr>
<td>Papers coated with PEDOT:PSS</td>
<td>-</td>
<td>10⁻² – 10⁻³ S cm⁻¹</td>
<td>-</td>
<td>-</td>
<td>[95]</td>
</tr>
<tr>
<td>(with/without TiO₂ / MWCNT)</td>
<td></td>
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<tr>
<td>Various papers</td>
<td>Lignosulfonate:</td>
<td>10⁸ – 10⁻¹⁰ S cm⁻¹</td>
<td>-</td>
<td>-</td>
<td>[41]</td>
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<td>PANI ink (1:1 and 1:4 ratios)</td>
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<tr>
<td>Flexo Silver flake ink</td>
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<td>795 – 2684 S cm⁻¹ (before calendering base papers)</td>
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<td></td>
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<td>786 – 1177 S cm⁻¹ (after calendering base papers)</td>
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<th>Thickness</th>
<th>Calculated Conductivity</th>
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<td>Ethyl cellulose-g-LiAMPS in MMA gel</td>
<td>-</td>
<td>1 – 1.3 mS cm⁻¹</td>
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<td>-</td>
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<td>(Ethyl cellulose 12.5 – 37.5 mol L⁻¹, MMA 0.125 – 0.5 mol L⁻¹)</td>
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<tr>
<td>(LiAMPS 0.5 mol L⁻¹, EGDMA 0.063 mol L⁻¹)</td>
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<td>NFC carbonized along with graphene oxide</td>
<td>-</td>
<td>649 ± 60 S cm⁻¹</td>
<td>-</td>
<td>-</td>
<td>[108]</td>
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<tr>
<td>Paper</td>
<td>Iron based catalytic ink</td>
<td>18 S cm⁻¹ (after calcination)</td>
<td>-</td>
<td>-</td>
<td>[100]</td>
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<td>CMC doped with 9% NH₄F</td>
<td>-</td>
<td>2.68 x 10⁻⁷ S cm⁻¹</td>
<td>-</td>
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<td>[91]</td>
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<tr>
<td>CMC doped with 20% CH₃COONH₄</td>
<td>-</td>
<td>5.77 x 10⁻⁷ S cm⁻¹</td>
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<tr>
<td>NFC/RGO composite (RGO 10%)</td>
<td>-</td>
<td>15.4 S cm$^{-1}$</td>
<td>-</td>
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<td>[97]</td>
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<tr>
<td>Amine modified NFC/RGO (10% RGO)</td>
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<td>71.8 S cm$^{-1}$</td>
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<td>NFC paper</td>
<td>ITO (sputter deposition)</td>
<td>12 Ω/sq</td>
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<td>AgNWs  (Mayer rod)</td>
<td>25 Ω/sq</td>
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<td>-</td>
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<td></td>
<td>CNTs (Mayer rod)</td>
<td>200 Ω/sq</td>
<td>-</td>
<td>-</td>
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<td>Photo papers</td>
<td>Screen ink 3% CMC and 10% carbon fibers</td>
<td>1.03 Ω cm</td>
<td>-</td>
<td>0.97 S cm$^{-1}$</td>
<td>[103]</td>
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<td>Screen ink 3% CMC and 0.5% MWCNT</td>
<td>0.57 Ω cm</td>
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<td>1.75 S cm$^{-1}$</td>
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<tr>
<td>Electrolyte of 4% MCC, LiOH and Urea</td>
<td>-</td>
<td>3.56 x 10^{-7} S cm^{-1}</td>
<td>-</td>
<td>-</td>
<td>[103]</td>
</tr>
<tr>
<td>Various papers</td>
<td>UV curable polymer preatreatment followed by inkjet printed CNT-PEG/PEDOT-PSS</td>
<td>917-2143 Ω/sq (3 layer prints)</td>
<td>-</td>
<td>-</td>
<td>[59]</td>
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</tbody>
</table>
3. CMC BASED HYDROGELS FOR THE SUBSTRATE AND PHOTO-DEGRADATION FOR SPATIAL TUNING

3.1 Introduction

Hydrogels are substances which absorb and hold a large amount of water. There are a variety of materials showing such capability. In the review for usage of cellulose based materials in printed electronics, it was noted that the cellulosic hydrogels are rarely utilized in the applications of electrical circuit generation. Apart from a reference of electrolytic gel, hydrogels were not recognized or appreciated for substrate development and process enhancement in printed electronics. Such materials can be of great usage if their swelling capacity can be tuned zonally. The zonal tuning of the hydrogels can possibly make them swell at different rates and let them receive different amounts of functional materials such as conductive inks. The water holding capacity can also make them a capable matrix for electrolytic components.

3.2 Cellulosic hydrogels

Since the discovery of water absorbing and swelling materials, we have utilized them for various purposes, mainly for cleaning or soaking up water from any wet surface. A further categorization of hydrogels is superabsorbent polymers if they can absorb and hold water more than 10 times the weight of dry mass under pressure (>0.67 g/cm²). The matrix of hydrogels is similar to a sponge, where there can be water present in between two molecules of a polymer. The polymer molecules are crosslinked at some points so that they cannot be separated completely by the water. Such materials can be used for extended duty applications in absorption of aqueous solutions such as sanitary applications, and as an aqueous solution supplier through controlled release of water for wound dressing and agricultural irrigation. Along with these properties, hydrogels provide secondary benefits such as the ability to hold and release small molecules and
shape change and surface modulation though opening or closing of the matrix. Based on the type of polymer and the crosslink, the hydrogel matrix shows different capacities for water holding. The local factors that control this water absorption and holding capacity are the amount of available water to be absorbed, ionic concentration,\cite{124} the pH of the solution,\cite{125} the temperature of the system,\cite{126} and the rate of water supply to the system vs rate of water loss due to evaporation.

Hydrogels are tunable materials where one can control water absorption capacity by controlling the rigidity of the gel matrix. A rigid matrix has less swelling capacity and hence less water absorption capacity. The increasing crosslinking can thus govern this property. A second aspect is the length of a crosslinker molecule. The crosslinker length controls the distance of separation of two polymer chain segments. The smaller the crosslinker molecule, the lesser the swelling ability as compared to longer crosslinkers.\cite{127} By selecting the polymers and crosslinkers of desired properties, one can achieve a stimuli responsive hydrogel.

Cellulose is a hydrophilic natural polymer. In plants, it is the most abundant polymer followed by hemicelluloses and lignin.\cite{128} In its natural form, it has crystalline and amorphous regions. The amorphous regions are highly water receptive as compared to the crystalline regions. If the cellulose chains can be separated from each other, the hydrophilicity of the material increases. The disruption of crystalline regions and addition of spacers in the form of grafted side chains can make it possible. The crystalline regions limit the swelling capacity of cellulose. They act similar to crosslinking\cite{129} at multiple sequential repeating units causing it to have no water penetration in between two successive crystalline regions/tie points. If there is gap between two tie points, the water can penetrate, and the water absorption capacity increases. Similarly, the grafted spacers prevent two cellulose chains from coming together and aligning with each other, thus reducing the chances of hydrogen bonding of multiple sequential repeating units. In other
terms, this is considered a reduction in crosslinking density. Further, charges developed on the cellulose or derivative cellulose cause the repulsion and allow more water to be penetrated.

### 3.3 Carboxymethyl cellulose

Carboxymethyl cellulose is an ether derivative of cellulose. Reaction of monochloroacetic acid and mercerized cellulose provides carboxymethyl cellulose (CMC). Alternatively, the sodium salt of monochloroacetic acid is reacted to obtain the sodium salt of CMC or CMC-Na (Figure 3.1).\textsuperscript{[130]} The salt form of the molecule makes it a water-soluble polyanionic polymer. In the cellulose chain, there are three hydroxyl groups per glucose unit. It is possible to substitute all of them with carboxymethyl groups. Based on the average number of substitutions, the degree of substitution can vary between zero and three. The degree of substitution (DS) plays an important role in solubility and rheological properties of CMC.\textsuperscript{[131, 132]} Higher DS would equate to lower crystallinity. A previous study has found it to have no crystallinity in CMC aggregates above DS 1.05.\textsuperscript{[131]} The thixotropic behavior of the aqueous solution of CMC is highly dependent on the uniformity of DS. The more uniform the DS, the lesser the chances of unsubstituted units in the chain. At a higher DS, the chances of finding unsubstituted blocks is lower, which can cause hydrophobic interactions. Above DS 1, thixotropy is not observed.

![Figure 3.1: Carboxymethyl cellulose (Sodium salt).](image-url)
The mechanical properties and rheological properties of CMC are also dependent on the molecular weight of the polymer.\textsuperscript{[133]} The higher the molecular weight, the higher the viscosity of the solution. Carboxymethyl cellulose displays high optical transparency,\textsuperscript{[134]} making it suitable for transparent films, coatings, and as a viscosity modifier. For viscosity modification, the concentration of the CMC plays an important role in the shear thinning or shear thickening behavior of the solution.\textsuperscript{[135]} The critical concentration is reported to be 1\%, below which CMC shows shear thinning for all shear rate ranges. Above a 1\% concentration of CMC, the solution shows conventional non-thixotropic (Newtonian) initial shear thickening followed by shear thinning above a critical shear rate. Thus, for high concentration mixtures, material mixing and transferring become difficult at lower shear rates. The glass transition temperature of the CMC is reported to be 75 °C for molecular weight 250,000.\textsuperscript{[79]} The electrical conductivity of CMC films is poor (1.26 × 10^{-8} \text{ S cm}^{-1})\textsuperscript{[79]} and it falls at the boundary of the insulator-semiconductor materials group.\textsuperscript{[136]} Though a typical insulator is considered to have conductivity less than 10^{-10} \text{ S cm}^{-1}, for low voltage electrical applications, dry CMC should be good as an insulator.

### 3.4 CMC based Hydrogels

Cellulose can be crosslinked by various methods and chemicals. Based on the nature of the additive, the process can vary. In the presence of PVA, physical crosslinking can be achieved by a freeze-thawing process.\textsuperscript{[137]} Similarly, ionic bonding of CMC is possible by introducing multivalent metals in the system.\textsuperscript{[138]} The multivalent metal ion bonds with two (or more) sites of carboxyl branches in CMC form a crosslinked structure. Lowering the pH of CMC is another way to achieve physical linkages through hydrogen bonding.\textsuperscript{[139]} A polymer complex network of polycationic polymers along with carboxymethyl cellulose is also possible.\textsuperscript{[140]}
Covalent bonding is suitable for more stable gels. A covalent bonded link is possible through a molecule bearing multiple sites for bonding. Aldehydes can react with hydroxyl groups on cellulose in an acid environment. Glyoxal\textsuperscript{141}, glutaraldehyde\textsuperscript{142} or dialdehyde cellulose (made by periodate oxidation)\textsuperscript{143} can be utilized as ether forming crosslinkers for binding cellulose molecules. Similarly, epichlorohydrine can form ether based crosslinks in a basic solution.\textsuperscript{144} Methylated nitrogen compounds are known to form ether crosslinks with cellulose.\textsuperscript{141, 145} Diisocyanates,\textsuperscript{146} divinyl sulfone\textsuperscript{147}, phosphate esters\textsuperscript{148} are other chemicals that can be used to form ester and ether bonded crosslinks with cellulose. Multicarboxylic acid group compounds such as maleic acid,\textsuperscript{149} and citric acid\textsuperscript{150, 151} are other groups of chemicals, which form ester linkages with cellulose. The acidic environment or catalysts such as sodium hypophosphite can be used in the process. However, the tri- and quadruple-functional carboxylic acids show the interesting ability to undergo cyclic anhydride formation at elevated temperatures.\textsuperscript{152} Anhydrides are more reactive than the carboxylic acids. Hence, they do not need the catalysts to form ester bonds with cellulose. More important, the cyclic anhydride crosslinking can be performed without the need for the solvent in the system.

Covalent crosslinking can also be performed through radical formation on a cellulose molecule. High energy radiation has shown ability to create radicals at various carbons in cellulose.\textsuperscript{139} The radicals are unstable, and they can lead to two different outcomes. If the polymer concentration is high enough, the radical can quickly bind to a neighboring polymer and form a crosslink. However, at lower concentrations, it leads to hydrolysis and degradation of the cellulose. Water plays an important role as it undergoes photo-excitation and photo-ionization and produces reactive species such as H$_3$O$^+$, H$_2$O$^+$, hydrated electron (e$^-$), H$^+$, and OH$^-$ radicals.
3.4.1. Water photo-ionization

In water photolysis, the excitation energy for water is 7.5 eV, and ionization energy is 12.5 eV.\[^{153}\] Though such energies are possible for photons in X-ray or higher energy radiations, one can still use a comparatively lower energy light such as UV and violet light to achieve similar results. This is possible through the mechanism of multiphoton absorption and water ionization.\[^{154}\] The photon energies between 3 eV and 3.5 eV, cause a (3+1)-photon resonance-enhanced multiphoton ionization (REMPI). This energy band is for the violet and near-UV light. For higher energy photons between 3.9 eV and 5 eV, a two-photon absorption mechanism was seen. The photo-excitation and ionization reactions are given in Equation 3.1 through Equation 3.4.

\[
\text{Equation 3.1: Photo-excitation of water and radical formation} \\
[H_2O] \rightarrow [H_2O]^* \rightarrow [H]^+ + [OH]^-
\]

\[
\text{Equation 3.2: Hydronium ion and hydrated electron formation} \\
[H]^+ + [H_2O] \rightarrow [H_3O]^+ + [e]_{hyd}^-
\]

\[
\text{Equation 3.3: Photo-ionization of water} \\
[H_2O] \rightarrow [H_2O]^+ + [e]_{hyd}^-
\]

\[
\text{Equation 3.4: Hydronium ion and hydroxyl radical formation} \\
[H_3O]^+ + [H_2O] \rightarrow [H_3O]^+ + [OH]^-
\]

Thus, formed hydronium ions and hydroxyl radicals can participate in cellulose degradation. The hydronium ions can lead to depolymerization of cellulose by breaking glycosidic links (Figure 3.2).\[^{155}\]
In the presence of a hydroxyl radical, the reaction takes place through hydrogen abstraction\textsuperscript{156} as shown in Figure 3.3. The resulting radical then reacts with nearby oxygen and then with $H^+$ ions in the solution. Finally, water molecule completes the reaction by forming a carbonyl group at the affected carbon (Figure 3.4). In this process, cellulose depolymerizes. However, if the reaction takes place at carbons 2, 3 or 5, the resulting output is oxidation of the respective carbon and not depolymerization. When hydrogen is abstracted from carbon 5, the endocyclic oxygen breaks the ring and results in the formation of an ester group at carbon 1.\textsuperscript{156}

Figure 3.2: Cellulose depolymerization by hydronium ion.

Figure 3.3: Hydrogen abstraction with hydroxyl radical.
Figure 3.4: Cleavage of glycosidic bond from the reductions of ground state oxygen and water. (Formation of carbonyl group).

3.5 Citric acid crosslinking

As mentioned earlier, citric acid can be utilized for hydrogel formation with cellulose and its derivatives. Citric acid is a naturally occurring molecule in citrus fruits.\textsuperscript{[157]} Its melting point is reported to be 156-157 $^\circ$C, and it decomposes above 175 $^\circ$C. Figure 3.5 shows the structure of the citric acid.

Figure 3.5: Citric acid.
The crosslinking mechanism is as shown in Figure 3.6. The mechanism suggests that the third carboxylic acid group on citric acid should not participate in crosslinking as it cannot form a third cyclic anhydride.

![Crosslinking Mechanism Diagram]

Figure 3.6: Carboxymethyl cellulose crosslink with citric acid by formation of intermediate cyclic anhydride in citric acid.

### 3.6 Photo-degradation of the CMC based hydrogels for zonal tuning

Various applications of hydrogels are possible though controlling the molecular alignment, pH, charges, and type of crosslinker in the hydrogel. If one can control the spatial tuning of the hydrogels, it would enable the possibilities such as shape controlling and surface tuning of the hydrogels. One of the ways to control the spatial behavior of hydrogels is though photographic
reactions. The light energy can be used to excite the molecules and form reactive species only at the photo-excited areas. Generally, photo-excitation results in states that are short lived and chemical changes that occur only in close radial vicinity of the generated species. This prevents system wide changes and allows spatial tuning. The photographic reactions allow the user to perform reactions without having contact with the material. Utilization of laser-based systems permit spatial precision and avoid the temperature changes for the whole material.

Cellulose is susceptible to radiation induced degradation, where depolymerization takes place. Previous studies have shown its ability to be processed by photolithography using UV radiation.\[158, 159]\ It is likely that the water or moisture in the cellulose goes through the photolysis process, leading to hydrolysis of cellulose. The rate of degradation should be dependent on the UV absorption of the system and the concentration of the cellulose. Such photodegradation should create the localized weak hydrogel matrix. The changes in the matrix can lead to zonal behavior of the hydrogels. As the material for hydrogel is transparent, it will have lower interaction with UV. To assist the degradation process, photo-active dyes can be used. The hydrogel system is water-based; hence, the dye should be water soluble. Moreover, if the dye is available from natural resources, it would enhance the bio-degradability, thus making a case for sustainability. Naturally occurring flavins are UV sensitive materials. One of them is riboflavin, commonly known as Vitamin B\textsubscript{2}. Riboflavin is UV sensitive and fluorescent.

### 3.6.1 Riboflavin assisted photodegradation

Riboflavin is vitamin B\textsubscript{2} utilized by our bodies. It is an orange colored molecule in its dry state, which shows solubility in water. In the presence of water, it absorbs UV light and fluoresces in the green-yellow region. The photo excitation of riboflavin (RF) at ground state results in the formation of a singlet excited state (\(^1\text{RF*}\))(Figure 3.7).\[160\] This is a short-lived state that follows
inter system crossing. The excited riboflavin non-radiatively decays to a triplet excited state ($^3$RF) that is able to activate further reactions. The triplet excited riboflavin can abstract hydrogen from a nearby molecule via a type I reaction (explained next). Such abstraction of hydrogen can then result in oxidation and bond breaking like the reaction shown in Figure 3.4.

