CHEMICAL MODIFICATION OF CELLULOSE FIBERS AND THEIR ORIENTATION IN MAGNETIC FIELD

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A thesis submitted in conformity with the requirements for the degree of

Doctor of Philosophy

Center for Biomaterials and Biocomposites Processing
Faculty of Forestry
and
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University of Toronto

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2011

Abstract

Studies that involve natural fiber orientation in a matrix were mostly based on regulating shear forces during mixing of fiber and matrix. This study attempts to propose a novel technique for orientating natural fibers like cellulose in a viscous polymer matrix such as polylactic acid (PLA) by applying the concepts of magnetism. Orientation of cellulose fibers in a PLA was achieved by modifying the cellulose fibers with a ferromagnetic entity and subjecting to a magnetic field. Chemically modified cellulose fibers (CLF) were oriented in dilute polylactic acid by subjecting the fiber and matrix to a magnetic field of \( \approx 4 \) T (Tesla). CLF and Microcrystalline cellulose (MCC) were oxidized with Hydrogen peroxide and further reacted with activated Ferrous sulphate heptahydrate (FeSO\(_4\).7H\(_2\)O) in order to form Cellulose-Fe complexes. Chemically modified CLF was characterized by spectroscopic, thermal and morphological methods. The results from X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR spectroscopy) agree that coordination bonds were formed between deprotonated and/or oxidized hydroxyl groups of cellulose and Fe\(^{2+}\).
ions. Powder X-ray diffraction (PXRD) was used to compare the crystallinity of unmodified and modified samples of CLF. Thermal properties of modified cellulose were studied using thermogravimetric analysis (TGA) and a differential scanning calorimeter (DSC). Scanning electron microscopy (SEM) results showed that there was minimal morphological change occurred to cellulose after treatment. It was also observed that the electrical conductivity of cellulose modified with Fe$^{2+}$ was higher than that of unmodified samples. The modified CLF was then mixed with polylactic acid diluted with dichloromethane and the fibers in the matrix suspension were subjected to a magnetic field of $\approx 4$T. The suspension was allowed to solvent cast inside a glass vial in the magnetic field. Morphological examination of the fiber matrix composites using confocal microscopy showed that CLF were successfully oriented along the flux direction of the magnetic field.
Acknowledgements

My deepest and foremost gratitude goes to my major advisor and project supervisor Prof. Mohini M. Sain for all his support and encouragement through the course of this project. Thanks are also due to Prof. Kristiina Oksman for co supervising this project.

I thank all the project committee members for their suggestions and comments that lead to constant improvement of this project thought its course of time. My sincere thanks to Dr. D.N Roy, and Dr. Robert Morris for their technical advice on various aspects of this project. Thanks are due to Dr. Ning Yan, Dr. Rana Sodhi, Dr. Tim Burrow, Dr. Illya Gourevich and Dr. David James for their assistance with various analytical instruments used in due course of this project.

Special thanks to my colleagues Mr. Jaganathan Ulaganathan, Miss Brenna Lattimore, Mr. Carlos Quijano, Mr. Sayed Abthgir, Mr. Sedric Pankras and other colleagues for helping me in various strides of this project and for being with me through thick and thin. Thanks are due to all faculty, staff and students at the Center for Biomaterials and Biocomposites, Center for Environment and Faculty of Forestry for making my stay at Toronto a wonderful experience.

I would also like to thank the Ontario Center of Excellence (OCE) and Materials and Manufacturing Ontario (MMO) for the financial assistance.

Finally I would like to thank my father, mother and sister for their unconditional support, encouragement and love.
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List of Abbreviations

AOM - Angular overlap model
ATR - Attenuated total reflectance
CFT - Crystal field theory
CNW - Cellulose nanowhiskers
CLF - Cellulose long fiber
CMC - Carboxymethyl cellulose
CT - X-ray computed tomography
DTG - Differential thermo gravimetry
FTIR - Fourier transform infrared spectroscopy
HEC - Hydroxyethyl cellulose
LFT - Ligand field theory
MCC - Micro crystalline cellulose
O/C - Oxygen to carbon
PLA - Poly lactic acid
PXRD - Powder X-ray diffraction
SEM - Scanning electron microscopy
TGA - Thermogravimetric analysis
XPS - X-ray photo electron spectroscopy
List of Symbols

∂ (delta) – Resistivity
µm- Micro meter
E” - Storage modulus
E’ – Loss Modulus
eV - Electron volt
G - Free energy
ΔG^0 - Change in free energy
ΔH^0 - Change in enthalpy
[I_o/I_c] – Integrated peak area of carbon divided by oxygen
K - Stability constant
K_{eq} - Equilibrium constant
Kv – Kilo volt
Pa.S - Viscosity
ΔS^0 - Change in entropy
S·m^{-1} – Conductivity
S^{-1} - Shear rate
S_o/S_o - Corrected sensitivity factor of carbon divided by oxygen
T – Tesla
Tan Δ - Storage modulus/Loss Modulus (E”/E’)
T_g - Glass transition temperature
T_m – Melting temperature
T_c - Crystalline temperature
v/v – Volume by volume
1. Introduction

1.1 Overview

Cellulose is the most plentiful, natural, biodegradable and renewable raw material available for versatile applications. Recently there was an ample interest in substituting cellulose in place of inorganic reinforcements/fillers in polymer based composites. This is due to the virtue of cellulose being biodegradable reinforcing agent as well as its adaptability to be tailored for high performance applications in composites (Chakraborty et al., 2005; Puglia et al., 2003; Said et al., 2005). The transformation is well sought after in the wake of stringent environmental concerns. These bio-based composites have soaring demand by automotive industry, construction application, manufacturing household products and in the field of packaging (Mathew et al., 2005; Gallagher et al., 2005).

This study combines the concepts of hydroxyl group modification of cellulose using a ferrimagnetic entity and achieve optimal orientation and dispersion of cellulose fibers in the polymer matrix by subjecting the modified cellulose into a magnetic field. The presence of a magnetic entity in modified cellulose is expected to provide an opportunity to manipulate orientation of fiber by virtue of magnetic properties of Fe$^{2+}$ ions. Studies have been conducted to impart paramagnetic properties in clay particles by cation exchange of Fe$^{2+}$ ions and thus orienting them in specified applications (Pingnon et al., 2003). However, there was only a modest attempt to introduce and apply the concepts of modifying cellulose with paramagnetic substance to facilitate orientation and thus improving mechanical properties (Larenjeria et al., 2006; Shokrieh et al., 2009; Nielsen et al., 2009). Since the OH$^{-}$ groups of cellulose are subjected to modification, there is a potential to reduce the hydrogen bonding between cellulose fibers that usually results in undesirable dispersion and negatively affects the strength properties of cellulose based bio-polymer composites (Kondo, 1997).
There have been only a few studies which explored the orientation of cellulose in a liquid medium. Mostly previous studies suggests about the orientation of cellulose fiber in low viscosity liquids such as water, chloroform and cyclohexane. Dong and Grey, (1997) observed that tunicin whisker suspension in cyclohexane was oriented in a 1 kHz electric field of 2000 V cm\(^{-1}\). In another study tunicin whiskers dispensed in chloroform were oriented along the flux direction of a magnetic field of 7T (Sugiyama et al., 1992). These studies mainly focused on cellulose fibers of dimension ranging from 1 to several micrometers in length and 10-20 nm in width, the solvents had lower viscosity and were seldom polymeric. Moreover, orientation was attained by subjecting cellulose fiber to magnetic field up to 20T. In polymer composite processing it is required that the fiber be aligned in the matrix to obtain desirable properties (Larenjeria et al., 2006).

Currently natural fiber orientation in composites mainly depends on flow properties of the matrix that is difficult to manage (Larenjeria et al., 2006). There is a gap in current knowledge to broaden the concepts of magnetic orientation of fiber to a viscous medium such as a polymer matrix. This study addresses such an effort to apply the concepts of magnetic orientation of cellulose fiber in a polymer matrix by surface modifying the fiber with a ferromagnetic entity. There have not been many studies in this field to align cellulose in a polymer matrix to manufacture biodegradable natural fiber composites. In this scenario it was speculated to be justifiable to modify cellulose fibers to impart magnetic properties and align them in a polymeric matrix. This study focused on modifying cellulose fibers using a ferrimagnetic entity and aligning them in a polymer matrix.

The modified cellulose fibers thus obtained based on this technique will be characterized and analyzed to determine modification, orientation, dispersion and dynamic mechanical properties of fibers and their composites using various instrumentation techniques.
A successful outcome of this study could give explanations in enhancing mechanical, optical, thermal and electrical properties of bio-based composites and commercialization of the concept. Patenting the new findings, prototype trials and the feasibility of technology transfer to industry could be sought. The scope of this research lies in conjunction with practical solution to enhance the properties of bio-based polymer composites and to impart environmental benefits by minimizing utilization of petroleum based polymers and value addition of bio-based composites.

1.2 Justification of the project

The properties of cellulose based composites are not only governed by factors such as fibers length and dispersion of fiber in the polymer matrix, but also the orientation of cellulose fiber in the matrix (Larenjeria et al., 2006). Studies have shown that fiber orientation has a crucial role in determining various properties of bio-fiber composites (Coban et al., 2010, Nielsen et al., 2009). In cellulose - biopolymer composite processing, the inability to control orientation and dispersion of cellulose fiber in polymer matrix pose a challenge (Nguyen et al., 2008). On this basis, even though the environmental and economical advantages are achieved by using cellulose as a filler or reinforcer in bio-based composites, the reduction of properties limits the application of cellulose based biopolymer composite’s potential end uses. In this scenario, it is sensible to modify the cellulose to attain improved orientation and dispersion in a biopolymer matrix to accomplish property enhancement. This study was based on the hypothesis that the use of iron based salts for modifying cellulose to impart magnetic properties onto cellulose by cation exchange and complex formation reactions and eventually will orient the fiber in a biopolymer matrix such as Poly lactic acid (PLA). Apart from fiber orientation this modification can also impart property enhancement of cellulose that could benefit in production of novel products and in other applications such as

- Security paper
• Magneto graphic printing
• Information / Data storage
• Magnetic filtering
• Magnetic shielding
• LCD substrate, etc.

Modification of cellulose for property-enhanced cellulose based biopolymer composites have been extensively studied. However knowledge and information on modification of cellulose that involves imparting magnetic properties for property enhanced application is less studied or not reported. Most of the studies that involve fiber orientation was based on controlling shear forces to make the fiber orient or dispersing unmodified cellulose in a using a low viscosity medium such as chloroform or dichloromethane. In the literature available, such orientation was established by introducing cellulose suspension in high magnetic field up to the rate of 10 to 20 Tesla (T). Generating a magnetic field of this magnitude is energy intensive. Achieving fiber orientation in a lower magnetic field in a viscous matrix have not been cited in literature or studied extensively.

1.3 Research questions and objectives

Currently there is a dearth in information of techniques used to modify cellulose to impart orientation. Using a magnetic entity such as iron for modifying cellulose fiber, orienting the fiber in a polymer matrix and its property enhancement, to the best of the authors knowledge have not been studied yet. The information obtained from this study could act as a bridge to available knowledge and the new findings revealed on magnetic orientation of cellulose.

The primary objective of this study was to modify cellulose fibers (CLF and MCC) by cations (Fe$^{2+}$) and using CLF fibers to produce fiber oriented bio-composites. The fiber orientation characters in different viscosity of PLA were also investigated.
The second objective of this project was to study the details of the effect of modification and its characterization.

The third objective of this study was to investigate the mechanism by which complex formation takes place between cellulose and Fe$^{2+}$ ions.

The fourth objective of this study was to characterize the thermal and dynamic mechanical properties by the help of a thermo gravimetric analyzer, Differential scanning calorimetry and a dynamic mechanical analyzer respectively. The electrical properties of the bio-composite will be analyzed

**1.4 Structure of the thesis**

The finding of the and results of the above objectives are presented in Chapters 2 to 7

The literature review on cellulose, biopolymers and cellulose-based complexes are explained in Chapter 2.

**Chapter 3** explains the mechanism of complex formation between cellulose and Fe$^{2+}$ based on complex formation theories and thermodynamics

Characterizations of cellulose modified by Fe$^{2+}$ salts are explained in **Chapter 4**. The results were also published in the Journal Carbohydrate Polymers (Sundar et al., 2010).

Thermal characterization and electrical properties of iron modified cellulose fibers and microcrystalline cellulose is explained in **Chapter 5**, the results are the base for the paper accepted for publication in Journal of Thermal Analysis and Calorimetry

Chemical modification of cellulose fibers by iron salt and their orientation in a magnetic field is explained in **Chapter 6**. Summary and conclusions and future work suggestions are given in **Chapter 7**
2. Cellulose, Biopolymers and Transition metal complex formation theories

2.1 Cellulose

Cellulose is regarded as one of the most abundant biological polymer available naturally. Cellulose is found in the cell wall of plant, some algae and bacteria (Bielecki and Krystynowicz, 2002). About 40-45 percentage of all the wood species constitute of cellulose. Cellulose comprise of anhydro glucopyranose units attached together by a β-1-4 glycosidic linkage with a degree of polymerization between 3500 and 12000 (Figure 2.1) (Sjostrom, 1993; Fengel and Wegener, 1984). The glycosidic bonds are formed when a molecule of water is eliminated from 1st and 4th positions of two adjacent monomers of cellulose (Lai, 2001). Cellulose biosynthesis in plants results in formation of micro fibrils which are flat ribbon like structures held together hydrogen bonds and vander waals forces. During biosynthesis, when monomer units are added to the polymer chain, they rotate 180° in relation to the adjacent molecule resulting in twofold screw symmetry (Brown, 1996). The glycosidic bonds between monomers of cellulose are hemi acetal in nature that can cleave in acidic and alkaline conditions. The functional groups present in cellulose can be oxidized to aldehydes, ketones and carboxylic groups (Lai, 2001).