![Figure 3.7: Riboflavin excitation after UV exposure.](image)

When the relaxation of the excited state of riboflavin is with fluorescence, riboflavin can engage in type I and type II reactions. In the type I reaction, two mechanisms can take place. The nearby molecule can transfer an electron to the riboflavin, or it can transfer a hydrogen atom. Sometimes, an intermediate stage of proton coupled electron transfer can be seen that results in a hydrogen atom transfer. This acquired electron or hydrogen is later transferred to the available oxygen, and riboflavin returns to the ground state. As the nearby molecules (substrate) get converted to radicals, they are susceptible to reactions. In the case of cellulose, it can become hydrolyzed and degrade. Type II reaction is physical quenching of the triplet excited riboflavin by the oxygen. It results in the generation of singlet oxygen ($^1\Delta_g$). The excited oxygen can oxidize nearby molecules, causing the degradation.
3.7 Photo-ablated hydrogels and their tuning

A study of the photo ablated/photo degraded hydrogels becomes necessary to understand physical and chemical changes occurring in them. The shape changes, and variation in water absorption capacity can then be utilized to create substrates for printed electronics to simplify the process of circuit making. In the next chapter, the CMC hydrogels are studied for their photo tunability, where we noticed that the transparency and spatial swelling changes can convert a thin hydrogel film into a lens shape. Such lenses can be used as commercial contact lenses with further study.
4. PHOTOINDUCED SPATIO-TEMPORAL RESOLUTION OF BIO-BASED THIN FILM HYDROGELS FOR CONTROLLED MORPHOLOGY, OPTICAL, AND GAS TRANSMISSION PROPERTIES

4.1 Abstract

This study targets spatio-temporal irradiation of cellulose-based hydrogels using a laser diode stereolithography 3D printer. The photodegradation addressable hydrogels (PAHs) are composed of carboxymethyl cellulose (CMC), citric acid, and riboflavin. Under irradiation, these PAHs engage in an unprecedented spatially resolved zonal swelling event. More specifically, the system shows marked, but controllable changes in swelling and thickness while concomitantly providing improved oxygen transmission rate values. These biocompatible and non-resorbable PAHs system provide selective control of material properties for the fabrication of biomedical devices such as highly functional and low-cost soft contact lenses, drug release devices, and wound healing dressings.

4.2 Introduction

The ‘smart properties’ of hydrogels is a topic of high interest to many fields. For example, such materials may provide controlled drug delivery triggered by porosity[124] and other bulk functional changes[161] (e.g., grafted spacers, functional molecules to direct drug holding and delivery). For example, hydrogels can be tuned for drug delivery[162-164] and wound healing by engaging in site-activated antimicrobial activity.[165]

Hydrophilicity, drug loading, and controlled delivery make hydrogels a suitable material for soft contact lenses by judicious control of their morphology and curvature leading to changes
in refraction/diopter strength. Due to the high-water content of the hydrogels, their direct contact with the cornea prevents irritation and inflammatory responses. Siloxane-based, hydroxyethyl methacrylate, and ethylene glycol dimethacrylate-based hydrogels have been commercially used to fabricate soft hydrogel contact lenses.[166, 167] Poly(acrylamide-co-sodium acrylate) based stimuli-responsive hydrogels have also been proposed for configurable contact lenses.[168]

The created hydrogels were citric acid crosslinked at elevated temperatures. The physical properties of the hydrogel, such as strength and swelling behavior, can be controlled by changing the degree of crosslinking.[133] Alternatively, they may be controlled by partial photo-degradation of the matrix because of the ability of cellulose to undergo structural modification from UV/photo-irradiation.[169, 170] With the addition of photosensitizers like riboflavin, degradation of polysaccharide chains can be initiated through a photo-excited state mediated by a sensitizer such as riboflavin.[171, 172] Another advantage of riboflavin is its bio-renewability, biocompatibility, and water solubility at low concentrations.[160] Unused riboflavin could be easily removed by washing in water. Thus, cellulose hydrogels can be degraded to form a weak gel matrix for controlled swelling (suggested schematics in Figure 4.1).
Previous studies have examined the photo-degradation of cellulose based films to create desired patterns, and of poly(ethylene glycol) based gels containing photodegradable molecules for cell culture and graphics generation. However, to date, hydrogels based on cellulose derivatives for photo-degradation have not yet been fabricated. We show that CMC, riboflavin, and citric acid, can control swelling by photo-degradation for the development of optical materials such as contact lenses. The lens thickness and shape can be controlled by zonal swelling.

4.3 Gel formulations and photo ablation

The gels were created using two different molecular weight CMCs. The amount of crosslinker (citric acid) varied from 1% to 15% to identify the amount of water absorption based on molecular weight, crosslinker and curing conditions. The gels G1 and G2 had CMC MWs of 700k Da and citric acid contents of 1% and 5% wt., respectively. Gels G3, G4, G5 and G6 were made from CMC at 250k Da molecular weight. The amount of citric acid was changed from 1%,
5%, 10% to 15% wt. Finally, gel G7 was created by the addition of 0.1% riboflavin as that of CMC in gel G5. The molar ratios of ingredients can be found in the Table 4.1. Later, these gels were dried into a film form followed by laser ablation at 90 mW and curing at 150 °C, 160 °C and 170°C for variable times. Laser ablation at 90 mW power produced films that displayed surface graininess and thus reduced film clarity. Laser ablation at lower intensities was also attempted to optimize film transparency.

It was observed that laser ablation of riboflavin sensitized film at 5 mW laser power to provide highly transparent films. There was no shape change effect seen on unsensitized films (no riboflavin) at lower laser powers. Figure 4.2 shows various gels cured at different conditions and processed under laser ablation. The higher molecular weight CMC gels were rougher on the surface and showed visible porous structures after swelling. The clarity, however, was not acceptable. On the other hand, lower molecular weight CMC showed a smoother surface and sufficient transparency. It was seen that a higher level of crosslinker and more curing time caused reduced water absorption capacity. Laser ablation leads to a reduction in film thickness (Figure 4.2a) at the ablation site. The more the ablation, the greater is thickness reduction. (The notation Lx in the Figure 4.2 suggests that there was (20 × x) scans of laser per micron thickness of the film.)

Thickness reduction is attributed to material losses due to ablation. The gels become weaker in ablated areas and absorb more water. Using the ablation pattern in Figure 4.2b, the cured gel shows curvature changes as observed in Figure 4.2c after swelling. Figure 4.2d through Figure 4.2f shows the preliminary lensing activity of specialized lens design. The films were riboflavin sensitized and treated at 3 mW laser power. Figure 4.2d is a direct image of the letters while Figure 4.2e and Figure 4.2f are through the lens shape mounted on a glass slide. The change in letter sizes
indicate the light bending at the center of the lens. The edges of lens and surrounding area show image distortion due to presence of thick and uneven water film between the glass and hydrogel. This distortion should not be mistaken for a lensing effect.

Table 4.1: Molar ratios for different gel compositions.

<table>
<thead>
<tr>
<th>CODE</th>
<th>CMC (MOL)</th>
<th>CITRIC ACID (MOL)</th>
<th>RIBOFLAVIN (MOL)</th>
<th>CMC MW. (KDA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1</td>
<td>36.803</td>
<td>-</td>
<td>700</td>
<td></td>
</tr>
<tr>
<td>G2</td>
<td>191.762</td>
<td>-</td>
<td>700</td>
<td></td>
</tr>
<tr>
<td>G3</td>
<td>13.144</td>
<td>-</td>
<td>250</td>
<td></td>
</tr>
<tr>
<td>G4</td>
<td>68.486</td>
<td>-</td>
<td>250</td>
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<tr>
<td>G5</td>
<td>144.583</td>
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<td></td>
</tr>
<tr>
<td>G6</td>
<td>229.631</td>
<td>-</td>
<td>250</td>
<td></td>
</tr>
<tr>
<td>G7</td>
<td>144.583</td>
<td>0.6643</td>
<td>250</td>
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</tbody>
</table>
To arrive at an estimate of focal length of the created lens, the object distance from the lens was measured (129 mm). The lens was placed at approximately halfway between this gap. The Equation 4.1 gives the distance of the virtual image as 89 mm. Finally, the focal length was estimated (Equation 4.2) to be 234 mm. The diopter (D) strength of this lens is thus estimated to be about 4, when the focal length (f) is measured in meters (Equation 4.3).

\[
\text{Image Distance} = \text{Object Distance} \times \frac{\text{Image Size}}{\text{Object Size}}
\]

Equation 4.1: Image distance calculation
\[ \frac{1}{Focal\ Length} = \frac{1}{Object\ Distance} + \frac{1}{Image\ Distance} \]

Equation 4.2: Focal length calculation

\[ D = \frac{1}{f} \]

Equation 4.3: Diopter calculation

Figure 4.3 shows various curing conditions and water absorption capacity of the gel films.

\[ S = \frac{W_s - W_d}{W_d} \]

Equation 4.4: Swelling ratio

The swelling was calculated according to Equation 4.4 in which S is the swelling ratio (water absorption) measured in grams of water per gram of dry gel. Ws is weight of swollen gel and Wd is weight of dry gel.
Figure 4.3: Effect of curing conditions and molecular weight on swelling behavior. a) G5 was cured for 150 °C, 160 °C and 170 °C for 2, 5, 10, 20, 30, and 40 min. b) all gels cured at 160 °C for 40 min. c) Gels G5 and G7 laser ablated with 20 layer 3D block and cured at 160 °C for 40 min. Passive exposure suggests effect of scattered light on unexposed G7 film. d) OTR values of different films.

The effect of curing temperature can be prominently observed following crosslinking. As temperature increases, the water absorption/swelling decreases due to increased crosslinking and hence loss of swellability (Figure 4.3a). Likewise, molecular weight reduction leads to a reduction in swelling (Figure 4.4). If crosslinker levels are increased, an exponential reduction in swelling is observed at the same curing conditions (Figure 4.3b). It was observed that 10% citric acid films of 250k Da CMC, cured at 160 °C for 30 to 40 min, resulted in 1.3-2.2 times more swelling and a smoother surface. Yet, a drawback of this approach was that films with lower levels of crosslinker
are delicate. Curing at a higher temperature does not provide much improvement. Very high crosslinking is detrimental and cause films to crack during water absorption. The laser ablation provides further enhancements for water absorption attributed to a weaker gel matrix. The addition of riboflavin has a higher impact on matrix weakening (Figure 4.3c) that endows the process with a very high specificity to targeted areas. Negligible change in water absorption due to passive exposure (scattered light) of nearby gel areas in riboflavin sensitized films was observed.

4.4 Oxygen transmission rates

Oxygen transmission rates (OTR), of great importance for contact lens applications, was dependent on the amount of water in the film. The higher the water content, the higher OTR. However, OTR was improved by laser ablation without much effect on swelling (Figure 4.3d). Riboflavin sensitized gels show a lower OTR than unsensitized gels, which is an effect from trapping oxygen by riboflavin molecules, that is possible when riboflavin is reduced by photo-excitation. Reduction of riboflavin leads to leucoflavin (dihydroriboflavin), which re-oxidizes in the presence of oxygen and produces lumichrome and lumiflavin.\[175\] Thus, the process of CMC hydrogels laser ablation shows potential for controlled swelling, controlled OTR, and shape control.
Figure 4.4: Swelling data for gels due to water absorption. The effect of different molecular weights of CMC, amount of crosslinker (Citric Acid) and curing conditions. Missing points in graph are due to disintegrated gels.
4.5 Improvement in film clarity

For optical applications for hydrogel films, the clarity is of most importance. The presence of surface gains and larger pores in the film can result in haze. It was observed that the hydrogel films form surface grains, which can be a result of formation of crystalline aggregates due to hydrogen bonding.[176] Higher pH of the solution can disrupt the hydrogen bonds, causing reduced grains and thus increased optical clarity. At close distances to the retina, even smaller particles can cause a higher impact on the distortion of light, resulting in optical haze. This distortion cannot be noticed from larger distances, and the film appears to be very transparent. Ammonium hydroxide can be used to raise solution pH. After dissolving CMC in the solution, the ammonia can be removed by boiling off the solution as its solubility decreases with increased temperature.[177]

To verify if this process dissolves the CMC grains completely and improve the smoothness, a 3D laser microscopy was performed. Figure 4.5 shows optical image and 3D laser scan of G5 films where the CMC was dissolved in water and in ammonium hydroxide. The number of big particles is reduced greatly after ammonium hydroxide treatment. The root mean square roughness of the films was measured 1.01 µm for CMC dissolved in DI water vs. the ammonium hydroxide assisted CMC dissolution showed roughness of 0.37 µm.
4.6 Solid State Nuclear Magnetic Resonance (SS-NMR) analysis

$^{13}$C CP-MAS NMR was performed on the samples of CMC film, G5 and G5 cured at 160 °C for 40 min (160/40). Figure 4.6 shows clear distinguishable peaks for carbonyl groups (179.2 ppm) and anomeric carbon (104.6 ppm). The peak for C6 carbon on cellulose (62.3 ppm) is slightly merged with its neighbor; however, the signals for C4 (82.2 ppm), C2, C3 and C5 carbons (75.6 ppm) cannot be resolved. Hence their individual contribution is hard to analyze. After heat curing, the carbonyl peak showed slight broadening, (4% increase) indicating ester linkages. At the same time, there was a slight reduction in anomeric carbon, indicating possible thermal degradation. Other peaks did not show considerable changes.
4.7 **Total carboxyl contents**

Total carboxyl contents of a hydrogel are the grafted carboxylic groups and ester bonds in the hydrogel. As the degree of crosslinking increases, the number of carboxyl groups on the hydrogel should increase. Figure 4.7a shows a comparison of carboxyl contents in hydrogel G5 before and after heat curing (160 °C). As the curing time changes, the carboxyl contents change. At 40 min curing time (condition 160/40), the carboxyl content on the hydrogel can be close to 1.75 mEq. of HCl/g hydrogel. At just 2 min curing (condition 160/2), the number can be near 0.25 mEq./g. While comparing different gel compositions, the carboxyl contents reduce if the initial amount of citric acid in the gel is lower (Figure 4.7b) irrespective of molecular weight of CMC.
Interestingly, the laser ablation of hydrogel showed increased carboxyl contents. This is possibly due to ablated cellulosic material, which changed the weight ratio of CMC to citric acid.

Figure 4.7: Total carboxyl contents. a) Comparison of uncured gel vs. level of curing. b) Comparison of initial citric acid contents, molecular wt. of CMC and laser treatment.

The increased carboxyl contents after laser ablation should have increased crosslinking and reduced the water absorption. However, the change in swelling behavior does not support that. This indicates more contribution towards grafting of the citric acid than towards the crosslinking.

4.8 Fourier Transform Infrared spectroscopy (FTIR) analysis

To gain information on chemical bonds in the hydrogels; CMC, G5 and G7 films were analyzed with FTIR before and after laser treatment. G5 films were also analyzed after curing at two different time intervals. Figure 4.8 shows absorption spectra for the films. The peaks between wavenumbers 3000 and 3500 cm\(^{-1}\) are from –OH stretching vibrations.\(^{[178]}\) After the curing of films at 160 °C, a peak at 2922 cm\(^{-1}\) started to resolve, which is attributed to C-H stretching vibrations. A peak around 1722 (1710-1730) cm\(^{-1}\) is due to the presence of carboxylic acid groups and ester
linkages. This peak is not visible in CMC films, which can be expected as the citric acid is not added. Figure 4.8a indicates that there is no change in bond types based on the time of curing. Figure 4.8b shows that laser ablation does not show a new type of bond formation in FTIR spectra.

Figure 4.8: FTIR spectra of CMC based hydrogel films. a) Effect of curing time on the films. b) Effect of laser ablation on the films.

4.9 X-ray Photoelectron Spectroscopy (XPS) analysis

To probe the chemistry of laser ablation, an XPS analysis of CMC, G5 and G7 films was run. The changes in carbon bonding and oxygen bonding support material degradations from ablation. In Table 4.2, the emergence of different bonds is recorded.
Table 4.2: XPS carbon (C 1s) and oxygen (O 1s) bonding percentages for various samples.

<table>
<thead>
<tr>
<th>Approximate BE (eV)</th>
<th>283.7</th>
<th>284.8</th>
<th>286.6</th>
<th>288.2</th>
<th>289.3</th>
<th>291</th>
<th>528.9</th>
<th>531.2</th>
<th>532</th>
<th>533</th>
<th>533.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon/Oxygen bond</td>
<td>C=C</td>
<td>C-C</td>
<td>C-O</td>
<td>O-C</td>
<td>O-C</td>
<td>Na-O</td>
<td>O=C</td>
<td>O=C</td>
<td>O=C</td>
<td>O=C</td>
<td>O=C</td>
</tr>
<tr>
<td>(Nitrogen in Riboflavin)</td>
<td>C-H</td>
<td>C-O</td>
<td>C-N</td>
<td>O-C</td>
<td>O-C</td>
<td>C=O</td>
<td>C=O</td>
<td>C=O</td>
<td>C=O</td>
<td>C=O</td>
<td>C=O</td>
</tr>
<tr>
<td>Code</td>
<td>C1x</td>
<td>C2x</td>
<td>C3x</td>
<td>C4x</td>
<td>C5x</td>
<td>C6x</td>
<td>O1x</td>
<td>O2x</td>
<td>O3x</td>
<td>O4x</td>
<td>O5x</td>
</tr>
<tr>
<td>CMC (250k Da) Powder</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td>Powder</td>
<td>14</td>
<td>63</td>
<td>16</td>
<td>4</td>
<td>3</td>
<td>0</td>
<td>10</td>
<td>21*</td>
<td>44*</td>
<td>25*</td>
<td>0</td>
</tr>
<tr>
<td>CMC (250k Da) Film</td>
<td>0</td>
<td>18</td>
<td>56</td>
<td>21</td>
<td>2</td>
<td>3</td>
<td>0</td>
<td>23</td>
<td>47</td>
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<td>0</td>
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<td>Citric Acid Powder</td>
<td>0</td>
<td>36</td>
<td>17</td>
<td>0</td>
<td>47</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>44</td>
<td>24</td>
<td>32</td>
</tr>
<tr>
<td>Riboflavin Powder</td>
<td>0</td>
<td>33</td>
<td>47</td>
<td>8</td>
<td>10</td>
<td>2</td>
<td>0</td>
<td>26</td>
<td>0</td>
<td>72</td>
<td>2</td>
</tr>
<tr>
<td>G5</td>
<td>0</td>
<td>32</td>
<td>45</td>
<td>16</td>
<td>5</td>
<td>2</td>
<td>0</td>
<td>16</td>
<td>19</td>
<td>48</td>
<td>16</td>
</tr>
<tr>
<td>G5 cured at 160 °C for 30 min</td>
<td>0</td>
<td>18</td>
<td>55</td>
<td>18</td>
<td>6</td>
<td>3</td>
<td>0</td>
<td>17</td>
<td>20</td>
<td>47</td>
<td>16</td>
</tr>
<tr>
<td>G5 L20</td>
<td>9</td>
<td>37</td>
<td>37</td>
<td>12</td>
<td>4</td>
<td>1</td>
<td>0</td>
<td>9</td>
<td>35</td>
<td>12</td>
<td>44</td>
</tr>
<tr>
<td>G5 L20 cured at 160 °C for 30 min</td>
<td>0</td>
<td>41</td>
<td>41</td>
<td>13</td>
<td>2</td>
<td>3</td>
<td>0</td>
<td>8*</td>
<td>34*</td>
<td>33*</td>
<td>24*</td>
</tr>
<tr>
<td>G7</td>
<td>0</td>
<td>21</td>
<td>54</td>
<td>17</td>
<td>6</td>
<td>2</td>
<td>0</td>
<td>24</td>
<td>46</td>
<td>27</td>
<td>3</td>
</tr>
<tr>
<td>G7 cured at 160 °C for 30 min</td>
<td>0</td>
<td>22</td>
<td>54</td>
<td>16</td>
<td>6</td>
<td>2</td>
<td>0</td>
<td>18</td>
<td>28</td>
<td>39</td>
<td>14</td>
</tr>
<tr>
<td>G7 L20</td>
<td>0</td>
<td>33</td>
<td>46</td>
<td>15</td>
<td>4</td>
<td>2</td>
<td>0</td>
<td>21</td>
<td>26</td>
<td>45</td>
<td>8</td>
</tr>
<tr>
<td>G7 L20 cured at 160 °C for 30 min</td>
<td>0</td>
<td>36</td>
<td>43</td>
<td>15</td>
<td>4</td>
<td>3</td>
<td>0</td>
<td>25</td>
<td>31</td>
<td>37</td>
<td>8</td>
</tr>
</tbody>
</table>

* Binding energy was lower by about 1 eV
The spectra for the respective films or materials are available in Figure 4.9 and Figure 4.10. In XPS spectra, due to overlap of binding energies, it is difficult to differentiate bonds.\cite{179-181} The peak is near 284.8 eV is assigned to C-C and C-H linkages in which citric acid shows near theoretical values for C-C linkages. Though citric acid was only 10% in hydrogels, low molecular weight contaminants in CMC show a stronger signal for C-C. The evidence of traces of low molecular weight contaminants was seen in the $^1$H-NMR spectrum of CMC (250k Da). At 1.19 ppm, a doublet of doublets was seen due to trace solvents in CMC manufacturing. The spectrum is available in Figure 4.11. The rest of the NMR spectrum for CMC was supported by the literature.\cite{182,183} These contaminants and adventitious carbon\cite{184} concentrate at the surface during film formation. C-C contributions diminish from CMC powder to CMC film due to a reduction in surface area and loss of volatile components during film formation. Heat curing of hydrogel films caused a C-C contribution to drop from 32% to 18%, indicating further loss by the change in vapor pressure due to heating. However, after laser exposure, the relative percentage increased by 5-6% compared to the G5 sample, which may mean that laser ablation contributes to the formation of new C-C or C-H bonded species. Subsequent heat curing of laser exposed samples gives further rise to these species.

C-O contributions (i.e., ether and alcohol groups) increased when the sample was simply heat cured. On the other hand, after laser ablation, the C-O link contribution was reduced by about 8%. Following heat curing, the effect was ~ 4% reduction in total. These changes can be due to the conversion of cellulosic OH groups into aldehyde or ketone groups during oxidation by hydroxyl radical action.\cite{185} Carbon contributing to O-C-O / C=O (the anomeric carbon, aldehyde and ketones) does not show considerable changes before and after curing; however, it shows a 4-5% reduction due to laser exposure. Thus, the anomeric carbon demonstrated the effects of
exposure and chain breaking during materials ablation. All samples show a 1-2.8% contribution of various species resembling carbonates whose signals are due to carbonates formed by dissolved CO₂ in water during gel/film formation.

Among these signals, a C 1s peak near 283.7 eV was observed for CMC powder, as well as for laser ablated samples that were previously seen in graphene oxide and attributed to C=C linkages. CMC powder should not have C=C bonds; hence, the signal is likely due to contamination or the presence of “loose” cellulose chains. Surface charge neutralization may vary for the chains leading to this peak that later disappeared after film formation due to negligible loose chains in the films. After laser ablation, the peak reappeared, indicating the breaking of chains or bulk detachment, which disappeared after heat curing. Thus, these loose chains must be volatizing or bonded by esterification. This peak did not appear for films containing riboflavin. Like films without riboflavin, in the films with riboflavin, laser exposure increased C-C groups, but the change was much higher (10%). C-O bond contribution after laser exposure was reduced by 8-10% (possible formation of aldehyde/ketone) with almost no change in the collective contribution of O-C-O bands (glycosidic links) and C=O (aldehyde and ketone).
Figure 4.9: C1s XPS spectra for various samples.
Figure 4.10: O1s XPS spectra of various samples.
Oxygen contribution to bonding carbon can be seen from the O 1s peaks. There were minor changes in uncured vs cured samples without laser ablation. However, after laser ablation, the relative contribution of hydroxyl and ether oxygen (C-O-R) (O4x Oxygen) decreased by more than 20%. The laser ablated sample, when heat cured, showed an increase in C-O-R contribution by 20%, for a net reduction of ~ 10%, which is from a reduction in glycosidic linkages. The change in C-O-R linkages was compensated mostly by carboxylic oxygen (O-C=O) (O3x Oxygen) and (O-C=O) (O5x Oxygen). Heat curing alone did not seem to change this oxygen considerably, but laser exposure caused a 28% increase that settled to ~ 8% after heat curing. The C=O species also decreased from laser ablation. On the contrary, the addition of riboflavin showed increased C-O-R after laser exposure while the C-O-C=O reduced by 20%, which indicates that the addition of riboflavin initiates different paths of CMC degradation: material ablation is prominent and fragmented chains are not retained. The possible regions of action could be carboxylic acid groups and carboxymethyl side chains.

Figure 4.11: CMC (250k Da) ¹H NMR (500 MHz, D₂O, δ): 1.19 (dd, CH₂).

4.10 UV-vis analysis

The XPS analysis provides us information about the dry material. The CMC is laser treated in paste like conditions. The UV-vis analysis of CMC can provide additional information about
the intermediate conditions of the gels before curing. Figure 4.12 shows UV-Vis spectra for CMC (250k Da) without and with addition of citric acid (gel G5 before curing). The laser treatment was carried out at higher solids content and then diluted for UV-vis analysis. CMC-L and G5-L are the gel samples with prolonged laser treatment.

Figure 4.12 shows that CMC gels show gradual increase in absorbance below 450 nm wavelength. The absorbance is considerably higher below 300 nm. The gel shows almost no absorbance in the visible range of the spectrum. The absorbance at laser wavelength (405 nm) is poor. The value observed was 0.007. This indicates that the laser is not directly exciting the cellulose and possibly water ionization is occurring before CMC degradation. This later can be
causing acid and hydroxyl radical species to degrade CMC. After laser exposure, the CMC shows increased absorbance below 284 nm. One of the reasons can be increased carbonyl species, which can be supported by excitation of electrons from $\pi$ to $\pi^*$ orbitals.\cite{190} This increase in carbonyl species is due to cellulose degradation. As seen in XPS spectra, the material is being lost from the cellulose backbone. It might be possible that aldehyde and carboxylic species are being generated as a result of oxidation and hydrolysis process. The addition of citric acid to the CMC results in higher absorbance below 230 nm. Further laser treatment causes increased absorbance below 240 nm, which must be an effect of multiple species with slight structural changes.

### 4.11 X-ray diffraction (XRD)

![Normalized X-ray Diffractograms](image)

Figure 4.13: XRD pattern: CMC film, G5 film without and with laser treatment and with curing at 160 °C for 30 min (160/30).

Both XPS and UV-vis data provide us good understanding of chemical changes occurring in the hydrogel. As CMC with lower DS tends to form crystalline aggregates, they can affect the optical properties and water absorbance.\cite{131,132} Figure 4.13 shows that laser treated films tend to
lose crystallinity. The crystallinity index for CMC film after laser treatment reduced from 19% to 15%. Similarly, the G5 film showed change from 20% to 16% after laser treatment. The crystallinity increases after heat curing, which is due to increased crosslinking. G5 film showed increased crystallinity after heat treatment, which was 36%. The laser treated G5 film showed crystallinity of 20% after heat curing, which is still lower than the film that was not treated with the laser. The reduction in crystallinity should increase the water absorbance of the gel, which concurs with the data observed in Figure 4.3c. The deconvolution of XRD signals is shown in Figure 4.14.
Figure 4.14: XRD deconvolutions for CMC films and G5 films before and after laser treatment and curing at 160 °C for 30 min (160/30).
4.12 Conclusion

In sum, this study describes a very compelling and unique approach to modulate several very key material properties. More specifically, CMC hydrogel properties can be controlled by incorporation of riboflavin that is then susceptible to an ensuing photoablation. Riboflavin acts as the photosensitizer to ensure that the photoablation occurs. The photoablation process increases the amorphous nature of the material giving rise to more water absorption. It was seen that riboflavin sensitized films can be treated at lower powers such as 3 mW while unsensitized films show no effect. Further research will focus on successful usage of this material and method combination for contact lens applications and drug delivery, packaging, and printing.

4.13 Experimental Section

4.13.1 Materials

The (250k Da) CMC was procured from Fisher Scientific, while the (700k Da) CMC was obtained from Sigma-Aldrich. Both varieties had a degree of substitution (0.9). Citric acid monohydrate, 1N Sodium hydroxide, and 1N HCl were purchased from Fisher Scientific. Riboflavin was obtained in dry powder form from Sigma-Aldrich.

4.13.2 Hydrogel Preparation Procedure

Citric acid was dissolved in deionized (DI) water. The weight of citric acid monohydrate was adjusted by considering the water molecules associated with it. CMC was added to it and dissolved under low shear to form a gel mixture. Riboflavin sensitized gels had a predetermined quantity of riboflavin dissolved in water followed by the addition of citric acid and CMC to the gel mix. The gels were de-aerated in a depressurizing chamber. The de-aerated gel was poured onto glass slides and kept on a laminar airflow table to cast where the air pressure was 0.5 inch of the water column. The gels were air dried for 24 hours.
The photo-degradation of the cellulosic material was achieved for these cast films. The gel films were re-wetted and exposed to the laser. Rewetting was required for photo-degradation of CMC and riboflavin\cite{175, 191} to undergo photoexcitation.

### 4.13.3 Deaeration procedure

The gels were de-aerated in a depressurizing chamber. The pressure was lowered until bubbles formed and the gel mixture overflowed from the beaker. At this stage, the vacuum pump was disconnected, and the container was sealed to prevent re-pressurization. This condition was maintained for 20-25 minutes. Finally, the vacuum was turned on for five minutes followed by re-pressurization.

### 4.13.4 Laser Ablation and Heat Curing

A Form1 3D stereolithography printer by Formlabs was used for laser exposure. The printer was controlled with the use of the software and API available on GitHub (https://github.com/Formlabs/OpenFL). The software controls laser power output, scanning rate, line spacing, and the number of laser exposures per layer of 3D printable material. It also allows changes in layer thickness based on material. The exposure patterns were designed as 3D blocks as the Form1 printer accepts the data in 3D image format. The laser exposes the available material according to the 3D mesh provided to the printer. Various laser powers were used such as 1mW, 3mW, 5mW, 10mW, 20mW, 30mW, 45mW and 90 mW. The scanning rate was kept constant at 600 mm per s. The laser spacing was 0.03 mm, and the layer thickness was 2.5 µm. The number of laser exposures per layer was based on the thickness of the dry film. 20 exposures (scans) per layer (pass) were given per 1 µm thickness of the dry film. For variation in thickness, the exposure numbers were changed in proportion. For exposures, the films were mounted on a clean resin holder tank and rewetted with a small amount of water (up to 10 times the weight of the film). The
films were occasionally rewetted to compensate for water loss due to evaporation during laser exposure. The output laser power was set to 90 mW for all material analysis. The lower laser powers were tried to see the effect on surface graininess and clarity. Multiple laser passes were provided based on the film thickness. Finally, the laser ablated films were dried at room temperature and were cured in an oven at temperatures of 150 °C, 160 °C and 170 °C for different periods of time.

4.13.5 Film formation with assistance of ammonium hydroxide

A set of 2% solution of CMC (250k Da) was prepared with and without ammonium hydroxide. The first solution was created without ammonium hydroxide, and the pH was noted as 7.12. The second solution was created by raising its pH to 12 by the addition of ammonium hydroxide. This solution was boiled, and evaporated water was replenished by the addition of DI water. At regular intervals, the solution was brought to room temperature, and its pH was checked. Finally, the process was stopped when the pH reached 7.15

4.13.6 Characterization

Film appearance was checked by visual inspection to determine if it was partly dissolved and broken or maintained its integrity. Visual inspection also helps in finding the surface texture and clarity of the film. The swelling behavior of the hydrogels was determined by the amount of water absorbed per gram of the dry gel. The cured gels were immersed in a large quantity of De-Ionized (DI) water for ~ 24 hours. Afterwards, the gels were removed from water and kept on bloating paper to remove surface water. The weight of the swollen gels was measured within a minute. Additionally, a gel composition with better handleability and film clarity was selected, as a potential candidate for pre-lens material. It was swollen in physiological saline (0.9% NaCl aqueous) solution[192] and its swelling ratio was determined.
The surface grains and roughness of the chosen films were performed using the 3D Laser Scanning Microscope ‘VK-X1000’ from Keyence. The images at 5x magnification were captured, and their roughness was measured.

The oxygen transmission rate was measured using Mocon’s Optech-O₂ Platinum, which gauges fluorescence of the sensor (adhesive type sensor provided by Mocon). When the OTR dropped and became stable and started to increase gradually, the test was stopped. The minimum value of OTR was considered the final value. OTR values were measured in cc/day at 23 °C at 50% RH, which were normalized for film thickness. The OpTech-O2 Film Permeation Cell was used to test hydrogel films. Because the operational surface area of the cell is 100 cm² and the film samples were small and delicate, an aluminum film mask was created with a 1 cm² window to hold and test hydrogel film samples. The laser exposed samples were smaller in size; hence, the mask area was reduced to 0.25 cm². To measure OTR, the film with the mask was mounted on the cell, and the cell was flushed with N₂ gas to create a gradient in O₂ levels. This caused atmospheric O₂ to dissolve in the films and transmit inside the cell. Every 15 seconds, a new measurement was taken, and data were collected.

¹³C Solid-state NMR experiments were performed on a Bruker Avance II spectrometer operating at 500 MHz 1H frequency equipped with 3.2 mm Bruker MAS E-free(TM) probe. The 90 degree pulse was calibrated at 3.15 us, and a 2000 ms cross-polarization contact pulse was used for RAMP-CP. The MAS spinning speed was 7 kHz. The FID signal has been acquired for 10 ms at ambient temperature, and 8192 scans were co-added per spectrum. NMR data were acquired and processed using Bruker Topspin 2.0 software. Samples were prepared by cutting small disks of the film and stacking them in the rotor.
The total carboxyl content of the films was obtained by first washing the crosslinked films in 1:1 DI water and an isopropyl alcohol mixture for 2 h. These films were dried and weighed. The films (20-50 mg) were then dissolved in 10 ml of 0.1 N sodium hydroxide (NaOH) solution. This solution was then titrated with 0.1 N hydrochloric acid (HCl). Laser ablated samples were very small, so they were dissolved in 1 ml of 0.1 N NaOH and titrated with 0.01 N HCl. Phenolphthalein was used as a titration indicator. The carboxyl content was calculated using Equation 4.5\[^{178}\]

\[
\text{Carboxyl content} = (V_r - V_s) \times \frac{N}{W_s}
\]

Equation 4.5: Total carboxyl contents

For Equation 4.5, the \(V_r\) is volume of HCl required to titrate the used volume of NaOH without the gel sample. \(V_s\) is volume of HCl required to titrate the gel sample. \(N\) is normality of HCl, and the \(W_s\) is the weight of the gel sample in grams.

The FTIR data were obtained using Bruker’s OPUS FTIR spectrometer with ATR. The data were obtained from wavenumber 400 till 4000 cm\(^{-1}\) with an interval of 2 cm\(^{-1}\) and 32 scans.

To determine the purity of the CMC sample, proton NMR spectra were obtained using a Bruker 500 MHz NMR spectrometer. The solvent used was Deuterated Oxide (D\(_2\)O). XPS analyses were done using a SPECS System with PHOIBOS 150 analyzer, <1eV resolution. The X-ray source was 10-14 kV Mg.

UV-Vis spectrum of the gels was acquired for 200-500 nm range with a 1 nm incremental step. To prepare the sample, DI water and dry ingredients (CMC, citric acid) were dissolved in water. The air bubbles trapped in the sample were removed under vacuum degassing, with multiple cycles of de-pressurization and re-pressurization. Finally, the UV-Vis absorbance spectrum was obtained for samples. The same samples were laser ablated for a prolonged period with 90mW laser power. The treated samples were again analyzed for the UV-Vis absorbance spectrum.
The X-ray diffraction data of the pure CMC film and the laser ablated CMC film were obtained using a Rigaku SmartLab diffractometer. The angle was changed to 0.05° per step. The diffraction data obtained for each sample were deconvoluted to obtain the area for amorphous peaks and crystalline peaks.
5. STUDY FOR POSSIBLE COMMERCIALIZATION OF CMC BASED CONTACT LENSES

5.1 Abstract

Contact lenses are vision correction medical instruments, which are being used by a number of people. There are a variety of contact lens types produced by different manufacturers. A short market survey was conducted by contacting different stakeholders in the contact lens market to understand the stability of the lens materials. This study will help in identifying preliminary focus areas if one wants to utilize laser ablated hydrogels for manufacturing contact lenses.

5.2 Introduction

Spatially resolved laser ablated CMC hydrogel films have shown the capability for further development of the contact lenses. Potential product development from laboratory technology needs to adapt to market needs. Peoples’ needs and their expectations from new technology can be different than those visualized by the inventors and developers of the technology. For better understanding of the current market needs for the contact lenses, we conducted an interview-based study with the support of the National Science Foundation’s iCorp program. 30 interviews were conducted with users, doctors, opticians and manufacturers in the contact lens sector.

5.3 Contact lens requirements and people’s experience on usage

Contact lenses are small medical aids used to correct the refractive defects of the eyes of a patient. These lenses are tiny and made to fit on cornea of an eye externally. The most important thing in this context is to have clear vision with maximum comfort for an eye. Various vision defects such as myopia, hypermetropia, astigmatism and presbyopia can be addressed using
contact lenses. Usage of contact lenses over prescription glasses is often preferred by various patients and doctors for their inherent advantages such as clarity of vision, edge to edge (full viewing range) uniformity of vision, and aesthetics.