![Figure 2.1 Cellulose chain with 1-4 β glycosidic linkage between adjacent monomers](image-url)

Figure 2.1 Cellulose chain with 1-4 β glycosidic linkage between adjacent monomers
The strong inter and an intra molecular hydrogen bond contributes to high strength properties associated with cellulose. These strong bonds also results in an orderly arrangement of the fibrils resulting in a crystalline structure within cell wall of a plant. However there are some areas where the orderly arrangements is loosely followed resulting in an amorphous region of cellulose. These regions are more reactive compared to crystalline region (Klemm et al, 1998). The two main forms of cellulose present are cellulose-1, which is originated from plants in its natural form and cellulose-2 which regenerated form cellulose -1. Cellulose-1 consists of two allomorphs α and β cellulose (Eichhorn et al., 2005, Hart and Atalla, 1984).
2.2 Micro crystalline cellulose (MCC)

Cellulose fibrils can be obtained from many natural sources such as wood pulp, cotton, ramie, bacterial cellulose etc. Cellulose structure arise from individual glucan chain combining to form long thread like structure called micro fibrils. These cellulose chains are held together by hydrogen bonds and Van der Waals force. Native cellulose consist of an amorphous and crystalline region resulting in a semi crystalline structure. Usually the amorphous region acts as defects and can be easily removed by treating native cellulose with mineral acids. The resulting product will be crystalline cellulose with synonyms such as whiskers, nanocrystals, microcrystalline cellulose, cellulose crystallites etc (Battista and Smith 1962, Samir et al, 2005). It is also observed that the aspect ratio and charge of these crystals varies depending on source and mineral acid used for treatment respectively. Native cellulose comprise of two crystalline forms, namely a one-chain triclinic structure I\(_\alpha\) and a two-chain monoclinic structure I\(_\beta\). The fractions of I\(_\alpha\) and I\(_\beta\) phases in any native cellulose samples depend on the origin of the cellulose. Studies have shown that microcrystalline cellulose has high tensile strength which is better than most of the reinforcements used in polymer composite manufacturing. Stability, inertness, biodegradability and higher mechanical properties make microcrystalline cellulose a good candidate in the manufacturing of biodegradable polymer composites.

2.3 Cellulose fibers (CLF)

Cellulose fibers or cellulose fibrous – Long (Product nomenclature by Sigma), is essentially cellulose fibers obtained from various sources such as wood, rice straw or cotton with a higher aspect ratio (Reddy and Yang 2006). The fibers used in this study were cotton linters obtained from Sigma Aldrich, product number C6663. These fibers have amorphous and crystalline stages embedded
within the fiber. The aspect ratio was 10.0–21.0 as observed using a scanning electron microscope.

2.4 Biopolymer polymer and their classification

Growing environmental consciousness in the past two decades have paved way to open up frontiers in developing new polymers which are environmentally benign (Mathew et al., 2005). These bio-based polymers are replacing the mainstream petroleum polymers that are currently dominate the market. The use of these environmentally friendly polymers is curtailed in a considerable extent due to its inherent performance limitation and production cost compared to conventional plastics (Sodergard and Stolt 2002). However the considering the life cycle analysis and environmental benefit, biopolymers will be having an upper hand compared to conventional plastics where it can be replaced. Bioplastics can be widely classified into (a) the plant polymers cellulose, polysachhrides, proteins etc and (b) the bio polyesters which includes Poly lactic acid (PLA), Poly hydroxy alkonoate, aliphatic and aromatic copolyesters. Among these biopolymers, PLA has a huge potential to be tailored for making biocomposites (Averous, 2008). This is due to PLA’s versatility to be manufactured from different renewable agricultural resources, biodegradability, and competitive market price. PLA has been commercially produced in large quantities by companies around the world such as Cragill Corporation (USA), Mitsui chemicals (Japan), Trofan (Netherlands), Boeringher Ingelheim (Germany) etc. Studies have proven that PLA is biodegradable as well as biocompatible. PLA can also be tailored for different properties by adding plasticizers, fillers, grafting with other polymers etc (Averous, 2008). Figure 2.3 gives a detailed account on the classification of bio based polymers.
2.4.1 Poly lactic acid synthesis

Lactic acid is known to humans for a longtime as they were present in fermented lactose. Industrial production of lactic acid began in early twentieth century and has been used in various industrial and pharmaceutical applications. Lactic acid has an l and d isomer. Commercially lactic acid is produced from fermentation of carbohydrates by bacteria. The isomers of PLA obtained by fermentation depends on the species of bacteria used which is usually a species of *Lactobacilli*. Bases such as CaCO$_3$, Ca(OH)$_2$, Mg(OH)$_2$, NaOH, or NH$_4$OH are added to neutralize the fermentation and to give soluble lactate solutions. This solution is evaporated, purified and acidified with sulphuric acid to obtain lactic acid (Sodergard and Stolt, 2002; Averous, 2008).
The cyclic dimer of lactic acid combine together to form lactide. The lactide formed can be from lactic acid with l or d isomers or a combination of both (Figure 2.4). The ratio of l and d racemic mixtures of lactide formed is determined by the bacteria used, feed stock, temperature and catalysts used in the process.

There are three different methods to produce PLA from lactic acid such as a) Condensation polymerization b) Dehydration and condensation c) Lactide ring opening reactions (Figure 2.5). Condensation polymerization produce short chain length PLA while dehydration condensation process produce PLA with higher chain length with the help of an enzyme. Lactide ring opening reactions are performed in presence of cationic and or anionic catalyst such as stannous octoate. The ring opening polymerization yields PLA with high molecular weight compared to other processes (Mathew et al., 2006; Sodergard and Stolt 2002, Averous, 2008).
2.5 Complex formation theories

The compounds that contain a central metal atom or an ion surrounded by other molecules or ions are called coordination complexes. Usually the complex can be charged, non-charged or neutral depending on the sum of charges of the central atom or the associated molecules or ions (Basolo and Johnson, 1986, Crabtree, 1994). The relevance of coordination complexes are very important in every day biological processes such as photosynthesis, oxygen transport in blood with the help of hemoglobin and various other processes. In general metal complexes are formed by the reaction of between a salt and some other ion or molecule. Many anions such as \(\text{NH}_3^-\), \(\text{CN}^-\), \(\text{NCS}^-\), \(\text{NO}_2^-\) form metal complexes (Basolo and Johnson, 1986). The complexes usually are stable in solutions but there are cases where there could be partial dissociation. The discovery of hexamine cobalt (III) Chloride, Co.Cl\(_3\) .6NH\(_3\), by Tassaert in 1798 marks the beginning coordination chemistry (Basolo and Johnson, 1986). The experimental observation at that time was not sufficient to support the bonding of these molecules based on valence of these molecules, which triggered scientists and
chemist to understand the structure and bonds formed between these coordination complexes. Other theories that tried to partially explain complex formation include Bolmstrand - Jorgensen chain theory, Werner’s coordination theory and Valance bond theory. However crystal field theory was strategic in explaining many properties of coordinated complexes based on spectroscopic, spacial and magnetic properties.

2.5.1 Crystal field theory

The crystal field theory (CFT) explains the formation of ligands based on positive and negative charges assigned to metal ions and charged ligands respectively. The ligands could also be negative end of uncharged polar ligands (Ballhausen, 1962). CFT totally eliminates the concept of covalent bonding but only the attraction resulting from charge differences. The energy of the bonds formed calculated using the classical energy equation that accounts for attractive and repulsive forces between particles (Basolo and Johnson, 1986).

Bond energy \( \propto \frac{q_1 q_2}{r} \), where \( q_1 \) and \( q_2 \) are charges of the interacting ions and \( r \) the distance between them. The spatial orientation of d orbital’s is cardinal to the understanding of CFT. The d orbital’s of the metals and ligands produces an effect termed as crystal effect. This can be illustrated with the help of an example of a complex such as Titanium hexa flouride \([\text{TiF}_6]^{2-}\). In a \( \text{Ti}^{4+} \) ion \([1s^2, 2s^2, 2p^6, 3s^2, 3p^6]\) there are no d orbital electrons (Syarkin and Dyatkina, 1964). The 3d orbital of the ion has identical energies and hence called degenerate orbitals. In the case of \([\text{TiF}_6]^{2-}\), six \( \text{F}^- \) ions are surrounded by \( \text{Ti}^{4+} \). The d orbitals of \( \text{Ti}^{4+} \) are more difficult to be filled due to the repulsion of similar charge from \( \text{F}^- \) ions. However in a 3 dimensional special orientation of this is concept is only hypothetical. \([\text{TiF}_6]^{2-}\) has an octahedral structure and the \( \text{F}^- \) ions reside in the x, y and z axis. The splitting of the five d orbitals resulting in degenerate orbital is the key in forming the bonds among the central metal ion (Figure 2.8)( Lee, 1983). The \( d_{x^2-y^2} \) and \( d_{z^2} \) orbitals points towards \( \text{F}^- \) ions and referred as \( e_g \) orbitals. The points between ligands namely \( d_{xy}, d_{xz}, d_{yz} \) orbital’s are called \( t_{2g} \) orbitals (Basolo and Johnson, 1986).
The energy levels of $t_{2g}$ orbital’s are different than $e_g$ orbitals. Having higher energy than that of $t_{2g}$ makes it difficult to place electrons in $e_g$ compared to $t_{2g}$. This phenomenon of degenerate d orbital’s having different energy levels is mentioned as crystal field splitting (Syrkin and Dyatkina, 1964, Lee, 1983).
splitting of d orbitals primarily occurs due to 3D arrangement of the atoms and influence of neighboring atoms and ions on individual ligands and metals. CFT can be explained by the help of sponge ball structure representing a metal ion. In the case of an octahedral system such as \([\text{TiF}_6]^{2-}\), The six F\(^-\) ions concentrate its total force on six particular points which will be pressing the sponge ball structure inwards and leaving positions which are not presses bulged outwards. In CFT the bulges represents \(t_{2g}\) orbitals and the depression represents \(e_g\) orbital's. The \(e_g\) orbital’s points towards the F\(^-\) ions and have higher energy (Figure 2.9). In a 3D arrangement the electrons will add to lowest energy shell. In the case of \([\text{TiF}_6]^{2-}\) ligands once the fluorine atoms are attached , the ligands add to shells which will be having lower orbital energy. These orbital's have lower energy than that of degenerate orbital's. CFT explains that the ligands do form because the formation of a complex is of lesser energy than that of separated metal ions and ligands. In crystal field theory the symmetry of the complex is the crucial factor that decides the d orbital splitting pattern which results in bond formation of the complex (Basolo and Johnson 1986).

\[\text{Energy} \quad \begin{cases} d_{z^2} \\ d_{xy} \\ d_{xz} \\ d_{yz} \\ e_g \\ t_{2g} \end{cases}\]

**Figure 2.8** Field splitting in d- orbitals representing high energy (\(e_g\)) and low energy (\(t_{2g}\)) molecular orbital’s. (Basolo and Johnson 1986).

2.5.1.1 Magnetic properties based on CFT
Magnetism is of a material is explained on the basis of unpaired electrons present in the shells. A metal ion containing 3d electrons will be having three unpaired electrons because there will be only one electron in each of the three out of 5d orbitals (Mabbs and Machin, 1973). With the support of hunts rule it is predicted that electrons will add one by one to each orbit before they are paired. So the presence of unpaired electron contributes to magnetic properties of a material (Jackubovics, 1987).

2.5.2 Ligand field theory

The term ligand field theory covers all the aspects of which an ion or atom is influenced physically by its adjacent ligands. Ligand field theory (LFT) includes the concepts of chemical bonding between ions/atoms and its adjacent atoms. Apart from bonding explained by in crystal field theory, ligand field theory also accounts for spectral, thermodynamic and magnetic properties of coordination compounds. For a particular central metal ion to be treated by ligand field theory, there should be a dependence of at least one of the physical properties on the nature of coordination environment (Ballhausen, 1962).

2.5.2.1 Geometric distortion based on ligand field theory

In a stable complex system the average energy of the system is expected to be correlated to the way in which electrons are distributed in $t_{2g}$ and $e_g$ orbitals. When electrons are added as a result of bonding the d electrons get filled in the orbit with lower energy, subsequently when there is more electrons they get added to the higher energy level shell. Due to this ligand field splitting, irregularities in properties such as bonding energy will evolve. When an electron occupies a higher energy orbital, lengthening of the metal-ligand bond could occur in the direction of the d orbital lobes involved in bonding. Geometric distortions occur like this could be explained with the help of ligand field theory (Basolo and Johnson 1986; Ballhausen, 1962).
2.5.2.2 Spectral properties based on ligand field theory

The spectral lines from a coordination complex can be either ligand field band or a charge field band. Ligand field band are related with transitions among the d orbital of the central metal ion. This can be well explained by ligand field theory. In an octahedral structured complex an excitation of an electron from $t_{2g}$ to $e_g$ can produce a spectral line which corresponds to ligand field band. Usually the spectral lines thus produced are in a range about 5000 cm$^{-1}$ to 40,000 cm$^{-1}$.

Charge transfer band arise due to charge transfer from central ion to ligand atoms or vice versa. Though charge field band can be explained by crystal field model considering central metal ion and ligands have positive and negative charge, it is more original to explain them based on ligand field theory as ligand field bands are also involved. The ligand field theory is better in explaining the mixing of charge between central ion and ligand on the basis of molecular approach rather than covalent complex approach. The charge transfer between central ion and ligand can result in change in oxidation number of the central ion hence called redox spectra.

2.5.2.3 Magnetic properties based on ligand field theory

The spin and angular momentum of electrons are related to magnetic dipole. Orbital angular momentum and spin angular momentum contributes to each other in an induced dipole. Different class of magnetic materials and their atomic scale dipole moments are given in table 5.1 (Mabbs and Machin, 1973).