There are various types of lenses in the market. The early lenses were made of PMMA (polymethyl methacrylate) but soon they were replaced by other materials due to the lack of oxygen permeability. Later rigid gas permeable lenses were introduced and finally the soft lenses came to the market. The rigid gas permeable (RGP) lenses are made from silicon-based polymers. The soft lenses are made from silicone and fluorosilicone based hydrogels. The monofocal lenses, bifocal and progressive lenses, toric lenses (for astigmatism) and scleral lenses are types of lenses required for different eye conditions. Generally, progressive lenses are required at old age when people face the problem known as presbyopia.

A patient’s primary concern over the usage of contact lenses is the comfort. We conducted various interviews of contact lens users to understand their experiences with the contact lenses. The majority mentioned eye comfort. The lens must fit well on the cornea and should not cause abrasion over the eyelids. Before adopting any type of contact lens or eyeglasses, patients visit their doctors to get eye examinations. The doctor then analyzes each individual case and suggests the suitable options for contact lenses. Generally, a pair of sample lenses is provided to the patient to try and see if there is any discomfort. In our interview, a person had mentioned having tried RGP lenses, but just within 5 minutes of usage, felt discomfort and hence moved to soft contact lenses. As the lens hardness affects comfort, doctors prescribe soft lenses for the majority of cases. The higher water content in soft lenses (35-65%) causes less abrasion on the cornea and eyelids. An ophthalmologist mentioned that, in certain cases such as orthokeratology, small children are prescribed rigid lenses to wear at night. This reshapes their cornea and corrects the astigmatism.
The treatment can also be given for myopia control. Another advantage of rigid lenses is the uniformity of the focal length of lens as one moves away from the center of lens towards the edge of the lens. In soft lenses, this uniformity is hard to achieve. The life of RGP lenses is much longer and can extend to a year or two. In scleral lens technology, which avoids direct contact with cornea, the RGP material is used. Scleral lenses hold tears over the cornea and avoid contact with lenses.

Another major factor that governs contact lens usage is the dry eye problem. The contact lens is a foreign body in an eye. In some people, this disrupts tear film formation on the cornea. As a result, they observe dryness in the eye. The extended usage of contact lenses can dry out eyes at the end of the day and cause the lenses to stick to the eyelids. People need to use eye wetting drops in such cases. Lens cleaning is also required every day. However, in extreme cases, the dryness of eyes is too disconcerting, and few people move away from usage of contact lenses. They prefer prescription glasses for daily wear. In our interview, we came to know a person who moved away from contacts due to weather conditions. The dryness of air worsens the dry eye issue. In such cases, the daily disposable lenses are preferred for certain special occasions and prescription glasses are used on a daily basis.

Like the dryness of eyes, the lenses can cause a lack of enough oxygen to the eyes. The invention of RGP lenses and soft lenses have solved this to a major extent. However, the different conditions of eyes, costs involved in manufacturing, and material limitations can lead to choices of different contact lenses by users. If the lens is not a good permeant of oxygen, the time period for daily usage of lenses is reduced. Lack of oxygen causes discomfort to the eyes. Some people who use colored lenses can face reduced oxygen due to presence of colored pigments. Ophthalmologists mentioned that oxygen permeation (Dk/t) values should be more than 24 for daily usage.193, 194 However, if they are below 34, the patient is not supposed to sleep with the
lenses. Swelling of eyes occurs at such low oxygen permeation. Above 34 Dk/t but below 125 Dk/t value, a person can sleep with contact lenses and can observer mild swelling of eyes. Above 125 Dk/t value of oxygen permeation, the lenses are good to wear overnight while sleeping. Our interviewee mentioned that they use the lenses for 8-12 hours a day, and few interviewees use them up to 16-18 hours/day. Thus, the oxygen transmission becomes very important for such cases.

In our interviews with different people, the points raised were the fitting of lenses, price of lenses, and the duration of usage. The edge to edge vision clarity was also important for people with a high number of diopters. If eyeglasses are used by people with a higher number of diopters for lenses, the distance between eyes and glasses causes a great image distortion at the edges of the glasses. Contact lenses solves this issue. People are also concerned with the storage and packaging of the lenses. Each lens comes with a separate package and if one wants to use a daily disposable lens, then the storage of lenses becomes a space problem. Instead, a monthly, half yearly or yearly disposable lens is preferred. The requirement of cleaning lenses does not seem to affect choices for long lasting lenses. Additionally, the daily disposable lenses can be very expensive such as $1/day vs about $5-10/month for monthly wear lenses. However, when the toric lenses are used, they are custom made to correct astigmatisms. They can cost about $300-400 for a year’s supply of monthly disposable lenses. Also, the time between ordering and receiving the custom lenses can be up to two weeks. A manufacturer mentioned that the lens material formula does not change drastically for its lifespan unless it is a specialty lens. The companies prefer selling the maximum number of pieces to increase the profit. On the other hand, doctors will prefer the daily disposable lenses from the perspective of hygiene and lower eye related problems. Thus, there will be much greater scope for daily disposable lenses if the prices can be reduced.
We asked about adaptation of new methods and materials for lenses and the advantage of biodegradable lenses for manufacturers and users. The primary concern of the manufacturers is the yield of the process where they can use less material for the production and if there is lower waste in the processing. Biodegradability can help sell products and help nature provided that the material is handleable or easily formable on the equipment. A manufacturer mentioned that mass production of lenses is done with molding technology where thousands of lenses are produced per minute.

The specialty lenses need specific curvature and are produced individually on the lathe machine, where the concave side is first cut from a block of material and then the piece is flipped to cut the convex side of the lens. If the material is not handleable, it cannot give good yields. If a new material or process is introduced, the mass manufacturer should get at least 3-4% price reduction per unit lens. In that sense, when millions of lenses are produced per year, the manufacturer will obtain a considerable advantage. Biodegradability will certainly be a good point from environmental and disposal perspectives. People sometimes tend to flush the used lenses which affect the sewer system. If a biodegradable material is introduced, this problem can be eliminated. However, the biggest concern is the disposal of the packaging material.

During our interviews, we learned that there is a possible market segment for animal eye care. At veterinary hospitals, ophthalmologists use the contact lenses as bandages for animal eye care. The ulcers caused in animal eyes are treated and then contact lenses are applied over the cornea to prevent abrasion with eyelids. Usually a week’s time is required for the healing process. The animal specific lenses are very expensive and can cost about $25/piece. There is potential for growth in this market segment if the prices can be reduced. Ophthalmologists use donated human contact lenses for avoiding costs. We think, as there is no tuning of refraction for the animal’s eye,
these lenses must be causing great discomfort. Ideally, the lenses should be made for the use with specific animal eye conditions.

We also learned that people can have different allergies to eyes and when the eyes are affected, they cannot tolerate the contact lenses. Some people can still keep using the lenses just to avoid the usage of glasses. Few people do not have enough time to order and wait for new pairs of glasses in case of eye infections. Therefore, advanced research on lenses is required. According to one of the manufacturers, innovation in sensor developments for disease detection can be added to the lenses. Electronic chips or chemical indicators can be incorporated for a new generation of lenses.

In conclusion, we learned that the contact lens market is an important segment of personal health. People tend to care more about the comfort and extended wear of the lenses. Higher oxygen transmission is required for new materials. Animal care can be a good market segment for lens fracturing. Lens disposal is one of the less identified issues by the stake holders of the lens industry, but the packaging reduction and disposal are identified issues. If we can develop new biodegradable lenses that can hold drugs for eye care and chemical or electronic sensors for disease detection, then it will be novel for marketing. Even without these valued additions, if the new material and technology can result in 3-4% price reduction, the manufacturers can consider adopting it. Few believe that our current technology can lower the manufacturing costs and reduce packaging.

5.4 Protein build study requirements

Contact lenses are in direct contact with corneas. The tears in eyes contain multiple antifungal enzymes and lubricating ingredients. These enzymes are proteins, and they get attached to the contact lenses causing blurry vision and eye irritation. The most prominent enzyme is the
lysozyme that protects eyes from bacterial infection. It is a common practice to study the buildup of lysozyme on contact lenses after prolonged period of usage. The commercially available contact lenses can show ~0 to 125 µg/cm² adsorption of lysozyme after 24 h. If the CMC based hydrogels show the protein buildup similar to the commercial products, the chances of market success increase.

5.5 Possibility of saving packaging material and waste reduction

In Chapter 4, it was seen that the spatially photo ablated hydrogels do not change shape unless they are hydrated. Up until this point, they are in a flat film form. Such films can be stacked in a bunch and packed in thin paper-based containers. Before the time of usage, one lens can be removed and hydrated to gain its shape. Compared to the current market available lenses, this process is space saving and promotes renewable and bio-degradable packaging.

The current market available contact lenses are pre-hydrated and are packed in individual plastic packs along with aqueous solutions to keep the lenses hydrated. Such small plastic packs take up more space, and they are mostly ended up in landfills, where they do not bio-degrade. If multiple dry lenses are packed in a container, the need for waterproof plastic containers will vanish, and the cost of packaging will be reduced.
6. CMC BASED HYDROGEL FOR MAKING ACTIVE SUBSTRATES AND LOCATION FIXING FOR TWO INKS IN PRINTED ELECTRONICS

6.1 Abstract

CMC based hydrogels are capable of photo-degradation. The degradation patterns created by UV light on the surface of the hydrogel can result in stronger and weaker surfaces. The weaker surfaces should be able to absorb more water and succumb to sudden changes in internal stress due to swelling and shrinkage (during drying). This property can be used to create an actively participating surface for generating electronic circuit patterns. In addition to the stress developed activity in hydrogels, utilization of UV active hydrophobic agents can be employed to reduce the hydrophilicity of the CMC films at selective regions. Both these properties can then be utilized for active substrates with self-distribution of ink and location fixing for two separate inks.

6.2 Introduction

Commercially available printing processes have their own advantages and disadvantages for printed electronic processes. The analog printing methods such as gravure, flexo and screen-printing give high quality and low-cost replication of circuit design. However, they lack in accepting on-demand changes to print designs. Inkjet printers with tradeoffs for speed can address this limitation. The hydrogel films, if laminated to a sturdy substrate, can provide the assistive ink patterning and distribution based on the zonal changes in water absorbance and bonding strengths of bulk material.

Here it is shown how UV assisted photo patterning of pre-crosslinked CMC hydrogel can be used to create a weak and extra absorbent zone or a relatively hydrophobic zone (if pre-treated
with pyridine). Previous studies of UV excited pyridine in water have shown that pyridine undergoes a ring opening reaction, giving rise to amine with an aldehyde end.\textsuperscript{[196]} The new chemical can react with cellulose and get fixated on the surface, resulting in a hydrophobic nature. Details of this mechanism are discussed later. However, using this mechanism can provide a means of treating the hydrogel only in certain regions, which are treated with UV light. If some areas are masked or protected from UV, there will not be changes in pyridine. The unmodified pyridine can then be removed from the surface by washing or vacuum evaporation, thus preventing further unwanted reactions.

6.3 CMC gel preparation and UV patterning

The swelling capacities of different hydrogel formulations (chapter 4) show that CMC with molecular weight 700k Da has the ability to provide a swelling ratio above 300%. It does that by forming a non-dissolving matrix at 1% citric acid levels with a lower heat treatment time of 2 min. It thus becomes a better choice than the CMC with molecular weight of 250k Da. A film of 150-170 µm was casted in a glass tray using gel G1 at 2% solids. The mixing and de-aeration was carried out using the procedure defined in chapter 4. The obtained gel film was cut into pieces for further experiments.

To achieve faster output for UV photolithography, a flood UV system was used with wider frequency spectrum and much higher power output. The UV system was a conveyor-based system, and the lowest speed of the belt resulted in a UV energy output of 0.288 J/mm\textsuperscript{2}. The UV absorbance for CMC is weak (Figure 4.12) in a 400 nm band but stronger in a 250 nm band. Thus, the flood UV system was able to provide similar or enhanced degradation with a reduced amount of time. In comparison, the time was reduced from several hours to a few minutes. It should be noted that with 90 mW laser power (405 nm wavelength) and chosen settings, the energy output for a Form
1 printer was 5 mJ/mm². Of course, the tradeoff for using a flood UV system is the inability to achieve fine patterns possible through a laser system. It also requires using an opaque mask for the photolithography process. The opaque mask (shadow mask) was created by aluminum foil by cutting out patterns on it. This mask was brought in contact with the gel to minimize the diffraction effects at the edges of the opening.

It was, thus, necessary to have a gel surface strong enough to resist sticking to the mask and resist its tearing off during the mask removal process. As the CMC chosen was of higher molecular weight (700k Da), gels have better surface strength than the lower molecular weight CMC. In order to improve the strength, these gel films were cured for 2 min and 5 min at 160 °C. The cured films were soaked in water before masking and UV irradiation.

It was observed that the UV treated films show degradation of cellulose and negligible degradation of citric acid. Thus, when carboxyl contents were tested, the degraded film showed increased carboxyl contents as shown in Figure 6.1. The curing retains some of the citric acid as crosslinks, while UV degradation causes the relative amount to increase due to ablation of CMC fragments.
Creating a relatively hydrophobic zone in the hydrogel through selective addition of hydrophobic chains is possible via UV activated pyridine hydration reaction. Pyridine is reported to be a UV sensitive molecule that can absorb UV light. In this process, it isomerizes to its Dewar forms\textsuperscript{[196, 197]} (Figure 6.2). The UV wavelength responsible for Dewar 1 form is identified in a previous study as 253.7 nm. Thus, the use of Form 1 printer is not possible for pyridine excitation. These Dewar forms get associated with the water molecules if present in their vicinity. It is shown that the Dewar 1 form can get hydrated with water followed by a ring opening, resulting in the aldehyde molecule, 5-amino-2,4-pentadienal (Figure 6.3). This aldehyde molecule can combine with nearby cellulose in various ways as shown in the Figure 6.4. The resulting structure can be highly crosslinked with an improved hydrophobic surface due to two factors: the first is the conversion of hydroxyl groups to ether linkages and the second, the presence of the unsaturated bonds and amine group, which are relatively less polar than the carboxylic acid groups and hydroxyl groups on the CMC.
Pre-hydrated hydrogel films were coated with pyridine. The pre-swollen state of film allows its pores to be open so that the pyridine can penetrate. This film was then blotted to dry the surface followed by a shadow mask. Masked film was UV irradiated to see yellowing of the irradiated areas. With multiple passes through the UV system, the reaction progressed by giving
visual indication of yellow saturation (Figure 6.5). After inputting UV energy of 1.44 J/mm², the process was stopped, and the film was dried for further analysis.

Figure 6.5: Pre-hydrated hydrogels soaked with pyridine. After UV treatment through an aluminum mask, the films turned yellow where exposed to UV. The films also showed photobleaching and partial solvent loss due to heat of the UV lamp.

### 6.4.1 NMR Analysis of UV treated Pyridine

To determine the chemical change in Pyridine after UV treatment, ¹H NMR analysis was performed with proton NMR. The solvent was D₂O, to allow a hydration reaction if the pyridine went through a Dewar form. The NMR spectra of the samples show three proton signals with multiplicities. Figure 6.6 shows the proton NMR spectra for samples with and without UV treatment. Table 6.1 has a list of signal shifts for carbons and protons. Considering the signal of 2,2,3,3-d(4)-3-(Trimethylsilyl)propionic acid sodium salt as the reference, the pyridine signals were found to be matching with the literature.¹⁹⁸ The signal near 8.57 ppm is attributed to hydrogen at the second position in the pyridine. The second set of peaks is near 7.78 ppm and is from hydrogen at carbon in fourth place. The final set of peaks is around 7.34 ppm and is from hydrogen at the third carbon. After UV treatment, some of the pyridine is expected to get converted to 5-amino-2,4-pentadienal, where nitrogen is expected to be attached to deuterium in D₂O. The quantum yield of UV reaction was reported to be 0.06, hence the signal strength for new products
was expected to be very low.\textsuperscript{[196]} With high magnification of the NMR spectra, the UV treated sample showed 4 additional peaks. A doublet at 9.06 ppm was attributed to the aldehyde at carbon 1 in the expected new compound. A triplet was detected at 7.27 ppm, which was partly overlapped by the strong signal from unreacted pyridine. It is possible to have another hidden peak. This signal can be from hydrogen at carbon 3 of a new compound. A doublet of doublets was detected at 5.85 ppm and the signals were likely to be from hydrogen at carbon 2. Finally, a triplet at 5.76 ppm could have been due to the proton at carbon 4. A fifth signal for proton at carbon 5 was not detected and it could have been hidden behind the residual peak of water centered at 5.45 ppm.

![Figure 6.6: 1H NMR of a) Pyridine (500 MHz, D\textsubscript{2}O, \(\delta\)): 8.57 (m, CH(2)), 7.78 (m, CH(4)), 7.34 (m, CH(3)). b) UV treated Pyridine for detecting traces of 5-amino-2,4-pentadienal (500 MHz, D\textsubscript{2}O, \(\delta\)): 9.07(d, CHO(1)), 7.27 (t, CH(3)), 5.85 (dd, CH(2)), 5.76 (t, CH(4)).](image)

Additionally, Heteronuclear Single Quantum Coherence Spectroscopy (HSQC) was used to find the corresponding carbon shifts. The signals were weak and hard to detect. Four signals were seen for carbons at position 1, 2, 3 and 4 as 194.4, 117.61, 163.38 and 102.39 ppm respectively.
Table 6.1: NMR $^{13}$C and $^1$H shifts, for pyridine and 5-amino-2,4-pentadienal in D$_2$O.

<table>
<thead>
<tr>
<th>CHEMICAL GROUP</th>
<th>CHEMICAL GROUP</th>
<th>$^1$H SHIFT</th>
<th>$^{13}$C SHIFT</th>
<th>COMMENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>PYRIDINE</td>
<td>CH(2)</td>
<td>8.57</td>
<td>149.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH(3)</td>
<td>7.34</td>
<td>125.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH(4)</td>
<td>7.78</td>
<td>138.3</td>
<td></td>
</tr>
<tr>
<td>5-AMINO-2,4-</td>
<td>CH(1)</td>
<td>9.07</td>
<td>194.4</td>
<td>Aldehyde</td>
</tr>
<tr>
<td>PENTADIENAL</td>
<td>CH(2)</td>
<td>5.85</td>
<td>117.61</td>
<td>C=C</td>
</tr>
<tr>
<td></td>
<td>CH(3)</td>
<td>7.27</td>
<td>163.38</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH(4)</td>
<td>5.76</td>
<td>102.39</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH(5)</td>
<td>-</td>
<td>-</td>
<td>Possibly hidden behind Pyridine and water signals</td>
</tr>
<tr>
<td></td>
<td>ND$_2$</td>
<td>-</td>
<td>-</td>
<td>Deuterated (no signal)</td>
</tr>
</tbody>
</table>

6.4.2 UV-vis analysis of Pyridine in water

Samples were analyzed with UV-vis absorption technique. The spectra in Figure 6.7 show that before UV treatment, the peak absorbance is at 256 nm. However, after UV treatment a new
peak is seen at 365 nm. This is possible with the presence of a conjugated double bond system formed through a pyridine ring opening.

![UV-vis absorption spectra](image)

Figure 6.7: UV-vis absorption spectra a) 500 ppm wt. Pyridine aq. b) 500 ppm wt. Pyridine aq. with UV treatment (5-amino-2,4-pentadienal).

### 6.4.3 Time of flight-Secondary ion mass spectroscopy (TOF-SIMS) analysis

TOF-SIMS can provide information about the presence of nitrogen on the surface. The relative densities of nitrogen containing ions can show the enrichment of the surface with 5-amino-2,4-pentadienal, which should be grafted and/or crosslinked with the cellulose as per the schema in Figure 6.4. The comparison of the negative ion intensities (normalized) in Figure 6.8 shows the increased levels of CN\(^{-}\), CNO\(^{-}\) and CH\(_{2}\)NO\(^{-}\) ions in the UV treated sample.

Figure 6.9 shows visual representation of the UV treated and masked samples of CMC films treated with pyridine. The presence of higher amounts of nitrogen on UV treated sample confirms that the 5-amino-2,4-pentadienal is remaining.
Figure 6.8: TOF SIMS, negative ion spectra for UV protected (masked)-pyridine treated CMC film and UV exposed-pyridine treated CMC film.
Figure 6.9: TOF SIMS, visual map of different negative ions. a) Image of a sample: the light yellow region is the UV exposed pyridine treated part of the CMC film, while the white region is UV protected. b) CN\textsuperscript{-} ion map showing high density in UV exposed region. c) CNO\textsuperscript{-} ion map showing high density in the UV exposed region. d) C\textsubscript{3}H\textsubscript{3}O\textsubscript{2}\textsuperscript{-} ion map showing high density in the UV protected region (cellulose exposed to air). MC: Maximum count per pixel. TC: Total count in image.

### 6.4.4 X-ray Photoelectron Spectroscopy (XPS) Analysis

The film treated with photo-hydrated pyridine was dried and used for XPS analysis. The drying process helps removing unreacted pyridine. Remaining traces of these small molecules should be removed in the XPS chamber during vacuuming process. Table 6.2 shows relative contributions of carbon and oxygen in different bond formations, while Figure 6.10 shows deconvoluted XPS spectra. Interestingly, the XPS analysis did not find any traces of nitrogen in
the films. This is only possible if the nitrogen levels are below the detection levels of XPS. Atomic detection levels of XPS are 0.1 atomic %, while the TOF-SIMS can be sensitive by 1-2 orders of magnitude. This suggests a miniscule quantity of 5-amino-2,4-pentadienal present in the matrix of the film. This is in concurrence with the literature reference of low quantum yields (0.06) from pyridine.

Table 6.2: XPS carbon (C 1s) and oxygen (O 1s) bonding percentages for samples processed through pyridine followed by UV treatment through mask.

<table>
<thead>
<tr>
<th>Approximate BE (eV)</th>
<th>283.2</th>
<th>284.9</th>
<th>286.4</th>
<th>288</th>
<th>289.4</th>
<th>290.9</th>
<th>530.9</th>
<th>531.7</th>
<th>532.8</th>
<th>533.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon/Oxygen bond</td>
<td>C=C</td>
<td>C-C /</td>
<td>C-O</td>
<td>O-C-O</td>
<td>O-C=O</td>
<td>O-C=O</td>
<td>O=CO=O</td>
<td>O=C</td>
<td>O-C=O</td>
<td>O=C</td>
</tr>
<tr>
<td>Code</td>
<td>C1_x</td>
<td>C2_x</td>
<td>C3_x</td>
<td>C4_x</td>
<td>C5_x</td>
<td>C6_x</td>
<td>O1_x</td>
<td>O2_x</td>
<td>O3_x</td>
<td>O4_x</td>
</tr>
<tr>
<td>Masked region  (No UV)</td>
<td>1</td>
<td>45</td>
<td>35</td>
<td>14</td>
<td>3</td>
<td>2</td>
<td>10</td>
<td>30</td>
<td>50</td>
<td>10</td>
</tr>
<tr>
<td>Unmasked (UV treated) region</td>
<td>1</td>
<td>50</td>
<td>32</td>
<td>12</td>
<td>2</td>
<td>2</td>
<td>15</td>
<td>29</td>
<td>39</td>
<td>17</td>
</tr>
</tbody>
</table>
From the Table 6.2, C-C/C-H (carbon C2\textsubscript{x}) bonding increased by 5% after UV treatment. This can be possible due to a grafted compound on the cellulose. There is also a possibility of adventitious carbon, and hence grafting confirmation needs additional confirmation. The increase in O1\textsubscript{x} signal and no change in O2\textsubscript{x} signal can be considered as an addition of carbonyl groups in the system. If the system did not have pyridine, then the O=C (oxygen O1\textsubscript{x}) signal should have been reduced after UV treatment as seen in Table 4.2 (oxygen O2\textsubscript{x}).
6.4.5 Water Contact Angle and Surface Energy

A good way to identify hydrophobicity of the surface is by checking its interaction with water. The hydrogel by its nature is hydrophilic and absorbs water. However, the surface of the film can resist water absorption if the hydrophobicity is increased. Films without any treatment with pyridine were considered control. After applying the pyridine, a sample was dried without UV treatment and another sample was UV-treated before drying. Figure 6.11 shows water contact angle data for the first 4 seconds with the film samples. UV treatment reduces hydrophilicity of the surface.

![Figure 6.11: Water contact angle](image)

The reduction in surface energy can be calculated with the Owens Wendt Method, where polar and non-polar liquids are used to find their contact angles with the chosen surface. Using the Equation 6.1 the surface energy of the substrate can be determined.

\[(1 + \cos \theta) \gamma_{LV} = 2\sqrt{\gamma_{SD}\gamma_{LD}} + 2\sqrt{\gamma_{SP}\gamma_{LP}}\]

Equation 6.1: Owens Wendt Equation for Contact Angle and Surface Energy relation.
Where, $\theta$ is the contact angle, $\gamma_{LV}$ is the surface tension of the liquid, $\gamma_{SD}$ is the dispersive component of the surface energy of the solid, $\gamma_{LD}$ is the dispersive component of the surface tension of the liquid, $\gamma_{SP}$ is the polar component of the surface energy of the solid, $\gamma_{LP}$ is polar component of the surface tension of the liquid.

Using DI water as a polar liquid and Di-iodomethane as a non-polar liquid, the surface energy of the hydrogel surfaces was determined. The polar component of surface tension for water is 51 dynes/cm and 0 dynes/cm for di-iodomethane. The dispersive component of the surface tension for water is taken as 21.8 dynes/cm and 50.8 dynes/cm for di-iodomethane.

Figure 6.12 shows graphs for the contact angle with di-iodomethane and calculated surface energy of the treated substrates.

![Graph a) Graph for di-iodomethane contact angle with control film (G1 – cured for 2 min at 160 °C) and with the films treated with pyridine (without and with UV treatment) b) Graph for calculated surface energy for the same films.

It is seen that the surface energy of the pyridine-treated and UV exposed surface is reduced by almost 30 ergs/cm$^2$. This change is seen in the polar component of the surface, causing it to be negligible as compared to the dispersive component. This information can be used to determine the surface tension of the inks while printing or coating. It is seen that the backside of the film,
which is in contact with glass during the casting process showed higher polar component. The reason could be the surface roughness induced trapping of the 5-amino-2,4-pentadienal on the surface of the hydrogel.

6.4.6 Surface Roughness

Understanding the surface roughness is thus important for the dried hydrogel films. The Table 6.3 shows a comparison of the hydrogel film surfaces before and after UV treatment for pyridine.
Table 6.3: Surface roughness of the G1 films before and after crosslinking with 5-amino-2,4-pentadienal.

<table>
<thead>
<tr>
<th>Film surface</th>
<th>Root mean square Roughness (µm)</th>
<th>Surface texture of the samples (magnification 10x)</th>
<th>Optical+Laser image</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1 top surface</td>
<td>1.98</td>
<td></td>
<td></td>
</tr>
<tr>
<td>G1 bottom surface</td>
<td>1.89</td>
<td></td>
<td></td>
</tr>
<tr>
<td>G1 top surface with 5-amino-2,4-pentadienal</td>
<td>2.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>G1 bottom surface with 5-amino-2,4-pentadienal</td>
<td>2.04</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
6.4.7 Water absorption

The film does not show considerable surface changes for the first 10 s wetting, except minor swelling. After that, the film starts to show wrinkling because of swelling. In Figure 6.13a to Figure 6.13d the film was directly mounted on the glass slide and treated to form 5-amino-2,4-pentadienal on the surface.

Figure 6.13: Surface wrinkle formation due to swelling over time. a) A wet film treated with UV to form 5-amino-2,4-pentadienal crosslinking, b) after drying, c) 10 s wetting, & d) 30 s wetting.

Therefore, it can be considered that a brief time (within few seconds) of aqueous contact should not cause considerable absorption in the film. After placing a drop of DI water (~ 8.3 ± 0.1
× 10⁻³ g) on the hydrogel surface for 2 s, 5 s and 10 s the water absorption on the crosslinked surface was about less than half of the uncrosslinked surface (Figure 6.14).

![Graph showing water absorption](image)

Figure 6.14: Amount of water absorbed by the hydrogel surface with and without 5-amino-2,4-pentadienal crosslinking.

### 6.5 Conductive pattern formation through utilization of photo-ablation and gel weakening

Simple photo-degradation of the hydrogel resulted in a weaker matrix. When the film was flooded with dilute ink of PEDOT:PSS (poly(3,4-ethylenedioxythiophene) polystyrene sulfonate), the mismatch in zonal swelling rates caused the ink polymer to be aligned with unexposed (no UV treatment) areas. Over a short period of time, the ink pattern became visible. Figure 6.15 shows the schematics of the process. After hydration, one can add an intermediate step of soaking in pyridine. This step can add hydrophobic properties to the photolithographic pattern.
After we flooded the sample with aqueous ink, time was needed for ink polymers to distribute on the surface. Figure 6.16 shows timely progress of the ink segregation.

Figure 6.16: Aluminum mask and timely progress of liquid ink patterning. a) Aluminum mask. Hydrogel surface flooded with 0.125% PEDOT:PSS ink b) after 10 s c) after 40 s d) after 60 s e) 75 s after flooding f) after 90 s g) after 105 s. h) Conductive traces after drying. White spaces are UV exposed areas, separated during fast drying. Inked area shrinks to form denser traces.

6.5.1 Effect of ink solids on the pattern formation

The PEDOT:PSS ink is a polymeric complex and thus susceptible to effects such as polymeric chain entanglement and film formation. This property is good for a uniform film formation and higher conductivity, and it is effective for the conventional printing process where the ink and substrate are not contributing to the ink distribution process. For the photo-ablated hydrogel self-distribution process, it is most important the polymer chains have lower entanglement before final pattern formation. Three concentrations, namely 1%, 0.5% and 0.125%,
of the PEDOT:PSS ink were chosen to see the effects on the pattern formation. As shown in the Figure 6.17 the inks at 1% and 0.5% solids had too much interaction among the ink polymers, causing a solid film and failing to separate the patterns. Only at the lower ink solids, the mechanism of the pattern formation worked due to enough mobility for the polymeric chains allowing them to be redistributed on the surface contours. For the 0.5% ink solids, it was noticed that a week pattern formation was visible.

Figure 6.17: Result of solids contents of PEDOT:PSS ink on the pattern formation. a) 1% solids, b) 0.5% solids and c) 0.125% solids in aq. suspension.

6.5.2 Effect of UV energy on the pattern formation

Conductive traces thus formed need a very good separation from each other. Hydrogel is a random network of fibers interconnected by ester linkages. If all the interconnections between two traces are not weak enough, the drying process cannot prevent electrical shorting. This fails the electrical circuit. Figure 6.18 shows the effect of UV energy on the ability to separate the conductive patterns from each other.
Figure 6.18: Dried hydrogels after ink flooding. UV exposures at various energy amounts a) 0.03 J/mm² (all neighboring lines are shorted due to insufficient breaking of connecting whiskers) b) 0.58 J/mm² (tiny whiskers are seen connecting two lines) c) 1.15 J/mm² (tiny whiskers are seen, however, they are not connecting the neighboring lines, the not shorting). As the irradiation energy increases, the separation becomes sharper.

With increasing energy for UV degradation, the gaps between the conductive traces go on increasing while the conductive traces become isolated, and unwanted interconnects are reduced. This can be indirectly correlated to the line raggedness of the pattern. The line raggedness is the edge waviness of any line. The whiskers arising at the edges contribute to the waviness of the edge. Thus, the lower the raggedness, the lower are the interconnects. Figure 6.19 shows the graphs for pattern separation and line raggedness.

Figure 6.19: Effect of increasing UV energy on a) Pattern separation and b) Line raggedness.

The effect of UV energy below 1.15 J/mm² resulted great variability in both the pattern separation and the raggedness. The reason is the fine whiskers or interconnects. Therefore, such
patterns cannot be used reliably for the generation of conductive traces. Above 1.15 J/mm² energy, the complete isolation of conductive traces from their neighbors was seen.

6.5.3 Effect of drying mechanism on pattern formation

Drying is an important process in pattern formation and separation. While it was seen that room temperature drying did not avail efficient pattern separation, the hot air drying the oven caused a pinning effect as shown in Figure 6.20, the wet film starts drying at the edges, causing the gradient of water/solvent. The center of the film retains higher amounts of water, causing the deformation of the fine structures isolated by degraded hydrogel. The effect was minimal for the IR drying where the water loss could be assumed to be relatively uniform over the surface.

![Figure 6.20: Schematics of the drying and pinning effect](image)

As seen in the Figure 6.21, the pattern separation gets affected due to the pinning effect. The image in Figure 6.21a shows the bending of the isolated features of hydrogel due to the water gradient. They tend to come closer and can result in interconnects. On the other hand, the IR drying showed reduced bending of straight lines. As seen in the graphs of Figure 6.19, the IR drying caused larger average gap widths while maintaining relatively similar line raggedness. The drying mechanism, however, does not considerably affect the average resistance of the conductive traces (Figure 6.21c).
6.5.4 Effects of initial swelling (water contents) on the pattern formation

Increasing amount of absorbed water in the hydrogel results in the increased swelling and more in the surface area of the film. It therefore should govern the shrinking of the material as the water is lost. While the material remains uniform, the tensile forces developed in the material should be uniform all over the surface except at the edges. With degradation of the material at selective regions, these areas should face increased tension towards the non-degraded areas. Therefore, the more water there is, the more there should be line separation and lowered line raggedness. To confirm this, three ratios of water to gel were chosen. At 10 g/g swelling, the conductive traces could not be isolated effectively. The interconnects resulted, in higher line raggedness. Figure 6.22 shows that 20 g/g and 30 g/g absorbed water for hydrogels (before UV patterning) caused similar pattern formation. Thus, increasing the water content above 20 g/g should be avoided to reduce the energy consumption for drying as it does not contribute much towards image generation.
6.5.5 **Effect of curing time on hydrogel films**

The hydrogel films were cured for 2 min and 5 min at 160 °C to see the effect on the pattern formation. However, the 5 min curing made the films tough, and they were not able to adhere to the substrate. As curing increases, the more hydroxyl groups of cellulose should get engaged in ester linkages, effectively reducing available hydrogen bonds to bind with the substrate. Thus, higher curing time cannot be useful for the process.

6.6 **Conductive pattern formation by utilizing surface crosslinking and photo-ablation**

Gel weakening and ablation technique shows self-distribution of aqueous ink through variation of zonal absorption. In this process, the pattern formed has the tendency to show fine whiskers of conductive traces at the edges. Also, the drying induced forces tend to induce slight waviness to the traces. Finally, the ink deposition is of only one kind, and the material’s ability to self-distribute the second ink can be hard to achieve.
By incorporating the surface crosslinking and improved hydrophobicity, one can modify the process of ink deposition. It would be possible to improve image fineness and utilize different kinds of electrically functional materials.

As suggested earlier, pyridine can form a surface crosslinking of the hydrogel, causing increased water contact angle. The crosslinking should reduce the water absorption and help in creating variation in swelling. As a result, the highly crosslinked surfaces should resist the swelling as compared to the low crosslinked or uncrosslinked surfaces. This can create a channel like structure to be filled with desired ink. One can then utilize the reduced water absorption of the crosslinked surface to selectively deposit another functional material on the uncrosslinked surface.

6.6.1 The amount of UV energy and the effect on channel formation

As the UV energy input goes on increasing, the amount of pyridine being converted should increase. At the same time, the cellulose degradation should form deeper channels in the hydrogel surface. In Figure 6.23, various levels of UV exposure and the final effect on ability to form channels filled with nano-silver ink (aq.) are seen. The UV energy was varied from as low as 35 mJ/mm² till 0.886 J/mm². While the conductive traces were formed at 0.354 J/mm² energy, the channels were not able to provide enough depth for continuous ink traces. At 0.709 J/mm² and above, the silver ink traces were relatively defect free with least resistance. A comparison of different UV treatments and resistance of silver ink traces can be seen later in Table 6.4.
It is possible that the non-image areas can also be treated with 5-amino-2,4-pentadienal, to resist water absorption. However, the cellulose degradation can reduce the channel depths. To see if there is considerable loss of depths, the samples were made with higher UV exposure energies for the channels and lower UV energy for the non-image areas. As seen earlier, the UV energy exposure of 0.354 J/mm² can form deep enough channels. If the non-image areas are treated with lower energy, such as 0.177 J/mm², the relative difference should turn the channel depths equivalent to Figure 6.23b. For all the consecutive steps of UV exposure, a similar difference should be reflected. As expected, the conductive traces were formed above 0.709 J/mm² for channel exposures. A visual comparison can be seen in Figure 6.24.
Figure 6.24: Effect of crosslinking of non-image areas at 0.177 J/mm² on ink deposition. UV energies used: for pattern formation: a) 0.354 J/mm², b) 0.532 J/mm², c) 0.709 J/mm², d) 0.886 J/mm².

The conductive traces can be compared based on their electrical resistance. Table 6.4 shows the comparison for silver ink conductive traces formed using UV treatments.