<table>
<thead>
<tr>
<th>Class</th>
<th>Structure on atomic scale</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamagnetic</td>
<td>Atoms have no permanent dipole moments</td>
<td>Noble gases, diatomic gases, H$_2$, N$_2$, many metals such as</td>
</tr>
</tbody>
</table>
### Angular overlap model (AOM)

This model is derived from ligand field theory mostly based on molecular orbital approach. This model interprets the d orbital splitting of metal ion in terms of weak $\sigma$ - and $\pi$- bonds formed with ligands compared to electrostatic attraction from crystal field theory. The orbital’s taking part in bond formation is mentioned as bonding orbital’s and those which doesn’t take part are called anti bonding orbitals. Usually the bonding orbitals are balanced by anti bonding orbital’s which have higher energy. The major features of AOM are as follows.

- **a)** Though the metal and ligand are mostly ions which take part in coordination complex, there is a considerable covalent relation ship between these two

- **b)** The bond energy is mostly calculated from metal’s s orbital’s and p orbitals involved in bonding however the interaction involving metals d orbital is neglected
c) The formal oxidation charges of metals can be considerably less as the s and p orbitals involved in bonding are covalent in nature which in turn allow the expansion of the d orbitals.

d) The extent of overlap and energy separation between metals d orbital and ligand orbitals determines the degree of interaction between metal and ligand.

e) The oxidation state of the metal and electro negativity of the ligand influences the energy gap between metal and ligand orbital’s

The theoretical background in complex formation is important for understanding the mechanism of Fe$^{2+}$ complexion with cellulose. The magnetic properties, coordination number and geometrical structure of the complexes formed can be explained on basis of these theories. A detailed literature review on complex formation of transition metals with ketones, aldehydes and hydroxyls are given in chapter 3 and 4.
3. Mechanism of complex formation of \( \text{Fe}^{2+} \) with modified functional groups of cellulose

3.1 Abstract

A survey of previous works done to explore and understand complex formation of hydroxyl and carbonyl groups with transition metals were explained in this chapter. The reaction mechanisms of complex formation of \( \text{Fe}^{2+} \) ions with the modified functionalities of cellulose were explored. Complex formation mechanism was studied and explained on the basis of orbital hybridization and thermodynamic principles. Possible mechanism for the magnetic properties shown by modified cellulose was explained on the basis of crystal field theory.

3.2 Complex formation of transition metals with selected functional groups

In literature, the associations between \( \text{Fe}^{2+} \) ions and cellulose functionalities have been studied marginally. However there are a few studies that attempt to explain the mechanism during coordinate formation between \( \text{Fe}^{2+} \) ions and cellulose based ligands. The influence of anionic and neutral ligands on the reactivity of cationic iron complexes towards methanol, ethanol, and propanol has been studied by using \( \text{FeCl}_2^+ \) as a cationic core. The cations were neutralized by respective alcohol groups (R-OH) to form complexes, e.g. \( \text{FeCl}_2^- (\text{CH}_3\text{OH})_n^+ \). The resulting structure was dependent on the outer electronic orbital configuration of Iron (Ar.d\(_6\), s2) that favors the formation of octahedral complexes (Trage et al, 2006). Bock et.al., (1971) have studied the structure and bonding pattern of metals with diketones using 2, 4 – pentanodione and transition metals and established that the diketone exist in an equilibrium between keto and enol form which will be reflected in the formation of complexes with metal. The tautomers contribute to formation of resonating bond between metal and the keto group based ligands. In \( \beta^- \) diketones, the possibility of coordination arising from
mono, di and poly nuclear complexes were studied (Figure 3.1). Depending on the nucleophilic nature of the ligand, diketone can possibily coordinate with one or more metal ions. This study has also shown that complexes with keto groups are replace with N, P and S (Skopenko et al., 2004).

![Figure 3.1 Metal bonding in diketones with similar and dissimilar ligand](Skopenko,2004)

Another study revealed that when sodium carboxymethyl cellulose was reacted with Cr$^{3+}$, gave two ligands it was also observed that two water molecules were bound to the metal atom. It was observed there was a strong covalencey in the $\sigma$- bonds formed between metal atom and the functional group of cellulose. Other characteristic of this complex was that apart from the carboxymethyl group, chelating sites were also formed through ether, carboxyl oxygen atoms and also secondary hydroxyl group. The bonds formed involving secondary alcohol group can be affected by stearic hindrance of the OH groups attached to adjacent C atom. However, in the presence of a cation (Transition metal) the geometric stability favors formation of ligands with metal involving these two adjacent OH group (El- Saied et al., 1994). Another study observed that hydroxyethyl cellulose (HEC) and carboxy methyl cellulose (CMC) can be complexed with FeCl$_3$, Fe(NO$_3$)$_3$, Fe$_2$(SO$_4$)$_3$ to form monoligand complexes. The Fe$^{3+}$ complexes formed were arranged spatially in tetrahedral coordination with HEC and CEC (Hosny et al., 1997). The same group of researchers have also studied
the complexes formed between Cr\(^{3+}\) and Ni\(^{2+}\), Co\(^{2+}\), and Cu\(^{2+}\) chlorides and hydroxyethyl cellulose (HEC). From the IR spectra it was predicted that HEC acted as negatively charged bidentate ligand in the case of Cr\(^{3+}\), Ni\(^{2+}\) and as a neutral ligand when complexed with Co\(^{2+}\), and Cu\(^{2+}\). It was also observed that the oxygen from primary and secondary ethoxy groups were involved in the complex formation. The geometrical structures for these compounds were expected to be in octahedral arrangement for Cr\(^{3+}\), Ni\(^{2+}\), Co\(^{2+}\) and square planar for Cu\(^{2+}\) based complexes (Hosny et al., 1995).

Bulky molecules like diaryl 1,2- diketone bis (2,6-diisopropylphenyl) glyoxal (L) were complexed with Iron and Nickel (Figure 3.2). The cations such as Fe\(^{2+}\) and Ni\(^{2+}\) can contribute to \(\pi\) overlapping with ligands and form aromatic rings (Spikes et al., 2008).

![Diketone bond arising from adjacent carbon atoms](image)

**Figure 3.2** Diketone bond arising from adjacent carbon atoms (Spikes, et al., 2008)

In another work the acetyl end groups of long chain polymers were reacted with methyl acetate in presence of a base to form \(\beta\)- diketones on the surface of the polymer. With the presence of more reactants in basic conditions the reaction continued to produce \(\beta\)- triketones. These keto groups were effectively complexed by metal groups to produce metal based polymers (Figure 3.3) (Zaw and Henry, 1995).
Earlier Iron has been used widely in preparation of wood preservative chemicals. Propyl gallate was complexed with Fe$^{2+}$ ions in laboratory titration. The Iron species distribution, stability constant (k) and coordination compounds formed at various pH were investigated. It was observed that iron propylgalate can complex with wood at acidic conditions and enhance the antifungal properties (Binbuga et al., 2005). Fe$^{3+}$ ions were complexed with cellulose fibres mostly from cotton, lyocel and modal to form hepta D- gluconate complexes. It was observed that at pH 8 and 13, the formation of complexes was on the peak. pH value of 13 has favored high degree of complex formation compared to 8. It was reported that at 13 pH 1150 mg of Fe$^{3+}$ was complexed with a Kg$^{-1}$ of cellulose (Kongdee and Bechtold 2004). In another study transition metal ions such as Co$^{2+}$, Cu$^{2+}$, Zn$^{2+}$ were complexed sodium D-gluconate and glycene. The complexes were introduced to cellulose in a pH ranging from 7-13. It was observed that due to cation exchange process the M$^{2+}$ (metal ion) complexed with cellulose leaving D-gluconate and glycene via cation exchange process. It was observed from the results that the formation of complexes depend on ligand charge, Solution pH, complex species and type of cellulose used. The study suggests at pH 7 and 11, there was a decreasing trend in complex formation. However at pH 13 higher rate in complex formation was observed for Cu$^{2+}$ and at pH 11-12 the same trend was observed for Zn$^{2+}$. The lower complex formation properties for Cu$^{2+}$ at pH 7 and 11 were due to formation of species that are not favorable for complex formation (eg Cu$^0$). A similar trend was observed for Zn$^{2+}$ due to formation of
Zincate above pH 13. The optimum pH for Zn\(^{2+}\) for complex formation was observed between 11-12 (Kongdee and Bechtold, 2009).

Acidified carrageenan and cellulose sulfate were reacted with iron salts to produce iron oxy hydroxides based polysaccharides. The formations of these complexes were dependent on pH. The stability of these complexes was studied from pH 7-13. It was observed that the stability of the complex was affected by charge of the complex and species formed at a given pH. The optimum pH for stability for these complexes were reported to be at 13 (Jones et al., 2000).

3.3 Experimental

3.3.1 Materials

Cellulose fibers (CLF) was purchased from Sigma–Aldrich, Canada. The cellulose was used without further purification. Sodium hydroxide (NaOH) of 1M strength was used for intra crystalline swelling of cellulose. Ferrous sulfate FeSO\(_4\).7H\(_2\)O (98% purity) obtained from Fluka Chemika and Hydrogen peroxide of 30% v/v strength was used. In high pH hydrogen peroxide dissociates and results in the formation of perhydroxyl anion. These anions are strong oxidizing agents due its high electron donating ability. Oxidized cellulose was mixed with a solution of FeSO\(_4\) and NaOH in the ratio 7:12 respectively. This mixture of solution is expected to generate Fe\(^{2+}\) ions that will eventually get complexed with oxidized hydroxyl group of cellulose. The detailed account of oxidation of cellulose and formation of Fe\(^{2+}\) ions are explained in chapter 5.

3.3.2 Fourier transform infra red spectroscopy (FTIR)

FTIR-ATR (attenuated total reflectance) analysis of Iron modified cellulose was performed using a Bruker Tensor 27 instrument. The samples were subjected to 45 scans/s and 4cm\(^{-1}\) resolutions. The absorption peaks from wave numbers 4000 to 400 cm\(^{-1}\) were analyzed.
3.4 Mechanism of complex formation of Fe$^{2+}$ with modified functional groups of cellulose

The hydroxyl groups of cellulose was oxidized using hydrogen peroxide. After oxidization, the results from FTIR have shown that there were peaks representing carbonyl groups that might have arisen from keto or aldehyde functional groups (Figure 3.4). The Fe$^{2+}$ ions are expected to complex with the oxygen of the carbonyl group that have arisen from oxidization of cellulose hydroxyl group to either keto or aldehyde group (Bock et al., 1971). The unreacted hydroxyl groups are expected to form complexes with iron involving cation exchange/substitution reactions (Spikes et al., 2008, Kongdee and Bechtold 2004).

Figure 3.4 Spatial arrangement of electron clouds in carbonyls, (Wade, 1999)

3.4.1 Reaction with alcohol and carbonyl groups

After oxidizing cellulose, peaks were observed for carbonyl groups around 1650 to 1750 cm$^{-1}$ representing ketones and or aldehydes. Peaks were also observed at 3500 cm$^{-1}$ essentially from hydroxyl (OH$^-$) groups (Figure 4.3). There were no characteristic peaks around 1550 cm$^{-1}$ representing carboxylic groups, which suggests that the oxidation of cellulose have not resulted in formation of any
carboxylic groups. Cellulose molecule have three alcohol group, When reacted with NaOH the OH\(^-\) group gets deprotonated and Na\(^+\) ion replaces the H\(^+\) ion. Further in presence of Fe\(^{2+}\) The Na\(^+\) get displaced and Fe\(^{2+}\) coordinated with the oxygen atom. Since Fe\(^{2+}\) has six electrons available in the d orbital Fe\(^{2+}\) complex with six adjacent oxygen atom available from OH\(^-\) groups.

\[
R-OH + Na \rightarrow R-O-Na^+ + \frac{1}{2} H_2
\]

\[
R-O-Na^+ + Fe^{II} \rightarrow R-O-Fe
\]

Oxidized cellulose with keto and or aldehyde groups were reacted with Fe\(^{2+}\) in the presence of NaOH. The carbonyl groups of oxidized cellulose can exist in keto or enol form in the presence of a strong base. The ratio of these mixtures depends on the equilibrium kinetics of the reactants. The enolate ion is a stronger nucleophile when compared to keto form. The reaction happens in such a way that when ketones react with a metal, their corresponding alkoxide is formed. The number of bonds formed with the metal depends on the unfilled orbital of the metal ion.

Figure 3.5 gives an illustration about the formation of keto and enol form of a carbonyl group in the presence of a strong base. The double bond between oxygen and carbon atom resonates between the C-C bond and C-O bond. When the double bond is shifted towards C-C, the oxygen atom will have an extra pair of electron available which makes it a stronger nucleophile.
In presence of a strong base such as NaOH, the lone pair electrons of the carbonyl group are shared with the metal to form complexes. Fe\(^{2+}\) forms an octahedral spatial arrangement when it forms a complex. To form an octahedral structure, it involves six sites for bonding.

3.4.2 Complex formation of Fe\(^{2+}\) with cellulose based on orbital hybridization

The energy level difference between 3\(^d\), 4\(^s\), and 4\(^p\) orbital are not significantly different and electron transition can take place between these orbitals with out much hindrance. These exchanges of unpaired electrons do not involve energy changes of any considerable magnitude. The maximum number of unpaired electrons that is possible in these orbitals are five in \(d\), one in \(s\) and three in \(p\) orbitals.

**Figure 3.5** Keto and enol forms of carbonyl group in presence of strong base, (Wade,1999)
Table 3.1 Electron distribution in Fe metal and ions

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Fe²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>↑↓</td>
<td>↑↓</td>
</tr>
<tr>
<td>d orbital</td>
<td>↓</td>
<td>↑</td>
</tr>
<tr>
<td>s orbital</td>
<td>↓</td>
<td>↓</td>
</tr>
<tr>
<td>p orbital</td>
<td>↑</td>
<td>↓</td>
</tr>
</tbody>
</table>

The maximum number of unpaired electrons that is possible is therefore nine in these orbitals (Crabtree, 1994). In iron there are six electrons in d shell, when in an ionic state of Fe²⁺ the two electrons in the s orbital are lost. The six electrons in the d shell are available for forming bonds. The majority of the complex compounds have a coordination number or the electrons in d orbitals numbering either four or six. Literature suggest that if the coordination number is six the corresponding complex will have an octahedral spatial configuration in the bonds formed with the central atom (Syrkin and Dyatkina, 1964). In the case for Fe²⁺, during complex formation the electrons will be added in the order two in d, one in s and three in p depending on the complex formed to give d²sp³ hybrid orbital’s with the orbital’s close to the atom directed towards six corners of a regular octahedron (Gustorf, et al., 1981).