Table 6.4: Comparison of UV energy and its effect on resistance of conductive traces.

<table>
<thead>
<tr>
<th>UV energy for channels (J/mm²)</th>
<th>Resistance for samples with untreated non-image (Ω/cm)</th>
<th>Resistance for samples with treated non-image (Ω/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.035</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>0.177</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>0.354</td>
<td>&gt;40 M</td>
<td>NA</td>
</tr>
<tr>
<td>0.532</td>
<td>&gt;40 M</td>
<td>NA</td>
</tr>
<tr>
<td>0.709</td>
<td>0.534 ± 0.201</td>
<td>0.730 ± 0.178</td>
</tr>
<tr>
<td>0.886</td>
<td>0.444 ± 0.165</td>
<td>0.506 ± 0.23</td>
</tr>
</tbody>
</table>

It can be noticed visually that the channels have a deeper yellow color than the non-image areas, which is due to higher amounts of pyridine being converted to 5-amino-2,4-pentadienal.
6.6.2 Effect of UV energy on line raggedness

Difference of depths in image and non-image areas is the governing factor for effective ink deposition and retention. Lower depths can permit the removal ink from image areas along with the ink removal from non-image areas. This causes the uneven ink deposition and lower sharpness of the lines. The line raggedness gives us comparison for sharpness and uneven ink distribution. Figure 6.25 shows how the effect of UV energy of exposure on line raggedness for silver ink traces. For the selected UV energies, it was seen that one can reach the line raggedness in the range of 50-100 µm for energies above 0.35 J/mm². For treated non-image areas, the energy requirement becomes higher than 0.7 J/mm².

![Graph showing the effect of UV energy on line raggedness](image)

Figure 6.25: Effect of UV exposure energy for image generation on line raggedness for silver ink traces.

6.6.3 Effect of initial water contents in the hydrogel on silver ink trace formation

The initial water content in hydrogel (before UV treatment) can affect the channel depths and result in deeper channels if the swelling is higher. To verify the effect, three levels of swelling
were chosen such as 4g/g, 7g/g and 10g/g water absorption in the hydrogel before UV treatment. The channels thus formed were attempted to be filled with silver ink. It was noticed that 7 g/g and 10 g/g water absorption caused too much water content in the bulk of hydrogel that prevented the settling of aqueous silver ink in the channels. As a result, none of the channels were able to retain silver ink. The samples with 4g/g water absorption were able to form silver traces.

6.6.4 Deposition of two functional materials

The deposition of silver ink through the earlier discussed method shows a prominent way of forming electrical circuits with a digital imaging process and an active substrate. Heavy ink deposition is possible though this method with highly viscous inks, a known limitation for an inkjet printer. However, if one can deposit a second functional material without the need for a print registration system, it can be a breakthrough for flexible electronics.

Earlier in the discussion, it was shown that surface crosslinked hydrogel reduced water absorption as compared to an uncrosslinked surface. Therefore, a quick application of an aqueous solution can show selectively high absorption at uncrosslinked areas. This property can be used to deposit another functional material at selective areas. If the silver ink is cured before the application of a second material, it gets rendered to a non-dissolving state in the aqueous medium. Here, an in-situ polymerization of pyrrole is demonstrated to form selectively high grafting at uncrosslinked areas of hydrogel.

Pyrrole is a volatile liquid that can polymerize after oxidation. It forms an electrically resistive polymer; however, upon oxidation, it shows conductivity. A process of chemical oxidation can be utilized to form a polypyrrole as shown by Shukla.\textsuperscript{[109]} Ammonium persulfate in aqueous solution can trigger the oxidation of pyrrole and result in polypyrrole (Figure 6.26). As
proposed by Shulka,[109] the polypyrrole can get grafted onto the cellulose by radical formation through oxidation.

![Chemical structure of polypyrrole](image)

Figure 6.26: Pyrrole polymerization and cellulose radical formation through chemical oxidation by ammonium persulfate.

As ammonium persulfate (APS) forms a clear aqueous solution, it can be applied onto the pyridine treated and selectively UV exposed hydrogel surface. If the zone is completely uncrosslinked, it should absorb a very high amount of aqueous solution within a short period of time, leaving a big difference between the concentrations of APS and the crosslinked surface.

Flooding such a surface with pyrrole can start the formation of polypyrrole. In Figure 6.27, various stages of deposition of silver ink and polypyrrole can be seen.
The process shows the successful concept of deposition of two materials at predetermined locations, where the locations are fixed by UV exposure. The polypyrrole deposition was not enough to show conductivity. With an increased amount of time for pyrrole treatment, one can achieve a dense enough deposition; however, the non-image areas also show some polypyrrole in the process.

### 6.6.5 Limitations on feature sizes

The features created through UV photo-ablation and surface treatment were analyzed on dry film using an electron microscope to determine the feature size and limitations to the current process. Figure 6.28 shows that during the photo-ablation process, the removal of material creates an edge effect at transition from the masked region to the unmasked region. This effect can cause the increased edge width by a few microns. Figure 6.28b shows the minimal width of the edge as 2.4 μm. Further to this defect, the mask removal process can cause the tearing off of the attached
surface skin of the hydrogel. This can lead to an increased edge width up to 7.2 µm. The mask related defects can be eliminated by usage of a laser UV source.

![SEM micrographs of Pyridine treated sample where the left side of line is UV treated and the right side is masked. a) Minimal defect at the edge (line), b) Increased edge width due to tearing off the surface layer during mask removal.](image)

Figure 6.28: SEM micrographs of Pyridine treated sample where the left side of line is UV treated and the right side is masked. a) Minimal defect at the edge (line), b) Increased edge width due to tearing off the surface layer during mask removal.

### 6.7 Conclusions

Hydrogel films show a unique capability of active zone formation through photo-ablation and surface crosslinking. The photo-ablation process can be used to deposit polymeric aqueous inks which can pose the challenge of nozzle clogging if trying to print with an inkjet system.

For deposition of metallic inks such as silver inks, a channel like temporary structure can be developed in the hydrogel through photo-ablation and surface crosslinking. Three zones can be created during this process. Where a channel is created to hold viscous silver ink, a surface is created to resist absorption of aqueous solutions, and a surface is left untreated to have higher absorption of aqueous solutions. This mechanism can be used for in-situ polymerization of pyrrole at untreated surfaces. Usage of pyridine for surface crosslinking permits the removal of unused material through volatization. With usage of the shown mechanism of deposition of two materials, print registration issues can be minimized by reduction of at least one printing station.
Current demonstration of two material depositions need two shadow masks aligned to create the desired exposure pattern. This might imply that registration of images/masks is still required prior to image generation. However, if a digital system with a power modulated laser is utilized, the image exposure can be achieved without the needs of masks and in single scan cycle where all three zones (unexposed image area, non-image area and channels) can be created with lower feature sizes.

Further research can allow discovery of an optimized process where high deposition of polypyrrole is possible while maintaining non-image areas unaffected. Other easily removable UV active crosslinkers can be discovered to enhance the process.

6.8 Experimental section

6.8.1 Materials

CMC with average molecular weight of 700k Da with degree of substitution 0.9, PEDOT:PSS ink with 1% solids and D₂O were purchased from Sigma Aldrich. Citric acid monohydrate, Pyridine, 2,2,3,3-d(4)-3-(Trimethylsilyl)propionic acid sodium salt, di-iodomethane and aluminum foil were purchased from Fisher Scientific. Nano-silver flexo ink (PFI-600, silver loading 60%) was purchased from Novacentrix. Pyrrole at 99% purity and Ammonium persulfate at 99% purity were purchased from Fisher Scientific.

6.8.2 Equipment

A mask was created from aluminum foil by cutting the design on it. A Fusion UV conveyor system with flood exposure capacity was made by Fusion Systems Corporation, containing H-type UV bulb (wavelength range 200-600 nm, power 120W/cm). The speed of the belt and time spent in the chamber were used to calculate the UV energy provided for the samples.
6.8.3 Hydrogel film making

The films named as G1 were made from CMC of 700k Da with 1% of the citric acid by weight. The CMC and citric acid were dissolved in DI water and a solution of 2% consistency was made. The weight of citric acid was adjusted by 9%, considering the monohydrate form. The gel mixture was poured in a flat container and de-aerated to remove all air bubbles. The mixture was allowed to dry for a week on laminar flow table to obtain films of 150-170 µm thickness. These films were cut into suitable pieces and cured for 2 min at 160 °C. The low curing provides enough handleability along with the high-water absorptivity (more than 300 g/g as per data in chapter 4).

6.8.4 Film treatment and lamination

The lightly cured hydrogel films were soaked in DI water for a predetermined amount of time to swell. The swelling was not allowed to reach equilibrium as the goal of the hydration was to get partial swelling with scope for additional liquid absorption from the water-based ink. This pre-hydrated film was blotted to remove surface water and laminated on the paper. For hydrophobic treatments, the pyridine was applied to the surface using pyridine soaked cotton wipes. The wiping was done 4 times.

6.8.5 Photolithography

The laminated film was masked with aluminum mask and UV exposed by flood UV light. The time of exposure was varied to achieve the targeted energy input per unit area. The UV mask was removed before further treatment.

6.8.6 PEDOT:PSS ink application

PEDOT:PSS ink was diluted to the required concentration using DI water. The inks thus obtained were used for flooding the hydrogel film surfaces after UV treatment. Ink weight to
surface area ratio was maintained as 0.1 g/cm², which was optimum for the processing where the ink does not flow to surrounding surface due to natural vibrations during processing.

6.8.7 Nano-silver ink application

Water based nano-silver ink (PFI-600) was applied on the wet hydrogel surface with a tissue wipe. After ink application, a wet tissue wipe was used to wipe the surface gently to remove the silver ink from non-image areas. The film was then cured at 160°C till all the water gets removed. Resulting ink traces were non-soluble in water.

6.8.8 Deposition of polypyrrole

A double shadow mask made of aluminum was used for the hydrogel treatment. After application of pyridine, a mask shaped ‘T’ was placed on the hydrogel film. A second mask with ‘U’ shaped opening was carefully placed on the previous mask. The film was photo-ablated and surface crosslinked with pyridine. A “U” shaped channel was formed in the process. The top mask was removed, and the film was again treated with UV light to crosslink the non-image areas, leaving the ‘T’ shaped zone uncrosslinked.

The film was once wiped with wet tissue, and silver ink was applied. After application and curing of nano silver traces, the dry hydrogel film surface was treated with an ammonium persulfate (APS) aq. solution at 10% solids (with 1% mol HCl as counter ion supplier) for less than 2 s. The solution was applied with a wet tissue to limit excessive application. The surface was blotted with tissue to remove as much APS from non-image areas (crosslinked with pyridine+UV treatment). Pyrrole was applied on this surface and then blotted out on first visual confirmation of polymerization. Finally, the film was dried to remove remaining moisture.
6.8.9 Characterization

The total carboxyl contents of the films were obtained by first washing the crosslinked films in 1:1 DI water and isopropyl alcohol mixture for 2 h. These films were dried and weighed. The films (20-50 mg) were then dissolved in 10 ml of 0.1 N sodium hydroxide (NaOH) solution. This solution was then titrated with 0.1 N hydrochloric acid (HCl). Phenolphthalein was used as a titration indicator. The carboxyl contents were calculated using Equation 6.2\(^\text{[178]}\)

\[
\text{Carboxyl content} = (V_r - V_s) \times \frac{N}{W_s}
\]

Equation 6.2: Total carboxyl contents

For Equation 6.2, the \(V_r\) is volume of HCl required to titrate the used volume of NaOH without the gel sample. \(V_s\) is the volume of HCl required to titrate the gel sample. \(N\) is the normality of HCl, and \(W_s\) is the weight of gel sample in grams.

Proton Nuclear Magnetic Resonance (NMR) of Pyridine mixed with D\(_2\)O was obtained from the Bruker 500 MHz system. 2,2,3,3-d(4)-3-(Trimethylsilyl)propionic acid sodium salt was added as a reference in the NMR samples. UV-Vis spectrum of the gels was acquired for the 200-500 nm range with 1 nm increments.

Sessile drop contact angle was measured from the images captured through the SEO Phoenix system. The laminated films on paperback were dried before measurements and then mounted on the table. A drop of DI water was placed on the surface. The images were obtained at the interval of 200 ms. An average of 3 readings was taken for the graph plotting. The same procedure was followed for contact angle with di-iodomethane.

Hydrogel dried films were used for surface roughness measurements. A 3D Laser Scanning Microscope ‘VK-X1000’ from Keyence was used to capture the images at 10x magnification and measure the roughness.
Time-of-Flight SIMS – ION-TOF SIMS 5 was used for mass spectroscopy and detection of nitrogen containing ions during TOF SIMS analysis. High mass resolution and high spatial resolution spectra were obtained using LMIG Bi\(^+\) primary ions.

X-ray photoelectron (XPS) analysis was performed on the films without laminating them on the paper substrate. XPS was performed on a SPECS System with PHOIBOS 150 analyzer, <1eV resolution. The X-ray source was 10-14 kV Mg.

Image fineness and ink deposition were analyzed with PIAS-II image quality analyzer from the Quality Engineering Associates (QEA) Inc.

Resistance of samples was measured with GW Digital Multimeter (GDM-8055) using two probe method.

Scanning Electron Micrographs were obtained using a Field Emission Scanning Electron Microscope – FEI Verios 460L. The sample stage was biased at 500 V, beam voltage was 2 kV, and current was 50 pA.
REFERENCES


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APPENDICES
APPENDIX A: LIGNIN CONTAINING NANOCELLULOSE BASED COATINGS
FOR PHOTO-ASSISTED PATTERN GENERATION

A.1 Abstract

Lignin containing cellulose nanofibrils can be used as coatings or to make paper samples, which are highly absorbent. They can be zonally converted to be non-absorbent using UV exposure. Such tuned surface can then be used to absorb aqueous materials at selective areas, allowing digital surface tuning for electrically functional pattern generation. The absorbed aqueous solution can contain an initiator for polymerizing a monomer. After application of a monomer on such a surface, it will polymerize and get linked with the specific zone. Here a polypyrrole pattern formation is demonstrated by using ammonium persulfate as oxidizer.

A.2 Introduction

Lignin is a natural polymer occurring in plants. The basic units or pre-cursors of lignin are identified as p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol. Lignin’s natural function is a binder in plant cell walls and it is a relatively hydrophobic material. The pulping process can be mechanical, chemical or a hybrid. During the chemical pulping process, the lignin is removed. Such pulp is finally bleached to remove the remaining lignin and make the pulp white in color. This process improves the hydrophilic properties of the pulp but reduces the yield of the pulp because of the loss of biomass. The yield of the pulp for mechanical processes can be 85-95%. For a hybrid process, it can be 55-85%, and for a chemical process, it can reduce to 45-55%. The core purpose of lignin removal is to improve the paper strength and whiteness.

Technological developments led to the discovery of nanofibrillate cellulose and cellulose nanocrystals. Mechanical grinding and chemical assistance such as TEMPO oxidation are used for production of cellulose nanofibers (CNF). The nano features of cellulose can lead to improved
mechanical properties of the material and provide a high surface area for various innovative applications. In the past few years, people have studied various feed stocks such as wood, cotton, crops, algae, and bacterial cellulose\[201, 202\] for micro and nanocellulose production. It has also been of great interest to maintain the lignin in the nano- and micro- fibrillated cellulose to take advantage of lignin’s hydrophobic nature.\[203-205\] Films, hydrophobic surfaces, and composites can be possible with such materials, where material densification and nanoscale interactions are availed due to a material’s high surface area.

Here it is shown that the lignin containing nano fibrillated cellulose can be utilized for the photo patterning and selective absorption of water over different zones, leading to the capabilities of zonal material deposition. The deposited material can be an initiator for polymerization of any monomer of interest. Using such a mechanism with in situ polymerization of pyrrole using aqueous oxidizing agent (ammonium persulfate) is possible.

A.3 Usage of L-CMNF for creating hydrophobic zones

Cellulose can get degraded with UV while the lignin can degrade by forming phenoxy free radicals.\[206\] It is possible that cellulose gets degraded and the phenoxy radicals get crosslinked with nearby radicals and form a water resistant structure. Anticipating this change in structure, we conducted a study with lignin containing cellulose micro-, nano- fibrils (L-CMNF) made from hemp hurds. Thin paper samples were made from L-CMNF samples with an average weight of 35 grams per square meter (gsm) as described in method. To determine how the processing conditions for LMNF affect the surface properties and water absorption, two different pulps - autohydrolyzed pulp and kraft pulp – were used where the amount of lignin in the pulp changed significantly. A new process of dual assymetric centrifuge (DAC) was used to manufacture the L-CMNF from hemp pulps. A detail of the manufacturing process and L-CMNF characterization can be found in
APPENDIX B Similarly, a variation in processing time and processing solids content was varied to determine the effect of change in morphology and crystallinity on the surface properties of the L-CMNF.

A.4 **UV treatment to the L-CMNF paper sample**

L-CMNF paper samples were UV treated for different UV energies and analyzed for water contact angle. A sample made from 5% solids (final stage of L-CMNF manufacturing) was chosen for surface roughness changes and XPS analysis to determine the changes in chemical composition and different bonding species.

A.4.1 **Water contact angle**

Water contact angle changes over a time period can give great insight on water’s spreading and absorption on the surface. Four samples of L-CMNF were chosen for study of UV treatment and water’s behavior on the surface. One of the samples was chosen to see the effect of variation of UV energy. Table A.1 shows different abbreviations used for L-CMNF samples.

Table A.1: Sample codes for different L-CMNF.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Pulping condition</th>
<th>DAC treated final solids</th>
<th>DAC treatment time</th>
</tr>
</thead>
<tbody>
<tr>
<td>AH L-CMNF3_20 min</td>
<td>Autohydrolyzed Hemp Hurds</td>
<td>3%</td>
<td>20 min</td>
</tr>
<tr>
<td>AH L-CMNF3_60 min</td>
<td>Autohydrolyzed Hemp Hurds</td>
<td>3%</td>
<td>60 min</td>
</tr>
<tr>
<td>AH L-CMNF5_60 min</td>
<td>Autohydrolyzed Hemp Hurds</td>
<td>5%</td>
<td>60 min</td>
</tr>
<tr>
<td>HK L-CMNF3_60 min</td>
<td>Kraft pulped Hemp Hurds</td>
<td>3%</td>
<td>60 min</td>
</tr>
</tbody>
</table>
To observe the behavior of water with respect to UV exposure energy, the ‘AH L-CMNF5_60 min’ was chosen with No UV exposure, 0.144 J/mm², 0.288 mm², 0.576 J/mm² and 1.152 J/mm² UV exposure energy. All other samples were treated for 1.152 J/mm² UV exposure energy.