The transition elements atoms can form both σ and π bonds. In a bond only one σ bond is permissible and the number of σ bond should not exceed the number of atoms surrounding them. It has been established that there can be six σ bonds in a d²sp³ hybridized orbital (Gustorf, et al., 1978).
**Table 3.2** Electron distribution during formation of Fe$^{2+}$ complex with ligand

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Fe$^{2+}$</th>
<th>Fe$^{2+}$-[O$_6$]</th>
<th>d orbital</th>
<th>s orbital</th>
<th>p orbital</th>
<th>Electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>↑↓</td>
<td>↑↓</td>
<td>↑↓ ↑↓ ↑↓</td>
<td></td>
<td></td>
<td></td>
<td>Fe$^{2+}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>↑↓ ↑↓ ↑↓</td>
<td></td>
<td></td>
<td></td>
<td>O$^-$</td>
</tr>
</tbody>
</table>

**Figure 3.6** Spatial distribution of proposed octahedral Fe$^{2+}$ complex formed with cellulose

Cellulose when oxidized with an oxidizing agents such as hydrogen peroxide, the hydroxyl groups is expected to get oxidized to ketone, aldehydes, or carboxylates, however, all the hydroxyl groups may not be oxidized depending on the reactivity of the hydroxyl group pertaining to amorphous or crystalline
region (Sjostrom, 1993). Oxidized cellulose may possess non substituted cellubiose unit, mono substituted cellubiose unit (2,3 or 6 derivatives), di substituted cellubiose unit (2-6, 3-6 or 2-3 derivatives) or fully substituted cellubiose unit (2,3&6 substituted derivatives). The Fe$^{2+}$ cations can react with these cellulose units depending on the functional group at 2,3 and 6 derivatives. For OH$^{-}$ ligands originated from cellulose, cation exchange occurs and electrostatic bonds will be formed. In presence of Ketones and aldehyde groups, complex formation reaction based on coordinate covalent bonds are expected to be formed (Gustorf et al., 1981, Kongdee and Bechtold, 2004, Kongdee and Bechtold, 2009). Once introduced to cellulose, the possibility of Fe$^{2+}$ to exist in cellulose can be:

a) Un coordinated form due to stearic hindrance or lest proximity to hydroxyl groups derivatives

b) Complex formation can take place with out satisfying all the possible coordination valencies of Fe$^{2+}$ (Max coordination number of Fe$^{2+}$ is 6)

c) If all possible vacancies (coordination numbers) are satisfied to form octahedral complexes (Figure 3.6) (Gustorf et al., 1981, Gustorf et al., 1978, Crabtree, 1994, Basolo and Johnson, 1986, Syrkin and Dyatkina, 1964).

3.4.3 Complex formation of Fe$^{2+}$ with cellulose based on Thermodynamics

Energy changes accompanying chemical and physical changes are best described by thermodynamics. These changes in energy levels are cardinal in describing a system at equilibrium. Equilibrium constant $K_{eq}$ is defined as

$$A + B \Leftrightarrow C + D$$

$$K_{eq} = \frac{\text{products}}{\text{reactants}} = \frac{[C][D]}{[A][D]}$$
The value of $K_{eq}$ gives information about if the products or reactants are more stable. If the value for $K_{eq}$ is greater than one the reaction is favored towards right in the equation and vice versa. From $K_{eq}$ value, free energy ($G$) and change in free energy ($\Delta G$) can be calculated. Change in free energy can be represented as

$$\Delta G = (\text{free energy of products}) - (\text{free energy of reactants})$$

The relationship between $\Delta G^0$ (Free energy change) and $K_{eq}$ is given by the equation

$$K_{eq} = e^{-\Delta G^0 / RT}$$

or

$$\Delta G^0 = -RT \ln K_{eq} = -2.303RT \log_{10} K_{eq}$$

Where, $R = 1.987 \text{ cal/Kelvin-mol}$
$T = \text{Absolute temperature in Kelvin}$
$e = \text{the base of natural logarithm}$

The equation suggests that a reaction is favored when $K_{eq} > 1$, ie if $\Delta G^0$ has negative value energy is released and vice versa. The equation also predicts the reaction proceed from higher energy state to lower energy state resulting a decrease in free energy. The two major factors contributing to change in free energy are change in enthalpy ($\Delta H^0$) and change in entropy ($\Delta S^0$). The relation between change in free energy, enthalpy and entropy can be correlated with the equation

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

If weaker bonds are broken and stronger bonds are formed, the reactions can be exothermic. If stronger bonds are broken and weaker bonds are formed the
reaction can be endothermic. Reactions tend to favors products with maximum entropy. A positive value in entropy change contributes favorable to (negative contribution) to change in free energy. In the case of ligand formation between Fe\(^{2+}\) and carbonyl groups, the bonds formed are stronger when Fe\(^{2+}\) cations are exchanged with existing H\(^+\) or Na\(^+\) ions possibly existing as tautomers in carbonyl group. Often a reaction is favored by enthalpy changes than entropy changes as the contribution of change in entropy to a reaction is less significant compared to change in enthalpy. So even if the freedom of motion is jeopardized, the ligand formation favors strong bond formation.

### 3.4.4 Magnetic properties on complex formation of cellulose with iron

Electromagnetic theories suggest that dipoles that are magnetic in nature align in opposite directions so that the field will cancel out. This does not hold good with materials such as ferromagnets. In these materials magnetic dipoles tends to align in same direction observing a quantum mechanical effect called exchange interaction. Under certain conditions, such as in ferromagnets, when valance electrons forms bonds between atoms by overlapping the orbitals the distribution of the charge of the electrons can be further minimized and thus attaining more stability by having parallel spins than having opposite spins (Neel, 1948, Mabbs and Machin, 1973). The difference in energy for the electrons attained either parallel or opposite spins are called exchange energy. The exchange interaction energy will be more in ferromagnetic materials when compared with dipole interaction. Spontaneous magnetization is a characteristic of ferri and ferro magnetic materials below Curie temperature (Jackubovics, 1987). In ferromagnetic materials the magnetic moments of electrons are arranged parallel where as in anti ferrimagnetic they are anti parallel. As the temperature increases towards Curie temperature they become less aligned and above Curie temperature they becomes paramagnetic were there is a random disorder in magnetic moment (Jackubovics, 1987; Mabbs and Machin,1973).
In formation of cellulose iron complex, the temperature is kept below 770°C which is the curie temperature of iron. The Fe$^{2+}$ ions act as a ferrimagnet with unequal opposite moments that imparts magnetic moment to the cellulose when modified. If the charge gets neutralized by complexing with cellulose then ferromagnetic properties may be exhibited by iron with parallel spins.

3.5 Conclusion

Oxidized cellulose when reacted with Fe$^{2+}$ resulted in formation of Cellulose-Fe complexes. The peak obtained from FTIR around 3800 and 3600 cm$^{-1}$ represents cleavage of primary and secondary hydroxyl groups. The theoretical rationales behind the formation of complexes were addressed on basis of orbital hybridization and thermodynamic principles. It was speculated that stability and reduction of free energy of the systems were the main reason for the formation of complexes. The final structures that have the least stearic hindrance and the least energy are favored. Magnetic properties of the Iron modified cellulose were due to unequal moments arising from Fe$^{2+}$ ions (Ferrimagnetic) or parallel moments of Iron atom (Ferromagnetic). The reaction was conducted well below curie temperature so that ferro or ferri magnetic properties were not lost.
4. Characterization of microcrystalline cellulose and cellulose fibers modified by iron salt

4.1 Abstract

Microcrystalline cellulose (MCC) and cellulose fibers (CLF) were treated with iron (Fe) based salt and the samples were characterized using analytical instruments to study the coordination complexes formed between cellulose and iron. The Fe-modified MCC and CLF were characterized by spectroscopic, thermal and morphological methods. MCC and CLF were oxidized and further treated with iron (Fe) based salt in a high pH medium to form coordination complexes. Both MCC and CLF were then analyzed using Scanning electron microscopy (SEM) to examine their surface morphology. The results have shown that there was no major change in morphology for MCC and CLF upon modification. The functional groups formed by modifying cellulose by iron salt were investigated using FTIR-ATR spectroscopy and the nature of the coordination bonds formed between cellulose and Fe ions were examined by X-ray photo electron spectroscopy (XPS). The results agree that coordination bonds were formed between de-protonated and or oxidized hydroxyl group and Fe ions. Powder XRD (PXRD) was resourceful to compare the crystallinity of unmodified and Fe-modified samples of MCC and CLF. Thermal stability of modified cellulose was studied using thermo gravimetric analysis (TGA). The results showed that there was an increase in percentage of residual mass and higher thermal stability for the Fe-modified MCC and CLF compared to unmodified samples due to the presence of iron.

4.2 Introduction

Cellulose is one of the most abundant naturally occurring bio-polymer. It is commonly found in the cell walls of plants and certain algae. In addition to plant cell wall, cellulose can be obtained from sources like tunicates (Angles and Dufresne, 2000, Sturcova, et al., 2005) and bacteria (Bielecki and Krystynowicz,
Cellulose from the bacterium Acetobactor xylinum is a product of its primary metabolism and forms a protective coating in contrast to the structural roles cellulose plays in plant cell wall (Bielecki and Krystynowicz, 2002). Recently, there has been a great deal of research interest in utilizing cellulose for various applications such as composite manufacturing due to its remarkable reinforcing capability, excellent mechanical properties, low density and environmental benefits. However, the reinforcing capability of cellulose can be compromised by the poor dispersion and lack of orientation of cellulose fiber in the polymer matrix (Larenjeria et al., 2006). Recent studies have shown that orientation of cellulose can be achieved by subjecting the cellulose fiber suspended in a solution to electromagnetic fields. Liquid suspension of cellulose when dried in an electric field was oriented in respect to the applied electric field (Bordel et al., 2006). Orientations of cellulose fibers in suspensions were reported when they were subjected to magnetic fields up to 20 T (Cranston and Gray, 2006, Kvien and Oksman, 2007, Sugiyama et al., 1992). In this scenario, it justifiable to modify cellulose with ferrimagnetic elements such as iron to induce further improvement in cellulose orientation in a polymer matrix. Such modification could enhance orientation of cellulose in lower strength electric and magnetic fields.

Cellulose has been modified to obtain various derivatives such as acetates and nitrates. Among the derivatives, cellulose-based metal complexes have attracted scientists due to its specific applications. Cellulose–metal complexes have found many foreseeable applications in drug delivery systems and initiators for free radical polymerization (Harcourt, 1972, Muller et al., 1971, Samal et al., 1984). However, to the best of our knowledge, there is only little information available regarding the synthetic routes used to produce these cellulose-metal complexes. When transition metal salts are reacted with cellulose, they form coordination bonds with functional groups at the 6th, 2nd and 3rd carbon positions of cellulose. Previous studies have revealed that it is possible to form coordination bonds involving transition metals and monosaccharides such as glucose, fructose and galactose (Cerchiaro et al., 2005). There have been studies on
derivatives of cellulose such as hydroxyethyl cellulose (HEC) and carboxymethyl cellulose (CMC), when reacted with iron salts they have produced cellulose–Fe coordination complexes (El-Saied et al., 1994). Transition metals will complex with de-protonated hydroxyl group of polysaccharides through oxo-bridges (Hosny et al., 1997). Cellulose, a polysaccharide having β (1–4)-linked glucopyranose units, the vicinal diol groups (2- and 3-hydroxyl groups) can be involved in the formation of diketone bonds in coordination with Fe$^{2+}$ (Godovsky et al., 1999). However, the primary hydroxyl groups of cellulose at C6 have the potential to form complexes with adjacent cellulose chain through Fe bridges (Figure. 4.5). The hydroxyl groups at C6 may not form Fe complexes with C2 and C3 of the same cellulose molecule owing to their steric hinderance (Kennedy et al., 1974). The specific objective of this study was to characterize the coordination bonds formed between Fe and modified hydroxyl groups. The functional groups formed upon modification, the nature of bonds, surface morphology and thermal properties of MCC and CLF was also investigated using FTIR, XPS, SEM and TGA, respectively.

4.3 Experimental

4.3.1 Materials

MCC (Avicel, PH-101) was purchased from Fluka, Biochemika and CLF was purchased from Sigma–Aldrich, Canada. Both MCC and CLF were used as obtained without any further processing. Ferrous sulfate FeSO$_4$.7H$_2$O (98% purity) obtained from Fluka Chemika and Hydrogen peroxide 30% v/v was used.

4.3.2 Oxidation

The dissociation of hydrogen peroxide at high pH results in formation of perhydroxyl anions that acts as an oxidizing agent (Zeronian & Inglesby, 1995). Such an oxidation can modify cellulose hydroxyl groups into oxycellulose. The hydroxyl groups can also get modified into carboxylic and or keto groups (Lewin & Ettinger, 1969). Twenty-five grams of MCC and CLF were soaked separately in 1 M NaOH and stirred at room temperature for 50 h to aid intra-crystalline swelling. 250 mL of hydrogen peroxide (30% v/v) was added to 1000 mL of
alkaline cellulose suspension and stirred for 15 h in room temperature (25 ± 1 °C) and pressure (Zeronian & Inglesby, 1995). The suspension was washed with distilled water three times and further vacuum filtered to obtain the fiber and used as such for further reaction with iron salts.