![Figure A.1: Water contact angle variation with time. a) Effect of UV energy for treating L-CMNF5_60 min, b) Behavior of water with on L-CMNF surfaces made with different processing conditions.](image)

Figure A.1a shows that untreated samples have a very high water absorption rate and within 10 s, all water gets absorbed in the surface. With UV exposure, the water contact angle improves by 20° or more. However, at UV energies lower than 1.152 J/mm², the water contact angle is not stable. There is a slow absorption of water seen. At 1.152 J/mm² exposure, the water drop sits on the surface without absorption.

For different L-CMNF samples, the water absorption changes are based on processing conditions (Figure A.1b). The ‘AH L-CMNF3_60 min’ showed faster water absorption and the lowest water contact angle before UV treatment. The contact angle improves if the DAC processing time is lower or the final solids of DAC process are higher. Similarly, the kraft pulped
hemp showed a higher water contact angle, which can be due to the changed chemical structure of lignin during the kraft process. For auto hydrolyzed pulp samples, the explanation for the change in the water contact angle can be related to the crystallinity of various pulp samples. As explained in APPENDIX B the crystallinity of ‘AH L-CMNF3_60 min’ was seen as 35% while it was higher for other samples. ‘AH L-CMNF3_20 min’ was seen as 41%. Similarly ‘AH L-CMNF5_60 min’ had crystallinity of 40%. The texture of 60 min processed samples was much finer than 20 min processed samples. The texture of 5% L-CMNF was coarser than the 3% L-CMNF.

A.4.2 X-ray Photoelectron Spectroscopy (XPS) study

XPS study was conducted on an ‘AH L-CMNF5_60 min’ sample before and after UV exposure. The UV energy used was 1.152 J/mm². It shows that there is a considerable loss of oxygen by UV exposure. After UV exposure, the carbon to oxygen ratio changed from 2.7 to 7.33, indicating more carbon species on the surface.

The comparison of C 1s spectra for both samples show increased C-C bonds by 26% and reduced C-O bonds by 22%. Also, O-C-O binds were reduced by 5%. In addition, the UV exposed surface showed traces of C=C species. With the loss of oxygen and increased C=C structures, the increased hydrophobicity can be explained. A comparison of bonding contribution is given in Table A.2: XPS carbon (C 1s) and oxygen (O 1s) contributions for ‘AH L-CMNF5_60 min’ sample before and after UV treatment, and the XPS deconvolution spectra are shown in Figure A.2.

Looking at the O 1s spectra, there was not a considerable change noticed in oxygen bonding with surrounding carbon.
Table A.2: XPS carbon (C 1s) and oxygen (O 1s) contributions for ‘AH L-CMNF5_60 min’ sample before and after UV treatment.

<table>
<thead>
<tr>
<th>Approximate BE (eV)</th>
<th>283.4</th>
<th>285</th>
<th>286.7</th>
<th>288.5</th>
<th>532</th>
<th>533.2</th>
<th>534.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon/Oxygen bond</td>
<td>C=C</td>
<td>C-C / C-H</td>
<td>C-O</td>
<td>O=C-O</td>
<td>O=C-O</td>
<td>C=O</td>
<td>O=O-C-O</td>
</tr>
<tr>
<td>Code</td>
<td>C1_x</td>
<td>C2_x</td>
<td>C3_x</td>
<td>C4_x</td>
<td>O1_x</td>
<td>O2_x</td>
<td>O3_x</td>
</tr>
<tr>
<td>Masked region (No UV)</td>
<td>-</td>
<td>50</td>
<td>40</td>
<td>10</td>
<td>12</td>
<td>82</td>
<td>6</td>
</tr>
<tr>
<td>Unmasked region (UV treated)</td>
<td>1</td>
<td>76</td>
<td>18</td>
<td>5</td>
<td>9</td>
<td>86</td>
<td>5</td>
</tr>
</tbody>
</table>
Figure A.2: XPS deconvolution spectra for ‘AH L-CMNFS 60 min’ samples. a) C 1s spectra before UV treatment, b) C 1s spectra after UV treatment, c) O 1s spectra before UV treatment, d) O 1s spectra after UV treatment.

A.4.3 Changes in surface roughness

Using a 3D laser scanning, the surface roughness of ‘AH L-CMNFS 60 min’ was checked for No UV exposure and UV exposure with 1.152 J/mm² energy. It was seen that the surface turned relatively smoother. The roughness value decreased from 5.21 μm to 4.99 μm (root mean square value). It can therefore be considered that the surface was bridging the gaps by crosslinking and forming a smoother film.

A.5 Selective deposition of polypyrrole

A selective UV exposure to the hemp coated paper samples can therefore be used for image generation and selective deposition of various water soluble materials. As a demonstration for the
selective deposition of polypyrrole, a UV treated sample of ‘AH L-CMNF3_60 min’ was chosen. Figure A.3 shows various stages of process.

![Image of various stages of formation of polypyrrole pattern](image)

Figure A.3: Various stages of formation of polypyrrole pattern on ‘AH L-CMNF3_60 min’ paper. a) Untreated paper sample, b) UV patterns exposed though an aluminum mask, c) Application of 10 w% Ammonium persulfate aq. where the material is absorbed only on unexposed paper, d) Application of pyrrole followed by drying of the paper. The polypyrrole is formed on unexposed paper.

A.6 Conclusion

The UV treatment of L-CMNF paper shows structural chemical modifications in the paper, which are possibly the crosslinking of lignin along with some loss of carbohydrates through degradation. Usage of UV exposure permits selective patterning though a contact mask (shadow mask). The unexposed paper surface remains highly water absorptive and absorbs aqueous solutions while the exposed surface does not absorb the material can ca be cleaned by wiping off. The absorbed material can be a reaction initiator for another material. Here it is demonstrated that ammonium persulfate can be absorbed in paper and used to polymerize pyrrole at unexposed areas.

A.7 Experimental section

A.7.1 Material

Futura 75 cultivar hemp hurds were used to manufacture hemp pulp by auto hydrolysis and kraft pulping. Pyrrole at 99% purity and Ammonium persulfate (APS) at 99% purity were purchased from Fisher Scientific.
A.7.2 Method

The L-CMNF samples were dispersed in DI water to have 0.15% consistency. The dispersed pulp was filtered through Whatman filter paper using a Buchner funnel. The paper sheet thus obtained was dried at room temperature for 24 h and then used for further testing.

UV exposure to the L-CMNF paper samples was provided through an aluminum mask (shadow mask) by placing the mask in contact with the dry paper sample and exposing the sample in a Fusion UV conveyor system (Fusion Systems Corporation, H-type UV bulb, wavelength range 200-600 nm, power 120W/cm).

The UV treated paper samples were treated with 10 wt% APS in aq. solution (with 1% mol HCl as counter ion supplier) for a second, and the excess liquid was blotted out. The sample was then flooded with pyrrole for a couple of seconds, and excess pyrrole was blotted out. The sample was dried in oven.

A.7.3 Characterization

Sessile drop contact angle was measured from the images captured through the SEO Phoenix system. The paper samples before and after UV treatment were mounted on the table. A drop of DI water was placed on the surface. The images were obtained at the interval of 200 ms. An average of 3 readings was taken for the graph plotting.

A 3D Laser Scanning Microscope ‘VK-X1000’ from Keyence was used to capture the images at 10x magnification and measure the roughness.

X-ray photoelectron (XPS) analysis was performed on the films without laminating them on the paper substrate. XPS was performed on a SPECS System with PHOIBOS 150 analyzer, <1eV resolution. The X-ray source was $10^{-14}$ kV Mg.
APPENDIX B: INNOVATING GENERATION OF NANOCELLULOSE FROM INDUSTRIAL HEMP BY DUAL ASYMMETRIC CENTRIFUGE

B.1 Abstract

Among nano-biomaterials, cellulose nanofibrils (CNF) possessing intrinsically appealing fiber dimensions on the nanometer scale and biocompatibility features arguably demonstrate the greatest potential for a variety of practical applications such as packaging, hygiene, food and healthcare products. Herein, a new class of nanofibers are introduced from a very green feedstock using an isolated mechanical processing technique, enabling on-site and on-demand production with a significantly reduced risk of environmental and toxicological concerns during the product life cycle. Serendipitously, we have shown that autohydrolyzed hemp hurds, the short fiber piths of the hemp plant, show the surprising and unparalleled tendency to generate nanocellulose. Hemp hurd fibers were pulverized in a high intensity dual asymmetric centrifugation (DAC) force was employed to defibrillate unbleached hemp cellulosic fibers into lignin containing cellulose micro and nanofibers (L-CMNF). The impact of biomass composition, chemical processing, and mechanical pretreatment as well as DAC pulverization time and solids content on the fibrillation, crystallinity, charge, and colloidal stability of L-CMNF were studied. Formation of L-CMNF caused reduced crystallinity from 50% to 29% while charge distribution increased from 4.5 to 13 ($\times 10^{-5}$ µ eq.Vol./L of p-DADMAC) with higher pulverization time at lower solids in the presence of lignin. Finally, SEM and TEM images evidenced the formation of L-CMNF. Thus, we offer the community a powerful new approach to CNF by pulverizing autohydrolyzed hemp hurds for very short times in an isolated DAC system.
B.2 Introduction

Since the discovery of cellulose nanofibrils (CNFs) in 1977 by a research manager at the ITT Rayonier Eastern Research Division (ERD Lab in New Jersey, USA, through using a milk homogenizer, nanocellulose has been exploited for numerous sundry applications. Nanocellulose, more specifically cellulose nanofibrils (CNFs), have been proposed for several commercial applications such as rheology modifiers for coatings, food products such as ice-cream, oil-wells, etc. Other highly studied applications of CNFs are in composite films for barrier and strength properties, food packaging, and gas and oxygen barrier films, coatings, and biomedical applications. Although developing new products and applications using CNFs have been rigorously studied, the literature details very few studies on cleaner and more energy-efficient production of nanocellulose. Indeed, production is key to any future commercial successes; if methods are not developed that are cleaner, more efficient, and less expensive, then the whole arena of CNF will be only an academic exercise. Producing a cleaner and contaminant-free (e.g., chemical extractives) CNF is, for example, a key requirement for biomedical-grade applications to avoid inflammation, allergenicity, and tissue rejection. Several of the most conventional, mainstream, and popular methods for preparing nanocellulose fibrils are high-pressure homogenization, disk refining, microfluidization, ultrasonication, steam explosion, and cryocrushing. Considering the current machinery and infrastructure limitations along with energy and cost effectiveness, we believe disk refining is the only process currently economical and practical enough for large volume production. These processes deliver mechanical shearing stresses to pre-obtained cellulose fibers, splitting them along the longitudinal axis and subsequent diminution into nanocellulose fibers of diameters less than 200 nm and lengths from 500 nm to several micrometers.
The dimensions of the CNFs vary widely based on the source of cellulosic material, type, and duration of mechanical treatment. Separation of cellulose fibers into nanocellulose can be a very challenging, energy-intensive, and time-consuming process.\textsuperscript{[202]} To minimize energy consumption, several pretreatments exist for cellulosic fibers aid defibrillation, including alkaline to remove lignin, an intractable polymeric “contaminant”, oxidation to resolve aggregation,\textsuperscript{[234, 235]} enzymes to reduce molecular weight or degree of polymerization,\textsuperscript{[236]} etc. However, all add to waste generation and the complexity of the nanocellulose production system.\textsuperscript{[227]} Some newer approaches are the ball milling method,\textsuperscript{[225, 237]} high shear homogenization at high pressure,\textsuperscript{[238]} biosynthesis,\textsuperscript{[239]} electrospinning,\textsuperscript{[240, 241]} etc. Most lab-scale studies on nanocellulose production focus on energy and time consumption, which generally are the highest cost factors.\textsuperscript{[227, 242]} However, in a recent techno-economic study, Asis et al.\textsuperscript{[232]} showed that the major cost-driver in nanocellulose production is the raw material. The oxidized (bleached) pulp that is being used to prepare nanocellulose represents more than 60% of the total manufacturing cost of nanocellulose.\textsuperscript{[232]}

Wood is considered a conventional source of cellulose for producing nanocellulose.\textsuperscript{[201, 243-246]} Currently, the most common raw material used to produce nanocellulose is bleached wood pulp.\textsuperscript{[247]} Other raw materials used to produce nanocellulose are agricultural biomass, marine animals (tunicates and valonia), algae, and fungi.\textsuperscript{[247, 248]} Industrial and agricultural biomass waste such as rice straw, bagasse, carrot pulp, onion skin, and hemp hurds can also be used.\textsuperscript{[247]} Recently, hemp hurds have been studied to produce nanocellulose using chemical and enzymatic pre-treatments following mechanical shearing.\textsuperscript{[249, 250]}

Industrial hemp (\textit{C sativa}) contains less than 0.3% content of delta-9 tetrahydrocannabinols (psychoactive substances), making it unsuitable as a narcotic, but very useful for a myriad of other
applications.\textsuperscript{[251, 252]} It consists of an inner core of less valuable short xylem ("hurd") fibers and an outer core of more valuable long phloem fibers ("bast").\textsuperscript{[253, 254]} The separation of hurds from bast fibers can be accomplished by using a traditional "retting" process for selectively removing binding substances such as pectin or through the application of a more modern decortication process. Hurd fibers are widely regarded as a low-value byproduct primarily used for animal bedding\textsuperscript{[255]} and hemp–lime\textsuperscript{[256]} construction applications.

The current unique work presents a novel, low energy, and chemical-free process for producing nanocellulose using low value agricultural crop waste (industrial hemp hurds) instead of relatively expensive wood pulp without any additional pretreatment. In the 2018 Agriculture Improvement Act, industrial hemp was removed from the Controlled Substances Act and allowed to be grown for research purposes. Most US states had already allowed such crops for research and commercial purposes. This change will promote the cultivation of industrial hemp as a potential high value raw material for commercial applications\textsuperscript{[257, 258]} such as tissue\textsuperscript{[259]} making.

Unlike the earlier production studies cited to date, we used a relatively new and exciting approach known as dual asymmetric centrifugation (DAC, FlackTek speed mixer, DAC 150.1 FVZ-K) that gives additional mechanical shear impact to fibrillate cellulose fibers into micro and nano-fibrillated cellulose (CMNF). In past, DAC has been explored for biomedical research such as sterile preparations of liposomes by homogenizing a rather concentrated blend of hydrogenated phosphatidylcholine, cholesterol and NaCl-solution.\textsuperscript{[260]} Hirsch et al. further expanded the use of DAC for sterile preparation of RNA-liposome.\textsuperscript{[261]} DAC has also been used for producing homogenized carbon nanotube-epoxy reinforced composite.\textsuperscript{[262]} In contrast to conventional centrifugation where samples have degrees of translational freedom around a central axis, sample holders are additionally turned around a secondary rotational axis during DAC (Figure B.1). This
results in continuous changes of high centrifugal acceleration characterized by high frequent motion and very strong shear forces. The combination of forces in different planes generates very high acceleration \((700 \times \text{gravitational acceleration at 3500 rpm speed})\), which makes DAC more like a high shear homogenizer than a separation technique.

Figure B.1: A dual asymmetric centrifugation process. Relative opposite rotations cause shearing action instead of centrifuge separation.

At such high accelerations, when ceramic beads are added inside the sample vial, a greater mechanical shear is permitted on viscous samples by increased density and rapid motion. Such high mechanical shear should be able to defibrillate fibers into nanoscale fibers in a shorter timeframe compared to conventional methods. A novel point of this work was the selection of chemical free, lignin-containing auto-hydrolyzed (hydrothermally processed)\(^{[263]}\) hemp cellulose pulps. In CMNF (cellulose micro/nanofibers) production using earlier studied methods, it was natural that a delignified, weak, swollen cellulose fiber wall was much easier to transform into CMNF than a strong, lignin-containing stiffer, de-swollen one.\(^{[264]}\) Surprisingly, in the current work, mechanical shearing force, lignin-containing hemp cellulose fibers were far more amenable
to transformation into CMNF compared to bleached wood fibers or agricultural fibers. One of the driving factors for this transformation is suspected to be the rigidity of fibers imparted by the lignin in the pulp.\cite{265, 266}

**B.3 Importance of application of DAC**

Cellulose micro-nano fibrils have a number of potential applications including use as rheology modifiers, composites, packaging, food thickeners, and biomedical scaffolding materials. However, the process of making nanocellulose is still a drain in terms of energy consumption, cost of raw material, and availability at the site of demand. Using DAC for producing nanocellulose is a breakthrough, allowing a greater flexibility in terms of availability of nanocellulose on-demand and on-site due to an easy setup and processability. DAC also provides a high level of convenience for producing nanocellulose without the specter of non-process contamination (e.g., chemical extractives) which would likely compromise use in biological/biomedical applications. The other novel aspect is that a different container can be used for each batch of production that opens its potential in the biomedical applications. It has already been discussed that the raw material for producing CMNF is a major cost factor (~60% of total cost) followed by fresh water and energy consumption.\cite{231} The auto-hydrolyzed hemp hurds (AH) fibers used in this study opens another opportunity for producing low cost sustainable CMNF for numerous potential applications.
B.4 Obtaining L-CMNF

In Figure B.2, the Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM) images show how the unprocessed fiber bundle became disintegrated into random micro and nano fibrils (20-170 nm wide) after DAC processing. It was observed that lignin containing (lignin content: 23.9%) AH hurd fibers could defibrillate into L-CMNF by using the DAC force for pulp at 3% consistency (Figure B.2). The time or processing and output consistency plays an important role, which can be seen as a difference in the bulk appearances shown in Figure B.2. With increased time of processing, the homogeneity of the pulp increases. The usage of DAC is also highly tunable with respect to total energy input, type of beads used for milling action, and intensity of shear forces. It has the ability to handle material from 10 g to 5000 g, thus endowing it with very high versatility at the laboratory bench-scale.
B.4.1 Impact of different raw materials

To observe the impact of fiber source and lignin on defibrillation, a batch of bleached (lignin content: 2.1%) and unbleached hardwood-kraft pulps (lignin content: 9.2%) were run using the same working conditions as AH pulp. However, no desirable nanocellulose-like features were obtained.