4.3.3 Preparation of cellulose–Fe complexes

The formations of cellulose–Fe bonds are based on in situ coordination bonds between Fe and its intermediate ions with modified 2, 3 and 6 hydroxyl groups in cellulose (Hegetschweiler et al., 1995). Cellulose–metal complexes were prepared by reacting oxidized cellulose with ferrous sulphate hepta hydride (FeSO$_4$.7H$_2$O). FeSO$_4$.7H$_2$O was pre-treated with NaOH to liberate Fe$^{2+}$ ions. The oxidation state of Fe in the presence of NaOH are depended on pH and the concentration of Fe$^{2+}$ ions (Godovsky et al., 1999). At R = 7/12 (R = ratio between FeSO$_4$ and NaOH) the proposed reaction produces Fe$^{2+}$ ions available to form complexes with modified hydroxyl groups of cellulose (Olowe, Marie, Refait, & Genin, 1994).

$$7\text{FeSO}_4 + 12\text{NaOH} \rightarrow 6\text{Fe(OH)}_2 + 6\text{Na}_2\text{SO}_4 + \text{Fe}^{2+} + \text{SO}_4^{2-}$$

Oxidized celluloses (MCC and CLF) were added to two separate solutions of NaOH (1 M) with 16.6 g of FeSO$_4$.7H$_2$O. The mixture was stirred for 7 h at room temperature (25 ± 2 °C). Then the reaction mixture containing cellulose fiber was filtered and washed several times in double distilled water until the pH became neutral. The reaction products were dried in an oven at 50 °C for 48 h and stored in an airtight container for further analysis.

4.3.4. Scanning electron microscopy (SEM)

Morphology of MCC and CLF before and after treatment was analyzed with an SEM. The morphological analysis was carried out using a Hitachi S-2500 scanning electron microscope. The samples were mounted on metal stubs using
double side adhesive tapes. Scanning electron micrographs of dried MCC and CLF samples (both control and treated) were obtained at an acceleration voltage of 15 kV. The samples were previously sputter coated with gold for 30 s using a Cressington plasma sputter coater.

**4.3.5 Fourier transform infrared spectroscopy (FTIR)**

FTIR analysis was conducted to study the functional groups present in MCC and CLF before and after chemical modification with iron salts. FTIR experiments were performed using a Bruker Tensor 27 instrument. An attenuated total reflectance (ATR) mode was engaged to obtain information on the surface functionalities of the cellulose fibers. The instrument was operated at 4 cm\(^{-1}\) resolution and samples were subjected to 45 scans/s. The spectra was recorded in an absorbance mode and thoroughly analyzed for all absorption peaks from wave numbers 4000 to 400 cm\(^{-1}\).

**4.3.6 X-ray photoelectron spectroscopy (XPS)**

XPS spectra were obtained by running the cellulose samples on a Thermo Scientific with a monochromatic Al-K\(\alpha\) X-ray source. The spot size used for analysis was approximately 400 \(\mu\)m. Charge compensation was provided and position of the energy scale was adjusted to place the main cellulosic C1s feature (C-O) at 286.5 eV. Samples were analyzed at a take off angle of 90° with respect to the surface.

A low resolution survey spectrum ranging from 0 to 1350 eV was obtained to survey the elements present in the sample. The spectra collected at low resolution mode for survey was at 150 eV pass energy. To characterize the relative atomic percentage, a high-resolution spectrum ranging from 280 to 300 eV, 524 to 538 eV and 700 to 750 eV binding energy was obtained for the C1s, O1s and Fe2p regions respectively. High resolution mode used 20 eV as pass energy to scan C, O and Fe regions. The bond analysis of was determined by
curve fitting the peaks for C1s, and Fe2p and deconvoluting the peaks into sub-peaks. The data was analyzed using Avantage onboard software supplied by Thermo Scientific with the instrument. The atomic ratio of oxygen to carbon (O/C) was calculated from corresponding peak area based on the equation

\[ \frac{O}{C} = \left( \frac{I_O}{I_C} \right) \times \left( \frac{S_C}{S_O} \right) \]

Where \( I_O \) and \( I_C \) are the integrated peak area for oxygen and carbon, respectively. \( S_C/S_O \) is corrected sensitivity factor.

4.3.7 Powder X-ray diffraction (PXRD)

The powder X-ray diffraction (PXRD) patterns of treated and untreated MCC and CLF were recorded using a Rigaku–Panalytical diffractometer which produce CuK-\( \alpha \) emission lines. A nickel filter was used to eliminate K-\( \beta \) X-rays. The diffractometer was operated at 40kV at 40mA in the range of 5–45°.

4.3.8 Thermal analysis

Thermal degradation characteristics of Fe-modified and unmodified MCC and CLF were analyzed using a TGA Q 500 series thermo-gravimetric analyzer. The ramping rate was 10 °C/min up to 700 °C in a nitrogen environment. The results were reported in percentage weight loss versus temperature. The percentage of residual mass before and after modification of MCC and CLF were compared to establish iron content present in Fe-modified samples.

4.4 Results and discussion

Fe-modified and control samples of MCC and CLF were characterized using SEM to understand its morphology. Five replicates from three different samples were analyzed and a wide range of distribution in the aspect ratio
(length/breadth) was observed for both MCC and CLF. The length of MCC ranged from 10 to 100 \( \mu \text{m} \) and the diameter ranged from 5 to 10 \( \mu \text{m} \). The aspect ratio for MCC was in the range of 3.0–7.5. In Figure 4.1 the visual inspection of these images indicated that there are no considerable morphological changes occurred on the MCC due to the treatment. The CLF analyzed using SEM ranged from 70 to 350 lm in length and 5 to 15 \( \mu \text{m} \) in breadth. The aspect ratio for CLF was in the range of 10.0–21.0. A comparison between SEM images of treated and untreated CLF showed that the cellulose fibers less than 20 \( \mu \text{m} \) in length are absent in the Fe-modified samples. These particles could very well be lost during washing the samples in order to bring the samples to neutral pH. Figure 4.2 showed slight stranding of fiber at the ends on CLF surface after NaOH treatment. The intercrystalline swelling by NaOH and stirring of cellulose might have resulted in damaging the ends of CLF fibers.

Pure, oxidized and Fe-modified MCC and CLF were examined by FTIR in ATR (attenuated total reflectance) mode. The spectra for MCC are shown in Figure 4.3. After oxidation of MCC peaks corresponding to carbonyl groups were observed at 1731.63 \( \text{cm}^{-1} \). The peaks of interest for Fe-modified MCC samples were at 3838 cm\(^{-1}\), 3742 cm\(^{-1}\), 1516 cm\(^{-1}\) and 490 cm\(^{-1}\).
Figure 4.1 Scanning electron micrographs of (A) unmodified and (B) modified microcrystalline cellulose (MCC)
Figure 4.2 Scanning electron micrographs of (A) unmodified and (B) modified cellulose fibers (CLF)
For oxidized CLF shown in Figure 4.4, the peaks of interest were at 1693.03 cm\(^{-1}\) related to carbonyl groups. For Fe-modified CLF, peaks were observed at 3841 cm\(^{-1}\), 3743 cm\(^{-1}\), 1517 cm\(^{-1}\) and 498 cm\(^{-1}\). The intense bands in the region of 4000–3000 cm\(^{-1}\) are attributed to free hydroxyl and bonded OH stretching vibrations (Coates, 2000). In the case of both Fe-modified MCC and CLF there were additional shoulders in this region. The two shoulder peaks formed in the region of 4000–3740 cm\(^{-1}\) are assigned to the cleavage of the primary and secondary hydroxyl groups involved in the coordination complex formation with Fe (Hosny et al., 1997). The strong peak from 3500 to 3000 cm\(^{-1}\) shows presence of unreacted hydroxyl groups in both MCC and CLF (Coates, 2000). The weak peaks from 1510 to 1520 cm\(^{-1}\) are characteristic to diketone and its metal–oxygen derivatives formed by coordination with Fe\(^{2+}\) ions resulting in diketone/quinone metal complexes (Wijnja and Schulthess, 2001). The Fe\(^{2+}\) ions are bonded to 2nd and 3rd hydroxyl groups of cellulose that have been oxidized to keto groups and or carboxylate groups upon treatment with hydrogen peroxide. The peak in this region (1510–1520 cm\(^{-1}\)) represents the asymmetrical vibration of O=C=C=O or bi dentate Fe\(^{2+}\) complex such as –C-O-Fe-O-C- engaged in coordinate bond formation (Bock et al., 1971) (Figure 4.5). The peaks observed around 490–510 cm\(^{-1}\) for both Fe-modified MCC and CLF are essentially from vibration of metal oxide bonds. These bonds are believed to be from de-protonated hydroxyl groups of modified cellulose and Fe\(^{2+}\) ions (Offiong, 1995).

X-ray photoelectron spectroscopy analysis was performed to determine the presence of elements in the unmodified and Fe-modified cellulose samples. In Figures 4.6A and 4.7A, a low resolution scan mode has shown that the primary elements present in the unmodified MCC and CLF were mainly C and O.
Figure 4.3 FTIR spectra of MCC-control, oxidized MCC and treated MCC.

Figure 4.4 FTIR spectra of CLF-control, oxidized CLF and treated CLF
A low resolution scan for pure FeSO$_4$.7H$_2$O was also obtained for elemental analysis. Peaks were obtained for C, O, S and Fe (Figure 4.8). The presence of iron was distinctive in the low resolution scan of Fe-modified cellulose samples (Figures 4.6B and 4.7B). A high resolution scan was completed on the C1s and Fe2p region of Fe-modified MCC and CLF to examine the Cellulose-Fe bonds. The oxygen/ carbon [O/C] ratio was calculated to determine the surface oxidation of the samples after modification (Allen et al., 1974). The oxygen to carbon ratio for Fe-modified MCC and CLF was higher than that of the unmodified samples suggesting the oxidation of hydroxyl groups (Table 4.1). The modification of hydroxyl groups to ketones and carboxylates resulted in addition of oxygen atoms resulting in higher O/C ratio in Fe-modified cellulose. High resolutions scan of the C1s region of Fe-modified and unmodified MCC and CLF was deconvoluted into three sub-peaks namely C1s-HR-A, C1s-HR-B and C1s-HR-C. The deconvoluted peaks of C1s region and their corresponding binding energy and bond type are shown in Table 4.2. The C1s peak at 284.87 eV corresponds to carbon hydrogen bonds while C1s-HR-A, C1s-HR-B and C1s-HR-C correspond to various carbon–oxygen bonds. These peaks have arised

![Figure 4.5 Schematic of proposed complex formation of Fe with cellulose](image-url)
from the basic structure of cellulose where carbon atoms are attached to hydrogen and from unreacted ketone and carboxyl groups and possibly from the cyclic hemi-acetal linkage structure in cellulose chain (Hon, 1984). The presence of peaks in the region of 700–730 eV showed the occurrence of coordination bonds of Fe with Oxygen in both Fe- modified MCC and CLF. Table 4.1 shows that the percentage of iron present in the modified samples was 1.95% and 1.85% for MCC and CLF respectively. The peak binding energy for Fe2p curves
for Fe-modified MCC was 710.39 eV and for CLF it was 710.51 eV (Tables 4.3 and 4.4). Representative images for deconvoluted Fe2p peaks are shown in Figures 4.9 and 4.10 for MCC and CLF, respectively. The high resolution peaks of interest in this region were Fe2p- HR-A and Fe2p-HR-B. The binding energy for Fe2p-HR-A and Fe2p-HR-B for modified MCC and CLF and their corresponding bond types were obtained from the data base for XPS spectral lines from National institute of standards and technology (NIST), USA.

**Table 4.1** Elemental analysis of modified and unmodified MCC and CLF using a low resolution XPS spectrum.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Elemental composition (%)</th>
<th>O/C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>O</td>
</tr>
<tr>
<td>MCC</td>
<td>57.86</td>
<td>42.14</td>
</tr>
<tr>
<td>MCC Treated</td>
<td>54.35</td>
<td>43.7</td>
</tr>
<tr>
<td>CLF</td>
<td>58.98</td>
<td>41.02</td>
</tr>
<tr>
<td>CLF Treated</td>
<td>54.69</td>
<td>43.46</td>
</tr>
</tbody>
</table>

**Table 4.2** Analysis of C1s peak from XPS spectra.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C1s</th>
<th>C1s-HR-A</th>
<th>C1s-HR- B</th>
<th>C1s -HR-C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[C-C]</td>
<td>[C-O]</td>
<td>[C=O]</td>
<td>[ O - C=O]</td>
</tr>
<tr>
<td></td>
<td>eV</td>
<td>%</td>
<td>eV</td>
<td>%</td>
</tr>
<tr>
<td>MCC</td>
<td>284.87</td>
<td>11.21</td>
<td>286.52</td>
<td>63.81</td>
</tr>
<tr>
<td>MCC (T)</td>
<td>284.87</td>
<td>14.85</td>
<td>286.44</td>
<td>60.77</td>
</tr>
<tr>
<td>CLF</td>
<td>284.90</td>
<td>15.41</td>
<td>286.50</td>
<td>59.85</td>
</tr>
<tr>
<td>CLF (T)</td>
<td>284.88</td>
<td>13.57</td>
<td>286.44</td>
<td>60.14</td>
</tr>
</tbody>
</table>
Table 4.3 Deconvoluted peaks of Fe2p region of modified MCC–Fe complex and corresponding bond type.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Binding energy (BE)</th>
<th>At.%</th>
<th>Bond type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe2p</td>
<td>710.39</td>
<td>24.76</td>
<td>Fe or Fe-O-</td>
</tr>
<tr>
<td>Fe2pA</td>
<td>709.55</td>
<td>36.37</td>
<td>Fe-O-</td>
</tr>
<tr>
<td>Fe2pB</td>
<td>711.50</td>
<td>14.70</td>
<td>Fe-[OH]-O</td>
</tr>
</tbody>
</table>

Table 4.4 Deconvoluted peaks of Fe2p region of modified CLF–Fe complex and corresponding bond type.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Binding energy (BE)</th>
<th>At.%</th>
<th>Bond type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe2p</td>
<td>710.51</td>
<td>26.45</td>
<td>Fe or Fe-O-</td>
</tr>
<tr>
<td>Fe2pA</td>
<td>709.68</td>
<td>34.88</td>
<td>Fe-O-</td>
</tr>
<tr>
<td>Fe2pB</td>
<td>711.46</td>
<td>16.45</td>
<td>Fe-[OH]-O</td>
</tr>
</tbody>
</table>
The numerical values for the resolved peaks, values for theoretical binding energy and corresponding bond type are represented in Tables 4.3 and 4.4. The data shows that both Fe2p-A and Fe2p-B peaks in MCC and CLF are based on iron–oxygen bonds (Bock et al., 1971, Cerchiaro et al., 2005). Oxygen atoms bonded to iron are essentially from the de-protonated and or oxidized hydroxyl groups of cellulose (Hegetschweiler et al., 1995; Skopenko et al., 2004). High pH and the presence of an oxidizing agent such as hydrogen peroxide oxidize the hydroxyl group of cellulose into ketones or carboxylates. Fe$^{2+}$ ions introduced to modified cellulose functional groups resulted in the formation of Fe-oxo bridged polyolato complexes (Hegetschweiler et al., 1995, Spikes et al., 2008).

Figure 4.8 XPS survey spectrum for ferrous sulphate hepta hydrate.

Fe-oxo bridged complexes were speculated to be arised from the coordination
between diketones with iron and from de-protonated hydroxyl groups of cellulose and iron. The FTIR peaks obtained at 490–510 cm\(^{-1}\) due to formation of metal–oxide bonds are in agreement with the result from XPS peaks of Fe–oxygen ranging from 700 to 730 eV. XPS was further helpful to identify the nature of bonds formed between oxidized and or de-protonated cellulose and iron. A high-resolution spectrum for the Fe region of FeSO\(_4\).7H\(_2\)O was also obtained to compare it with the peaks obtained from the Fe region of modified MCC and CLF. The peak binding energy for Fe2p region was 711.11 eV corresponding to pure FeSO\(_4\).7H\(_2\)O. It should also be noted that in Fe-modified MCC and CLF, the peak for Sulphur was absent confirming the absence of residual FeSO\(_4\).7H\(_2\)O.

![Figure 4.9 High resolution XPS peak of Fe2p region of modified MCC](image-url)
Crystalline peaks of MCC and CLF were recorded using a Powder X-ray diffractometer. The PXRD pattern for both Fe-modified and unmodified MCC exhibit diffraction peaks at 16.2° and 22.18° which represents crystalline structure of cellulose 1 (Figure 4.11) (Nelson, 1964). Sharper PXRD peaks corresponded to higher crystallinity of the sample. However the intensity of the peak for Fe- modified MCC was lower compared to unmodified samples. The lower peak intensity of modified MCC might have arised due to treatment with NaOH (Nelson,1964, Oh et al., 2005). The crystalline region of MCC could have dismantled due to treatment with NaOH. Figure 4.12 showed that for both Fe-modified and unmodified CLF, the peaks at 14.5° and 16.3° were wide, a sharp peak was observed at 22.58° representing the crystalline region of CLF. There were no comparable differences in peak intensity for both CLF samples. Thermal characterization of MCC and CLF can provide insight into the processability of the fibers when mixed with a polymer. The thermograph results for both Fe-
modified and unmodified MCC and CLF shows that there was a weight loss at 100–105°C due to evaporation of moisture.

For untreated MCC the degradation occurred at a temperature range between 304 and 348°C. The results from the DTG thermogram (Figure 4.13) shows that and the peak degradation temperature for unmodified MCC was at 330.5 °C. For Fe-modified MCC the degradation temperature range was from 339.5 to 371.5 °C and the peak degradation was at 360.3°C. The result clearly shows that the thermal stability increased by modification of MCC with iron salts. The percentage weight of fiber residue after heating up to 700 °C was ≈ 8% higher for Fe-modified MCC when compared to unmodified. This implies that there was presence of iron in Fe-modified MCC which was not degraded when the samples were heated up to 700 °C. The higher percentage of residual mass in Fe-modified MCC is assumed to be from iron–cellulose complex as well as from unbounded iron.

![Figure 4.11 PXRD patterns of untreated and treated MCC.](image)

Figure 4.11 PXRD patterns of untreated and treated MCC.
Figure 4.12 PXRD patterns of untreated and treated CLF.

Figure 4.13 TGA and DTG thermograms of unmodified and modified MCC.
The TGA–DTG thermo-gram of unmodified CLF showed that the degradation temperature range from 330.0°C to 371.1 °C and the peak degradation occured at 351.3 °C (Figure 4.14). For Fe-modified CLF the degradation started at 339.9 °C and ended at 379.30 °C. The result shows that the degradation temperature was higher for CLF treated with iron salts. The percentage of residual mass was \( \approx 4\% \) higher for treated CLF which confirms the presence of complexed and or unbound iron in the sample. For both MCC and CLF the samples treated with iron salts showed a higher thermal stability compared to the untreated samples.

![TGA and DTG thermograms of unmodified and modified CLF.](image)

**Figure 4.14** TGA and DTG thermograms of unmodified and modified CLF.

### 4.5 Conclusions

Cellulose, when treated at high pH with an oxidizing agent, can result in the oxidation of hydroxyl groups into ketones or carboxylates. These functional groups can readily form complexes with transition metals. FTIR spectroscopy and XPS suggest that complex formation between modified cellulose hydroxyl
and Fe ions. Results from FTIR spectroscopy supported the formation of diketone linkages from both MCC and CLF, with Fe to result in complex formation. The presence of iron changed the degradation temperature upon modification. The resulting modified samples of MCC and CLF may be used for many applications such as property enhancement in composite manufacturing, magnetographic printing and manufacture of security paper. The research using these cellulose samples modified with iron for manufacturing fiber oriented composite films by solvent casting the fiber–polymer matrix in a magnetic field is discussed in Chapter 6.
5. Thermal characterization and electrical properties of Fe-modified cellulose fibers and micro crystalline cellulose

5.1 Abstract

Thermal properties of polylactic acid (PLA) filled with Fe-modified cellulose fibers (CF) and microcrystalline cellulose (MCC) were studied using thermo gravimetric analysis (TGA), differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). The Fe-modified CLFs and MCCs were compared with unmodified samples to study the effect of modification with Fe on electrical conductivity. Results from TGA showed that the degradation temperature was higher for all composites when compared to the pure PLA and that the PLA composites filled with unmodified celluloses resulted in the best thermal stability. No comparable difference was found in glass transition temperature ($T_g$) and melting temperature ($T_m$) between pure PLA and Fe-modified and unmodified CLF and MCC based PLA biocomposites. DMA results showed that the storage modulus in glassy state was increased for the biocomposites when compared to pure PLA. The results obtained from a femtostat showed that electrical conductivity of Fe-modified CLF and MCC samples were higher than that of unmodified samples, thus indicating that the prepared biocomposites have potential uses where conductive biopolymers are needed. These modified fibers can also be tailored for fiber orientation in a matrix when subjected to a magnetic field.

5.2 Introduction

Polymer composites have been found to have indispensible applications in various fields such as automotive parts, aerospace, construction and others (Larenjeria et al., 2006, Alemdar and Sain, 2006). The recent shift towards
environmentally friendly materials has paved the way to the development of biodegradable polymers and reinforcers in composites for tailored applications. Among biopolymers, polylactic acid (PLA) has been widely considered as a potential substitute for fossil fuel-based plastics. Mechanical properties of PLA are comparable to polystyrene for stiffness and strength (Petersson et al., 2007). PLA can be a synthesized form of lactic acid, which is derived from renewable agricultural raw materials such as corn, maize, wheat etc., that have undergone fermentation. Bio-based reinforcers in composites range from wood pellets and wood fiber, to micro and nano cellulose fibers (Alemdar and Sain, 2008b). Due to its abundance and remarkable reinforcing capacity, cellulose has been widely accepted as a reinforcer for polymer composites. The reinforcing capacity of cellulose depends on various factors, such as fiber dispersion and orientation. Studies show that orienting cellulose fiber in a matrix can be achieved by applying shear force. Cellulose whisker can orient in a plane perpendicular to shear direction for low shear rates and along the shear direction for higher rates (Kvien and Oksman, 2007). However, the optimization of fiber motion under flow condition is complicated and extremely difficult to achieve (Larenjeria et al., 2006). It is also reported that mechanical properties were improved when composites with oriented fiber were tested along the fiber axis, even at a fiber content as low as 10% (Larenjeria et al., 2006). Another path to orient cellulose fiber is to subject the reinforcing cellulose fiber to a strong magnetic field (usually up to 20 Tesla (T)), in a matrix suspension. However, such an orientation of cellulose can be achieved only if the fibers are at the nano scale (Cranston and Gray, 2006). It is predicted that micron-scale cellulose fibers can be oriented through the modification of cellulose using magnetic entities such as Fe and thus is speculated to improve the mechanical properties of the composites. The high energy required to orient cellulose fibers under a magnetic field can be considerably reduced by modifying the available hydroxyl sites of cellulose to form complexes with Fe. Modified cellulose-metal complexes have been used in medicine in the past and also have the potential to be used in magneto-graphic printing, manufacturing of security paper and other advanced composites (Sugiyama et al., 1992 ; Kim et al., 2006). Studies have shown that the thermal
Properties of polymers will change with the addition of fillers (Huda et al., 2005). However, there is only very limited information on thermal properties and the effect of iron modified, cellulose-based PLA composites. The ultimate objective of this research is to orient micro-scale Fe modified cellulose fibers in a polymer matrix. This paper evaluates the thermal properties of unmodified and iron modified MCC- and CLF-based PLA composites prior to fiber orientation. Thermal analysis techniques such as TGA, DSC, and DMA were used to characterize the thermal properties of the Fe modified cellulose-PLA composite. The electrical conductivity of the modified fibers was compared with unmodified fibers using a femtostat. The results are discussed.

5.3 Experimental

5.3.1 Materials

Microcrystalline cellulose (MCC) Avicel, PH-101, was purchased from Fluka, Biochemika, Switzerland and cellulose fibers (CF) were purchased from Sigma-Aldrich, Canada. Both materials were used as obtained, without any further processing. Two different types of cellulose, CLF and MCC, were used due to their higher aspect ratio and elevated crystallinity, respectively. Poly lactic acid (PLA) was used as a matrix for the composites. PLA was obtained from NatureWorks™, Cargill Dow LLC. This biopolymer has a density of 1.24 g/cm³, a melting temperature of 160–170°C, and a glass transition temperature between 55-60°C.

5.3.2 Modification of cellulose

Both celluloses (MCC and CLF) were soaked in NaOH for intra-crystalline swelling and then oxidized using hydrogen peroxide 30 percent v/v. The oxidized hydroxyl group of cellulose was reacted with a mixture of Ferrous sulfate (FeSO₄·7H₂O) (98 % purity) and NaOH. The ratio of FeSO₄ to NaOH was 7:12 to liberate Fe²⁺ ions. The liberated Fe²⁺ ions formed metal complexes with cellulose (Skopenko, Amirkhanov, Sliva, Vasilchenko, Anpilova, and Garnovskii, 2004). Hydroxyl groups of cellulose at 2, 3 and 6 positions are involved in the formation
of cellulose-Fe bonds. The bonds formed are based on in situ coordination between the Fe and its intermediate ions (Sundar et al., Hegetschweiler, et al., 2004).

5.3.3 Compounding of cellulose with PLA

Fe-modified and unmodified MCC and CLF were loaded on to PLA. The loading of fiber to the matrix was 10 percent of the total weight of the mixture. The mixture was compounded using a brabender mixer at 180°C for 15 min at 60 rpm.

5.3.4 Profiling and extrusion of PLA-Cellulose composite

The prepared compound was profiled at 190°C and 50 rpm into rectangular blocks of 35.0 mm × 12.04 mm × 2.02 mm for DMA using a DSM Micro 15, USA extruder.

5.3.5 Electrical conductivity of modified cellulose

The conductivity of Fe-modified MCC and CLFs was compared to unmodified samples using a Gamry FAS2 Femtostat. Fe-modified and unmodified cellulose samples were pressed into discs of 5.5 mm diameter and 0.2 mm thickness. A potential difference ranging from 0.5 to 1.5 V was applied to the sample. The variation in current (I) on constant voltage was recorded by monitoring potential differences between the reference electrode and the counter electrode attached to the sample. Conductivity of the sample was calculated by taking the inverse of resistivity.

\[ R = \frac{\partial \times L}{A} \]

where R is resistance, \( \partial \) is resistivity, L is the length between electrodes and A is the surface area of the sample.

5.3.6 Thermogravimetric analysis of cellulose-PLA composite

Thermal properties of PLA-Fe-CLF and PLA-Fe-MCC composites were compared to unmodified composites (PLA-CLF and PLA-MCC) and to pure PLA
using a TGA Q 500 series thermogravimetric analyzer (TA-Instruments, USA). The temperature ramping rate was 10°C/min up to 700°C in a nitrogen environment.

5.3.7 Differential scanning calorimetry (DSC) of cellulose-PLA composite

The glass transition temperature ($T_g$) and the melting temperature ($T_m$) for the Fe-modified and unmodified biocomposites as well as for the pure PLA were characterized using a Q1000 differential scanning calorimeter (DSC) (TA Instruments, USA). The sample weight was ≈ 5-7 mg and the materials were first equilibrated at 35°C and then ramped to 250°C using a heating rate of 10°C/ min.

5.3.8 Dynamic mechanical analysis (DMA) of cellulose-PLA composite

The composites and PLA profiles obtained from extrusion were subjected to a dynamic mechanical analysis using a TA Q800 (TA Instruments, USA). The storage modulus ($E'$) and tan delta ($\delta$) as DMA was run in dual cantilever mode. The sample dimensions were 35.0 mm in length, 12.04 mm in width and 2.2 mm in thickness. The samples were heated from 35 to 150 °C with a heating rate of 3.0 °C/min; the strain amplitude was 30 A° at a frequency of 1 Hz.