Figure B.3 shows a comparison among unbleached, bleached hardwood kraft pulp fibers, and AH pulp fibers after DAC processing. It was definitively shown that only the AH pulp was able to defibrillate into nanoscopic fibers. This result demonstrated that hemp hurd fibers have unique structural properties that endow them with the opportunity to fibrillate. The rigidity of the material is proposed to be one of the driving factors,[266] which likely arises from the presence of a high amount of lignin (23.5%) as compared to unbleached hardwood kraft pulp (8.5%), whereas the bleached pulp has almost no lignin in it. This is a critical finding for future work the discovery of which has a number of useful ramifications for future nanomaterials applications.
Kraft pulping removes lignin from the ligno-cellulosic biomass. Therefore, Kraft hemp pulp was applied for understanding the impact of reduced lignin content (14.5% lignin) on nanofibrillation in the DAC. Similarly, a batch of PFI mill treated hemp pulp was used to determine if DAC shows any differences in output. We observed that both Kraft and PFI treatment could still maintain the raw material’s ability to form L-CMNF (Figure B.4). There was no significant difference in morphology of the nanofibers after pre-treatments although chemically untreated fibers showed more lignin on the surface.

**B.5 Characterization of the L-CMNF**

It is evident from Figure B.2, Figure B.3 and Figure B.4 that hemp is able to form L-CMNF in the DAC, which is likely from the intrinsic rigidity afforded by the high levels of lignin.[266] It is well known that the charged groups inside the fiber wall of cellulose repel each other, resulting in osmotic swelling pressure in the fiber wall. The cellulose in the cell walls of the wood fibers is
lamellar in structure, which lose their crystalline alignment when fibers swell.[267] Therefore, the effect of water content was studied for DAC processing. Two consistencies were targeted for the studies with two periods of processing, starting at 10 wt.% solids and reaching 5 wt.%. Another condition was starting at 6 wt.% solids and reaching 3 wt.%. It was observed that at higher water contents, fibrillation was better.

**B.5.1 Surface charge development during fibrillation**

![Graph showing surface charge development during fibrillation](image)

<table>
<thead>
<tr>
<th>Solids/Process time</th>
<th>pH (0 min)</th>
<th>pH (20 min)</th>
<th>pH (60 min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hemp Auto, 3%</td>
<td>6.70</td>
<td>6.67</td>
<td>8.48</td>
</tr>
<tr>
<td>Hemp Auto, 5%</td>
<td>6.71</td>
<td>6.4</td>
<td>7.36</td>
</tr>
</tbody>
</table>

Figure B.5: a) Charge distribution and b) pH of DAC-treated hemp fibers for 20 and 60 minutes at 3% and 5% consistency.

The colloidal stability was seen to be the function of surface charges and pH changes, which changed dramatically for 3% pulp. As shown in Figure B.5a the p-DADMAC demand, for streaming potential neutralization, increased almost 3 times (4.5 to 13 μ eq.vol/L) and the pH of the pulp slurry became alkaline after 60 min (Figure B.5b). This change could be attributed to increasing exposure of the responsible functional groups of lignin and cellulose due to fibrillation, which were otherwise trapped inside the bundled fibers. For lesser processing times (20 min), the
3% pulp showed better colloidal stability and lower sedimentation (Figure B.6a and Figure B.6b) than the 5% pulp. However, after 60 min of processing, the difference in sedimentation was much lower. The sedimentation trials were conducted for an hour after making the suspensions. After 24 h of sedimentation, all samples showed the same sedimentation. Sedimentation levels in the vials indicated that the impact of initial solids was more than that of the processing time.

![Sedimentation images](image)

**Figure B.6:** a) sedimentation of DAC-treated hemp fibers for 20 and 60 minutes at 3% and 5% consistency, b) graph of the sedimentation.

**B.5.2 Changes in crystallinity after DAC treatment:**

In general, crystallinity of fibers decreases as it undergoes shearing stress to produce CNF or CMNF. Earlier studies have shown similar reductions in crystallinity of cellulose under high shear stress,\[268\] which can be seen as the breaking up of fibrillar bundles between crystalline regions. The 3% AH pulp showed changes in the crystallinity index (CI) from 50% to 35% after
an hour of processing Figure B.7 shows that the reduction in CI is significantly higher (reduction in CI by >5%) for 3% pulp than 5% pulp.

![Graph showing crystallography (XRD) of DAC-treated hemp fibers.](image)

**Figure B.7**: Crystallography (XRD) of DAC-treated hemp fibers.

Though the processing of hardwood pulp did not produce L-CMNF, it is worth noting that the presence of lignin in unbleached hardwood pulp showed higher reductions in crystallinity (CI: 38% to 31%) than the bleached hardwood pulp (CI: 55% to 52%). This shows that the source of cellulose and rigidity/stiffness due to the lignin present in the pulp plays very important roles in providing sufficient mechanical shear force to defibrillate cellulose in the DAC system. Though the detailed mechanism of mechanical shearing with the help of ceramic beads was not studied, lignin presence supplements the shearing action of ceramic beads.

Looking at the graphs in Figure B.7, it can be seen that after DAC processing, the crystalline peak around 16.5° starts to resolve from its neighbor at 14.3°. This separation indicates breaking of crystalline structures to expose (101) and (10\(\overline{1}\)) planes. With increased time of DAC processing, the resolution of these peaks increases. A list of the these peaks can be seen in the
Table B.1 where respective peak is assigned to crystal plane (Miller indices)\cite{269} of cellulose. In all conditions, the peak at 22.3° is a major peak for (002) plane with a merged peak for (021) plane. Table B.1: Crystallinity indices and list of major crystalline peaks resolved for different hemp autohydrolyzed samples processed through DAC.

<table>
<thead>
<tr>
<th>Time for DAC processing (min)</th>
<th>Final solids (%)</th>
<th>Crystallinity (%)</th>
<th>Miller indices and 2 Theta position (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NA (Unprocessed)</td>
<td>50</td>
<td>101 (14.3°) 10\overline{1} (16.5°) 021 and 002 (22.3°) 040 (34.7°)</td>
</tr>
<tr>
<td>0</td>
<td>5</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>20</td>
<td>5</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>6</td>
<td>4</td>
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<td>60</td>
<td>5</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>6</td>
<td>2</td>
</tr>
</tbody>
</table>

*Minor crystalline peaks are ignored from adding in table*
Figure B.8: Crystallinity of mechanically and chemically pretreated hemp fibers followed by DAC treatment.

Figure B.8 shows the relation of crystallinity with pre-treatments for the hemp pulp. A pre-chemical and mechanical treatment were carried out using sodium hydroxide in conjunction with sodium sulfide and PFI-mill refining respectively before DAC treatment. The refining of AH pulp resulted in a decrease in freeness (From 673 CSF to 128 CSF) and softer and less rigid pulp. It was observed that chemical pre-treatment of hemp hurds with NaOH and Na₂S, also known as Kraft pulping, resulting in softer pulp due to the swelling of cell walls of hemp fibers. This hemp Kraft pulp (HK), after being treated mechanically in the PFI-mill, resulted in more defibrillation and lesser rigidity. After 60 minutes of DAC treatment of pre-treated hemp fibers (HK and PFI-refined fibers), no significant difference was observed in the morphology of L-CMNF (Figure B.4), except that of chemically untreated fibers that had more lignin on their surfaces. The crystallinity results also support the morphology result explanation (Figure B.8). A significant reduction in crystallinity was observed in L-CMNF (60 min DAC treated fibers) after NaOH and Na₂S pre-treatment (CI: 35% to 29%). Pre-refining, on the other hand, did not show significant change (less than 5% difference) in crystallinity after 60 min DAC processing.
B.6 Conclusion

This study provides an innovative and robust way to prepare nanocellulose using more sustainable and less processed hemp hurds waste. The mechanical high-speed dual asymmetric centrifugation of hemp auto-hydrolyzed pulp has shown formation of nanocellulose, which is confirmed in SEM and TEM images. The charge distribution, sedimentation and crystallinity also witnessed the formation of nanocellulose in DAC process. Lignin, being a 3D molecule binding the cell wall, is supposed to limit the swelling of the fibers and limit the fibrillation. Corresponding to this theory, lignin should have hindered the formation of nanocellulose. However, in the current study, a de-lignified hardwood pulp was not able to produce nanocellulose fibrils in the DAC, which is reverse of the theory and earlier studies. It is therefore believed that the presence of higher lignin in the pulp assists the defibrillation process by making the fibers comparatively stiffer. A higher amount of processing leads to the generation of increased levels of nanocellulose in the presence of lignin.

B.7 Experimental section

B.7.1 Material

Futura 75 cultivar hemp hurds, dew retted and decorticated, was procured from the Netherlands. The obtained hurds were prepared by passing it through a 9.5 mm slot size screen to remove fines. The final hurds were 15-30 mm in length, 4-6 mm in width and 1-2 mm in thickness with 42% cellulose and 27.4% lignin contents. Hardwood chips were 40-50 mm in length, 30-40 mm in width and 3-5 mm in thickness with 44.2% of cellulose and 26.9% lignin contents. Further, bleached hardwood fibers from market pulp has 77.6% cellulose and 2.1% lignin contents.

Distilled water was used for autohydrolysis, washing, and all other purposes. Sodium hydroxide and sodium sulfide were purchased from Sigma-Aldrich.
B.7.2 Method

Auto-hydrolyzed pulp was obtained by adding distilled water to the hemp hurds in the ratio 8:1 and incubating for 3 hours at 160 °C in a 20 L stainless steel pulping reactor (Greenwood Instruments, LLC, Andover, MA, USA). Kraft pulping was carried out using 12% active alkali to achieve 25% sulfidity (NaOH+Na2S) (as Na2O) with a solid to liquor ratio of 1 to 8 (hemp) and 1 to 4 (hardwood), at 160 °C, 620-690 kPa for 3 hours in the pulping reactor. After separating the fibrillated hemp fibers from the liquid phase (black liquor), they were washed with distilled water. Washed fibers were refined for more fibrillation in two stages (first pass at disc gap of 0.1mm and second pass at a disc gap of 0.05 mm) in a disc refiner. On the other hand, hardwood Kraft pulp fibers were refined in three stages (first pass at 0.2 mm, second pass at disc gap of 0.1 mm, and third pass at a disc gap of 0.05 mm) to accommodate the longer fiber length. After dis refining, these pulps were screened with 0.15 mm slotted screen to remove any other unwanted materials. The obtained hemp fiber pulp (10 wt.% and 6 wt.%) was transferred to the closed plastic sample vial suitable for the DAC mixer containing 40 ceramic beads. The ceramic beads were standard 6 mm pharma media purchased from FlackTek, Inc. To obtain nanocellulose fibers by defibrillating hemp fibers, the DAC mixer was run at 3000 rpm for 20 and 60 minutes. Stepwise dilution of cellulose samples with water was done after every 5 min interval of the DAC process to avoid the cushioning effect due to entangled fibers and increase the shear between fibers. For every experiment the final solids contents were half of the starting solids content due to addition of water. This resulted in a final product consistency of ~5 wt.% and ~3 wt.% from the samples begun with 10 wt.% and 6 wt.% consistencies respectively.

The 24 g (dry) pulp fibers were first disintegrated into a 2 L water for 15000 rotations using a Lorentzen and Wettre model 93401 disintegrator. The excess water was drained using a Buckner
funnel to form a pulp cake at 10% consistency. This cake was used in PFI mill for refining for 5000 revolutions.

B.7.3 Characterization

Compositional analysis of cellulose and lignin contents were determined according to the laboratory analytical procedure (LAP) (NREL/TP-510-42618) or the ASTM E1758-01 (2015) standard. The estimation of acid insoluble lignin was done according to TAPPI T222 om-11 (2011) standard and the LAP-010 as per ASTM E1690-08 (2016) standard methods, respectively.

Freeness of the pulp was measured using TAPPI standard ‘T 227 om-99’ for Canadian Standard Freeness (CSF).

Charge estimation on fibers was carried out using the colloidal titration method. The colloidal charge of 200 mL suspension of fibers in diluted water at 0.01% consistency was evaluated by titration using a CHEMTRAC ECA 2000 P streaming current analyzer. The charge neutralization points of fibers were determined by the addition of cationic polymer (poly (diallyl dimethylammonium chloride (p-DADMAC/poly-DADMAC)) to the suspension. A sedimentation test was carried out by diluting the fibers at 0.5wt.% consistency and then leaving the samples on a maintained flat surface for one hour.

The crystallinity of cellulose samples was determined using an X-ray diffraction of the powdered form of the samples. The samples were freeze dried to remove the water. The obtained cakes were broken into pieces and ground into powder. The grinding was done using a FlackTek DAC mixer, without use of any grinding beads. The abrasion of the cake pieces turned them into powder after a minute of grinding at 3000 rpm. X-ray diffraction spectra were obtained with a Rigaku SmartLab diffractometer. The angle was changed to 0.05° per step. The diffraction data
obtained for each sample was deconvoluted to obtain the area for amorphous peaks and crystalline peaks.

To check morphology, the samples were diluted at 0.05 wt.% and coated on aluminum foil before being analyzed with scanning electron microscopy (SEM) under FEI XHR-VERIOS 460L field emission SEM and transmission electron microscopy (TEM) using JEOL JEM-2000FX S/TEM at 200kV in TEM mode.
APPENDIX C: XPS SPECTRA FOR POLYPYRROLE FORMATION

When polypyrrole is formed by oxidation of pyrrole in the presence of ammonium persulfate, the affected surface turns black. This is an indication of the polypyrrole formation. However, more information can be obtained using XPS spectra of the affected surface before and after polypyrrole formation.

C.1 G1 films with polypyrrole

Figure C.1 shows a comparison of C 1s and O 1s spectra for G1 films before and after polypyrrole formation. Details of the C and O engagements in different bond formations can be seen in Table C.1.

Table C.1: XPS carbon (C 1s) and oxygen (O 1s) bonding percentages.

<table>
<thead>
<tr>
<th>Approximate BE (eV)</th>
<th>284.1</th>
<th>285</th>
<th>286.6</th>
<th>288.1</th>
<th>289.4</th>
<th>291.2</th>
<th>531</th>
<th>532.3</th>
<th>533</th>
<th>534.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon/Oxygen bond</td>
<td>C=C</td>
<td>C-C / C-H</td>
<td>C-O</td>
<td>O-C- O / C=O</td>
<td>O- C=O</td>
<td>O- CO=O</td>
<td>O=C</td>
<td>O- C=O</td>
<td>O- C=O</td>
<td>O-C=O</td>
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<tr>
<td>Code</td>
<td>C1x</td>
<td>C2x</td>
<td>C3x</td>
<td>C4x</td>
<td>C5x</td>
<td>C6x</td>
<td>O1x</td>
<td>O2x</td>
<td>O3x</td>
<td>O4x</td>
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<td>G1</td>
<td>0</td>
<td>26</td>
<td>50</td>
<td>19</td>
<td>4</td>
<td>2</td>
<td>29</td>
<td>51</td>
<td>18</td>
<td>3</td>
</tr>
<tr>
<td>G1 with polypyrrole</td>
<td>14</td>
<td>36</td>
<td>31</td>
<td>14</td>
<td>4</td>
<td>2</td>
<td>29*</td>
<td>19*</td>
<td>44*</td>
<td>7*</td>
</tr>
</tbody>
</table>

* Slight shifts of 0.2 to 0.5 eV due to conductive environment of polypyrrole

The presence of C=C in films with polypyrrole is expected as the system must be giving rise to unsaturated bonds. Similarly, C-C linkages increase from 26% to 36% after polypyrrole formation. These links should be the bonds between two pyrrole rings. Relative contributions of C-O, and O-C=O decrease after polypyrrole formation. If O 1s deconvolutions are compared, a major decrease in O-C=O species is seen where contribution decrease from 51% to 19%. On the
other hand, O-C linkages increase from 18% to 44%. Thus, there might be a loss of carboxyl groups during the polypyrrole formation.

Figure C.1: XPS spectra for G1 films. a) C 1s deconvolution for untreated film, b) C 1s deconvolution for film with polypyrrole, c) O 1s deconvolution for untreated film, d) O 1s deconvolution for film with polypyrrole.

C.2 ‘AH L-CMNFS_60 min’ paper with polypyrrole

Figure C.2 shows C 1s and O 1s spectra for ‘AH L-CMNFS_60 min’ paper with polypyrrole. Similar to G1 film, the C=C contribution is seen as present, and was not seen for the paper sample without polypyrrole (Figure A.2 and Table A.2). The relative percentages of C and
O bonding contributions are given in Table C.2, where a row is copied from Table A.2 for easy comparison.

Table C.2: XPS contributions for ‘AH L-CMNF5_60 min’ paper without and with polypyrrole.

<table>
<thead>
<tr>
<th>Approximate BE (eV)</th>
<th>C=H</th>
<th>C-O</th>
<th>C=O</th>
<th>O-C=O</th>
<th>O=CO=O</th>
<th>O=CO</th>
<th>O=C</th>
<th>O=O-C</th>
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<td>535.2</td>
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</tbody>
</table>

| Carbon/Oxygen bond | C1 | C2 | C3 | C4 | C5 | C6 | O1 | O2 | O3 | O4 | O5 |
|--------------------|----|----|----|----|----|----|----|----|----|----|----|----|
| ‘AH L-CMNF5_60 min’ | -  | 50 | 40 | 10 | 0  | 12 | 82 | 6  |    |    |    |    |
| ‘AH L-CMNF5_60 min’ with polypyrrole | 18 | 40 | 26*| 11*| 5  | 1  | 30*| 24*| 28*| 12*| 5* |    |

*Shift of 0.5 to 0.8 eV due to conductive environment of polypyrrole

From oxygen bonding contributions, it can be seen that there is increased carboxyl content, which can be due to oxidation due to APS.

![Figure C.2: XPS spectra for ‘AH LCMNF5 60 min’ samples a) Deconvolution for C 1s, b) Deconvolution for O 1s.](image-url)
APPENDIX D: FUTURE WORK

Utilization of selective hydrophilicity and UV degradation/crosslinking for generating images is possible to solve various limitations of current printing processes. The issues related to ink viscosity, solids levels, and image registration can be minimized by creating an active substrate. The substrate used contains bio-degradable plant based materials and thus it can lead to improved sustainability. It is demonstrated that the hydrogels from cellulosic materials are capable of forming optical elements such as lenses with unconventional processes.

For further development, a detailed study on ink and material interaction can be done to use natural polymer based conductive aqueous inks. Alternatives to pyridine can be searched to reduce the volatile organic content (VOCs). A laser based digital writing system can be developed for fine patterning with selective UV wavelengths so that energy requirements and behavior of material to individual wavelengths can be studied. Also, this will permit contactless imaging and reduce the defects originating from contact masks.

The cellulose based hydrogel contact lenses can be a low cost renewable alternative to synthetic hydrogels. A study of toxicity and eye comfort can be pursued in the future, along with the ability to deliver the drugs.