5.4 Results and Discussion

The presence of Fe-cellulose complexes upon modification of CLF and MCC were established by the results from XPS. In Figure 5.1, the XPS spectra (low-resolution mode) of unmodified cellulose, modified cellulose and pure FeSO$_4$ are shown. The results show the presence of Fe in modified cellulose samples. The XPS spectrum of modified cellulose samples does not show any peaks for sulphur, which is present in the spectra for FeSO$_4$. This suggests the absence of residual FeSO$_4$ present in modified cellulose and also that the Fe present is chemically bound to cellulose (Sundar et al., 2010).
Table 5.1 Degradation, glass transition, melt temperature and tan delta peak temperature of PLA and the prepared composite materials

<table>
<thead>
<tr>
<th>Materials</th>
<th>Degradation temp (°C)</th>
<th>T&lt;sub&gt;g&lt;/sub&gt; (°C)</th>
<th>T&lt;sub&gt;m&lt;/sub&gt; (°C)</th>
<th>Tan (δ) peak temp.(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA</td>
<td>322.1</td>
<td>64.5</td>
<td>150.5</td>
<td>70.6</td>
</tr>
<tr>
<td>PLA-CLF</td>
<td>354.6</td>
<td>64.7</td>
<td>150.5</td>
<td>71.6</td>
</tr>
<tr>
<td>PLA-Fe-CLF</td>
<td>344.7</td>
<td>66.0</td>
<td>148.7</td>
<td>71.9</td>
</tr>
<tr>
<td>PLA-MCC</td>
<td>368.6</td>
<td>64.9</td>
<td>148.4</td>
<td>71.1</td>
</tr>
<tr>
<td>PLA-Fe-MCC</td>
<td>343.3</td>
<td>64.5</td>
<td>148.4</td>
<td>71.4</td>
</tr>
</tbody>
</table>

In Figure 5.2, the FTIR spectra of modified CLF and MCC were compared to unmodified cellulose. The peaks around 1510 to 1520 cm<sup>-1</sup> are expected from the asymmetrical vibration of diketones and/or bidentate ligands based on the formation of Fe-cellulose coordinate complexes. The peaks observed in the region of 3700 to 4000 cm<sup>-1</sup> are suggested to result from the cleavage of primary and secondary hydroxyl groups of cellulose when they are involved in coordination complex formation with Fe.
Figure 5.1 Low resolution XPS spectra for a) unmodified cellulose b) Fe-modified cellulose and c) pure FeSO$_4$.7H$_2$O
The peaks observed around 495 to 500 cm$^{-1}$ essentially arise from metal oxygen bonds (Sundar et al., 2010, Offiong, 1995). Results from FTIR spectra were helpful in establishing the association of Fe to cellulose through coordinate complex formation.

Thermograms from TGA-DTG for CLF-based PLA composites are presented in Figure 5.3. The peak degradation temperatures for the tested materials are also presented in Table 5.1 According to the results, (Figure 5.3A), among CLF-based composites the addition of CLFs showed positive impacts on degradation temperatures. The peak degradation temperatures were highest for composites with CLF at 354.6°C, the Fe-modified composite showed 10°C lower degradation.
Figure 5.3 TGA analysis A) CLF based PLA composites B) MCC based PLA composites
Figure 5.4  TGA analysis (A) Comparison between untreated CLF and MCC based PLA composites (B) Comparison between Fe-treated CLF and MCC based PLA composites
at 344.7°C, and the PLA have the lowest at 322.1°C. The reason for the higher thermal stability in the PLA-CLF biocomposite might be that the CLFs were not treated with NaOH as had been done for the Fe modified composites and thus resulted in less structural damage and chain cleavage [10]. However, in the case of PLA-Fe-CLF biocomposites, the cellulose fibers when treated with NaOH for bulking and further treatment with FeSO₄ could have resulted in loss of crystalline regions and/or cleavage of the molecular chains resulting in lower degradation temperature than that of PLA-CLF composite. Figure 5.3B shows similar trend when MCC is used, The degradation temperature was highest for the PLA-MCC composite 368.6°C and this temperature was decreased to 343.3°C for PLA-Fe-MCC further to 322.1°C for pure PLA. The higher degradation temperature of PLA-MCC compared to PLA-CLF could have aroused due to the higher crystallinity of MCC to that of CLF.

Figures 5.4A and B show the comparison between Fe-modified and unmodified CLF and MCC in a PLA matrix. The difference between peak degradation temperature for unmodified MCC and CLF was ≈ 15°C, however there was not much difference in peak degradation temperature for Fe-modified samples. The higher degradation peak for unmodified MCC when compared to CLF might have arisen from the presence of higher crystalline regions.

DSC was helpful in comparing glass transition temperatures (T₉) and melting temperatures (Tₘ) of the pure PLA and produced composite materials. Figure 5A shows the results for the endothermic curves for PLA, PLA-CLF and for PLA-Fe-CLF. The endothermic T₉ peaks observed were not considerably different among the different materials. The T₉ peaks were between 63 and 67°C for all the samples. The T₉ peak intensity for PLA-Fe-CLF, and PLA-CLF was higher when compared to neat PLA. The reason for the higher peak intensity for PLA-Fe-CLF is speculated to depend on the heat required to raise the temperature of Fe present in the composite upon modification. The melting temperatures for all composites were comparable, however Tₘ for PLA-CLF and pure PLA was ≈ 2°C
Figure 5.5 DSC for (A) CLF based PLA composite (B) MCC based PLA composite.
Figure 5.6 Storage modulus from DMA analysis (A) CLF based PLA composite (B) MCC based PLA composite
Figure 5.7 DMA analysis $\tan \delta$ peak temperatures A) CLF based PLA composites B) MCC based PLA composites
Figure 5.8 Electrical conductivity of Fe-modified and unmodified cellulose (a) CLF (b) MCC
higher than the other samples. Both MCC- and CLF-based samples had a wider crystalline temperature ($T_c$) ranging from 110 to 130°C. However, the $T_c$ peaks were comparatively sharper for neat PLA and the PLA-MCC composite, which is also believed to be due to the higher crystallinity of MCC.

The dynamic mechanical properties of the CLF- and MCC-based PLA composites were studied to provide information on molecular interaction between the fiber surface and polymer and also the viscoelastic behaviors of PLA. Storage modulus ($E'$) and tan $\delta$ curves were recorded in relation to temperature. In Figure 5.6, the results show that both Fe-modified and unmodified composites have considerably higher storage modulus before $T_g$ than that of neat PLA. The MCC and CLF acted as reinforcement for the PLA by improving the storage modulus and thus the mechanical properties (Nakagaito et al., 2009, Lewitus et al., 2006). Figure 5.7 represents the tan $\delta$ curves for the produced composites and PLA. The results show that the tan $\delta$ peaks from pure PLA were in a slightly lower temperature range when compared to PLA with both Fe-modified and unmodified cellulososes but this difference is not significant (Mathew et al., 2005, Oksman et al., 2003, Iwatake et al., 2008). These results indicate that there is no molecular interaction between the PLA and used cellulososes.

Electrical conductivity of modified and unmodified cellulose was compared using a femtostat. The cellulose samples were pressed into a disk of uniform diameter and the electrodes were connected to the farthest ends of the sample. The current (I) was measured for different constant voltages (V). The conductivity of cellulose was found from the equation $\sigma = L/RA$, where $\sigma$ is conductivity, $L$ is the length between electrodes, $R$ is resistivity and $A$ is the surface area of the sample. The results shown in Figure 5.8 explain that for set voltages, modified CLF and MCC have better conductivity than that of the unmodified samples. At 1V, modified CLF had a conductivity of $1.8 \times 10^{-8}$ S·m$^{-1}$ while unmodified had a conductivity of $6 \times 10^{-8}$ S·m$^{-1}$. For MCC the conductivity was $2.2 \times 10^{-8}$ S·m$^{-1}$ for modified and $4.5 \times 10^{-8}$ S·m$^{-1}$ for unmodified samples at 1V. The higher electrical conductivity of CLF may be explained by a greater number of reactive sites compared to MCC to attach Fe$^{2+}$ to the surface.
5.5 Conclusion

The focus of this work was to study the thermal properties of PLA-based biocomposites with an addition of unmodified and Fe-modified microcrystalline cellulose (MCC) and cellulose fibers (CF). Electrical conductivity of Fe-modified and unmodified cellulose that were used in making PLA based biocomposites were also studied. The results showed that the addition of small amounts (10 percent wt) of MCC and CLF had a positive impact on the degradation temperature of PLA and that the unmodified cellulosics demonstrated better thermal stability than the Fe-modified cellulosics. This is expected due to the higher crystallinity attributes of unmodified MCC and CLFs.

The addition of MCC and CLF did not demonstrate as high of an impact on the composites glass transition temperature ($T_g$) or melt temperature ($T_m$) and were comparable between PLA filled with Fe-modified and unmodified cellulose. Furthermore, the addition of Fe-modified and unmodified CLF and MCC increased the storage modulus in the glassy state but had no significant effect from the softening temperature of the PLA. The addition of the MCC and CLF did not change the tan delta peak position, thus indicating that no molecular interaction occurred between the PLA matrix and the two different cellulosics (MCC and CLF) used.

The electrical conductivity was higher for both Fe-modified cellulosics (MCC and CLF) when compared to unmodified cellulose. These Fe-modified cellulosics have the potential to be used in conductive biopolymer composites and in the production of fiber oriented polymer composites.
6. Chemical modification of cellulose fiber by iron salt and its orientation in a magnetic field

6.1 Abstract

Cellulose fibers in a PLA (Poly Lactic Acid)-dichloromethane matrix were oriented in a magnetic field of 4.7T (Tesla). Cellulose fibers were oxidized and further modified with iron (Fe) based salts to obtain Fe-modified cellulose. Results from Fourier Transform infrared Spectroscopy (FTIR) and X-ray electron photo spectroscopy showed the presence of coordination complexes. It was observed that the viscosity of the PLA-dichloromethane matrix increased when cellulose fibers were loaded. Confocal microscopy images indicated that the cellulose fibers were oriented in 0.3 g, 0.5 g and 1.0 g concentrations PLA in 10 ml dichloromethane when subjected to a magnetic field.

6.2 Introduction

Bio-based composites and materials are highly sought after by industries seeking ways to increase environmental sustainability. However, there is an inherent requirement for bio-based composites and materials to be tailored for niche applications, in part due to inferior properties that may be exhibited by these composites (Sain and Panthapulakal, 2006, Angles and Dufresne, 2000). Cellulose fibers have been used in bio-based composites due to their availability and enhanced physical properties when compared to other plant-based fibers (Alemdar and Sain, 2008). Cellulose fiber combined with a bio-based plastic such as PLA result in a completely degradable composite. These biodegradable materials have a great potential to be used in packaging, semi-structural applications, disposable cutlery, and other useful products (Mathew et al., 2005, Jayamol et al., 2001).

Cellulose is usually used as a filler or reinforcement in composites. The reinforcing capacity of cellulose fiber in composites can be determined by several
factors, such as fiber length, loading, dispersion and fiber orientation (Larenjeria, et.al, 2006, Helbert et al., 2001). Studies have shown that the aspect ratio of fiber plays a significant role in the reinforcing properties of a composite. Lower aspect ratios can result in the fiber added to a matrix behaving as a filler rather than as a reinforcing fiber (Samir et al., 2005). Factors such as fiber length and loading can be tailored to attain desired properties. However optimum orientation and dispersion of fiber in a matrix is hard to achieve (Larenjeria, et.al, 2006).

Previous studies have shown that when a tunicin whisker suspension in cyclohexane was oriented with a 1 kHz electric field of 2000 V cm$^{-1}$ the tunicin whisker suspension showed increasing birefringence with increasing field strength (Dong and Grey, 1997). In another study, cellulose whiskers obtained form tunicin were dispensed in chloroform and subjected to a magnetic field of 7T. The suspension was allowed to dry inside the field and the results showed that the fibers were oriented along the flux direction. It was also observed that the control samples prepared outside of the magnetic field presented a random orientation (Sugiyama et al., 1992). Cellulose nanowhiskers (CNW) in the dimension order of 5-55 nm separated from microcrystalline cellulose were mixed in water soluble Poly vinyl alcohol. A 0.2 wt.% suspension of CNWs in water and PVA was dried inside a horizontal bore magnet of 7T. The film obtained upon evaporation of water from PVA was analyzed to infer that the fibers were oriented in relation to the flux direction (Kvien and Oksman, 2007). However, these studies were dealing with cellulose fibers of short dimension and the solvents had lower viscosity and less polymeric. Moreover, orientation was attained by subjecting cellulose fiber to magnetic field up to 20T. In polymer composite processing it is required that the fiber be aligned in the matrix to obtain desirable properties (Larenjeria et al., 2006).

There have been only a limited number of studies in this field to align cellulose in a polymer matrix. In this scenario it was justifiable to modify fibers that have lengths up to 300 µm and align them in a polymeric matrix. This study focused on modifying cellulose fibers (CLF) using a ferrimagnetic entity and aligning them in a polymer matrix.
6.3 Experimental

6.3.1 Materials
CLF was purchased from Sigma Aldrich, Canada and was used as obtained without any further processing. Poly lactic acid obtained from NatureWorks™, Cargill Dow LLC was used as a matrix to align the cellulose fibers. The density of PLA was 1.24 g/cm³, the glass transition temperature was between 55-60°C, and the melting temperature was 160–170°C. Analytical grade Dichloromethane was used as a solvent for PLA which was obtained from Sigma Aldrich. The solvent was used to dilute PLA in order to reduce viscosity. During solvent casting, dichloromethane was mixed with PLA and then evaporated to obtain the bio-polymeric composite.

6.3.2 Developing Cellulose – Fe complex

Cellulose was converted to oxycellulose using 30%v/v hydrogen peroxide. Perhydroxyl anions originating from the dissociation of hydrogen peroxide, acted as an oxidizing agent. Thus obtained oxycellulose was reacted with ferrous sulphate hepta hydride (FeSO₄.7H₂O), which was pre-treated with NaOH to liberate Fe²⁺ ions. When mixed at a ratio of 7:12 for FeSO₄. 7H₂O to NaOH, FeSO₄.7H₂O liberated Fe²⁺ ions (Olowe, Marie, Refait, & Genin, 1994).

\[ 7\text{FeSO}_4 + 12\text{NaOH} \rightarrow 6\text{Fe(OH)}_2 + 6\text{Na}_2\text{SO}_4 + \text{Fe}^{2+} + \text{SO}_4^{2-} \]

The liberated Fe²⁺-ions formed metal complexes at deprotonated and/or oxidized hydroxyl sites of cellulose at 2, 3 and 6 positions. It is predicated that an in situ coordination occurs between the Fe and its intermediate ions and deprotonated or oxidized hydroxyl groups (Hegetschweiler et al., 1995, Skopenko et al., 2004).
6.3.3 Profiling of Cellulose-PLA- dichloromethane solution

PLA-samples weighing 0.3 g, 0.5 g and 1 g were mixed in a 10 ml dichloromethane solution. PLA was allowed to dissolve in dichloromethane in closed glass vials to prevent evaporation. The solution was kept for 24h. After mixing PLA and dichloromethane, the solution was vigorously shaken using a vortex mixer. After 24 hrs, 0.1g of Fe-modified cellulose fibers was added to each vial of PLA – dichloromethane solution. The vial containing PLA-dichloromethane and Fe-modified cellulose was sonicated using an ultrasound sonicator for 30 minutes.

6.3.4 Rheology of Cellulose-PLA- dichloromethane solution

The viscosity of the three different concentrations of PLA dichloromethane samples loaded with Fe modified cellulose were compared to a PLA – dichloromethane solution with no cellulose added. The solution was analyzed with an AR2000 rheometer using a 40mm 2° cone and plate attachment. The gap between the cone and plate was set at 61µm. The samples were conditioned for 5s before the experiment began. The test method was steady state flow with shear ramping from 1 to 10 Pa.S. A solvent trap was used to prevent evaporation of dichloromethane during the analysis. Five points per decade were selected and the maximum point time was set at 30 s. The experiment was performed at 25°C. The data was analyzed using rheology advantage instrument control AR software provided with a TA AR2000 Rheometer.

6.3.5 Cellulose orientation in PLA- dichloromethane solution

The vial of PLA- dichloromethane solution loaded with Fe-modified cellulose was introduced into a vertical bore magnet of a nuclear magnetic resonance (NMR) spectroscope. The magnet used was from a Varian 200 MHz NMR and it had a field strength of ≈ 4.3 T.
6.3.6 Confocal microscopy

The samples obtained after fiber orientation was analyzed using a Leica TCS SP2 confocal microscope. The microscope used Argon (Ar) ion laser at 480nm. A 20× M Plan dry lens with 0.4 numerical aperture and 50× HCPL Fluotar lens with 0.8 numerical aperture were used as eye pieces. The output power was set at 30 milli volts. The fluorescence emission was collected from 505 to 530 nm.

6.4 Results and Discussion

Formation of Fe-cellulose complexes upon modification of CLF by FeSO$_4$.7H$_2$O was established through Fourier transform infrared spectroscopy (FTIR) and X-ray photo electron spectroscopy (XPS) as described in associated previous studies (Sundar et al., 2010). In Figure 6.1, the XPS spectrum (low-resolution mode) of unmodified cellulose shows that the major elements present are carbon (C) and oxygen (O). Peaks for iron (Fe) are present in the XPS spectrum obtained for modified cellulose, which is shown in Figure 6.2 The sulphur peak is absent in the XPS spectrum of the modified CLF sample, suggesting the absence of residual FeSO$_4$ after the modification. The absence of sulphur (S) peaks also suggests that the Fe is chemically attached to cellulose fibers (Olowe et al., 1994). In Figure 6.3, the FTIR spectra obtained using an ATR mode for modified and unmodified CLF were compared. The FTIR spectrum of modified CLF showed peaks in the range of 1510 to 1520 cm$^{-1}$ which are expected to have arisen from the formation of diketones and/or bidentate ligands formed between Fe and Oxidized hydroxyl groups of CLF.
Figure 6.1 Low resolution XPS of unmodified cellulose with C and O peaks. Peaks for Fe and S are absent.

Figure 6.2 Low resolution XPS peak of Fe-modified cellulose fibers showing Fe, C and O peaks
Peaks and sub-peaks were also observed in the region of 3700 to 4000 cm\(^{-1}\), which may have arisen from the primary and secondary hydroxyl group cleavage (Coates, 2000, Hosny et al., 1997).

Another band in the region of 495 to 500 cm\(^{-1}\) represents the metal oxygen bonds formed during ligand formation (Offiong, 1995). Both XPS and FTIR were resourceful to establish the formation of metal complexes between iron and oxidized cellulose.

![FTIR spectra of Fe-modified, oxidized and unmodified cellulose fibers](image)

**Figure 6.3** FTIR spectra of Fe-modified, oxidized and unmodified cellulose fibers (reproduced from Sundar et al., 2010)

The viscosity of PLA-dichloromethane loaded with Fe-modified cellulose fibers was decisive in orienting the fibers in a magnetic field. It was observed that at three concentrations of PLA, the viscosity of the system changed considerably.
Figure 6.4 Viscosity plots a) 0.3 g, b) 0.5 g and c) 1.0 g PLA in 10 ml dichloromethane loaded with modified and unmodified cellulose fibers.
Figure 6.5 Confocal microscopy images of A) 0.3 g, B) 0.5 g and C) 1.0 g PLA in 10 ml dichloromethane loaded with Fe-modified cellulose fibers oriented in a magnetic field.
Figure 6.6 Unmodified cellulose fibers in a PLA (1.0g) dichloromethane (10ml) matrix in a magnetic field.

The results obtained from the AR2000 viscometer for three different concentrations are shown in Figure 6.4.

The results show that for all three concentrations, the viscosity of neat PLA was less than that of the samples loaded with cellulose fibers. There was a sharp increase in viscosity as the concentration increased from 0.3 g of PLA to 1 g of PLA in 10 ml dichloromethane. In Figure 6.4A it was observed that there was no considerable difference in viscosity for a given shear rate between treated cellulose and untreated cellulose in PLA. However, the trend showed that from shear rate (S\(^{-1}\)) 1 to 4, the viscosity decreased exponentially; thereafter the viscosity was to decrease steadily for shear rates above 4 S\(^{-1}\). The viscosity for neat PLA was lower compared to PLA loaded with treated and untreated cellulose. In Figure 6.4B, the viscosity plot indicated that for treated cellulose in PLA, the initial viscosity was lower compared to untreated cellulose. This could have arisen from the entanglement or stacking of fibers which might have resulted in additional frictional forces during the measurement. The viscosity for neat PLA was observed to be lower than that of PLA loaded with cellulose for all given shear rates. In Figure 6.4C, the treated cellulose fiber in PLA showed lower
viscosity for a given shear rate compared to untreated cellulose. At a shear rate of 1 S⁻¹, the viscosity was 7.9 Pa.S and 6.4 Pa.S for untreated and treated cellulose in PLA, respectively. The lowering of viscosity might have been caused by one or more factors, including (a) more entanglement of fibers in untreated cellulose, (b) the swelling of cellulose with NaOH and (c) smoother surface and fiber breakage/damage from further modification of cellulose and (d) uneven evaporation of solvent, dichloromethane in which PLA is dissolved. The viscosity for neat PLA was observed to be lower compared to both treated and untreated cellulose loaded in PLA-Dichloromethane. The viscosity at shear rate 1 S⁻¹ was 2.1 Pa.S for neat PLA.

PLA-dichloromethane loaded with treated and untreated cellulose was mixed thoroughly inside a vial using a sonicator and further on with a vortex shaker. The three samples with vials of PLA samples weighing 0.3 g, 0.5 g and 1 g in a 10 ml dichloromethane solution were introduced to the inner bore of a superconducting magnet. The PLA-dichloromethane loaded with cellulose fiber was allowed to cast inside the vials by letting dichloromethane evaporate inside the bore of the superconducting magnet. The vials were removed from the magnetic field once dichloromethane was evaporated completely. A film of PLA with cellulose fiber was formed inside the vial, which was carefully removed for further morphological analysis. A Leica confocal microscope and scanning electron microscope were used to characterize the orientation of the cellulose fiber in the PLA matrix. From the images obtained, it was observed that for all three different concentrations of PLA in dichloromethane loaded with cellulose fibers were oriented along the magnetic flux with a field intensity of 4.7 T. It was also observed that the unmodified cellulose samples were not oriented when subjected to the magnetic field. The results show that Fe-modification of cellulose was critical in orienting the samples along the flux direction. Previous studies showed that cellulose nano-fibers from tunicin whisker could be oriented in high magnetic fields from 7 to 20T in very low viscous liquids such as chloroform and cyclohexane. Overcoming the viscous forces of the matrix where the fibers are loaded is very crucial in fiber orientation by magnetic field. This study suggests that to overcome the viscous forces of a polymer matrix to align fibers, modification of
fiber surfaces with a ferrimagnetic entity such as Fe will be crucial. The modification will also eliminate the need for a high-intensity magnetic field up to of 20 T to create fiber-orientated bio-based films.

6.5 Conclusion

The objective of this work was to create fiber- oriented bio-based films. The addition of Fe-modified and unmodified cellulose to PLA matrix increased the viscosity of the blend when compared to neat PLA. It was observed that untreated fibers contributed to higher viscosity in PLA-dichloromethane matrix. Fe-modified cellulose fibers were oriented in three different concentrations of PLA (0.3 g, 0.5 g and 1 g of PLA in 10 ml dichloromethane): Furthermore it was also observed that unmodified cellulose fibers were not able to overcome the viscous forces of the PLA-dichloromethane matrix when subjected to a magnetic field of 4.7 T for the given concentrations and did not show any orientation. The Fe-modified, cellulose-based, fiber-oriented biocomposites have the potential to be used as a foundation for the manufacturing of higher quality fiber-orientated composites, conductive biopolymer composites, electrically active biopolymer films and magnetographic printing.
7. Conclusion

7.1 Executive summary

The objectives of this project to modify cellulose and re-defining orientation of cellulose fibers in a biopolymer matrix were successfully accomplished.

In previous studies, mostly cellulose fibers were oriented in low viscous liquids such as water, chloroform and cyclohexane. In this study, an attempt to use higher viscosity matrix such as PLA to manufacture biodegradable composites were successfully accomplished. The current gap in knowledge that limits magnetic orientation of cellulose fiber in a biodegradable viscous polymer matrix such as polylactic acid was effectively addressed.

The conclusions of this works is as follows

I. Cellulose fibers and microcrystalline cellulose were bulked in presence of NaOH at 13 pH. Further available hydroxyl groups of cellulose were oxidized to carbonyl groups. These oxidized groups were complexed with Fe$^{2+}$ ions. XPS and FTIR were resourceful to determine the extent of complex formation.

II. The mechanism of complex formation between Fe$^{2+}$ ions and oxidized cellulose was studied. Hydroxyl groups of cellulose when oxidized was expected to form ketones, aldehydes, carboxylates or existed as unmodified hydroxyl group. FTIR spectra shows the presence of
carbonyl groups on oxidized cellulose. Adjacent carbonyl groups are expected to form diketone bonds when complexed with Fe \(^{2+}\) ions. The coordination number of Fe \(^{2+}\) is six and expected to form an octahedral geometry when the valencies are fully satisfied. However there is a chance that all the valencies may not be satisfied resulting in a different spatial geometry. In the reaction, the actual number of carbonyl ligands complexing with Fe \(^{2+}\) may be less than six due to stearic hindrance.

III. Thermal properties showed that addition of neat cellulose fibers into PLA matrix have increased the degradation temperature and thus improving the thermal stability of the composite. However when cellulose fibers were modified with Iron, the thermal properties speculated by lowering of crystallinity.

IV. For iron-modified cellulose (MCC and CLF), it was observed that the electrical conductivity was higher when compared to unmodified cellulose.

V. Iron modified cellulose fibers was successfully oriented in three different concentrations of PLA (0.3 g, 0.5 g and 1 g of PLA in 10 ml dichloromethane). Unmodified cellulose when loaded in the same concentration of PLA was unable to overcome the viscous force of PLA-dichloromethane matrix in a magnetic field of 4.7 T.

This was a pioneer work where cellulose was modified by iron salts and further oriented the fiber in a biopolymer matrix in a magnetic field.

7.2 Study limitations

Unavailability and lack of access to a stronger magnetic field was detrimental at determining the orientation of fiber in different magnetic field strength.

The composites prepared could not be tested for its mechanical strength using an universal testing machine due to the restriction of samples size that could be introduced to the bore of the magnet.
Rapid evaporation of dichloromethane during viscosity studies using a cone and plate parallel plate rheometer was minimized to the maximum possibility by using a solvent trap.

### 7.3 Recommendations

Designing/modifying an extruder for continuous production of totally biodegradable fiber oriented composites/films can be sought after. Mathematical modeling using classical physics equation for magnetic field strength, viscosity parameter and cellulose loading to optimize orientation and the effect of each parameter on orientation and its correlation can be studied. Mechanical and degradation testing of PLA-cellulose based fiber oriented composite is necessary to be studied to compare with conventional literature which asserts improvement in properties due to fiber orientation. This study could qualify as a foundation to other fiber-oriented composites with diverse polymers systems. Manufacturing of conductive biopolymer composites, electrically active biopolymer films and application of Fe modified cellulose in magnetographic printing can be explored.
References


Ballhausen, C.J., (1962), Introduction to ligand field theory, Mc graw hill book company, New York, USA

Basolo, F. and Johnson, R.C., (1986), Coordination chemistry, Science reviews, British library cataloguing in publication data.

Battista, O.A and Smith, P.A (1962), Microcrystalline Cellulose, Industrial engineering chemistry, 54.9


Coban, O., Bora, M. O., Sinmazcelik, T. and Gunay, V. (2010) Effect of fiber orientation on viscoelastic properties of polymer matrix composites subjected to thermal cycles. Polymer Composites, 411-416

Crabtree, R. H., (1994), The organometallic chemistry of the transition metals, John Wiley and Sons, New York, USA


Nickel\textsuperscript{II} and Copper\textsuperscript{II} complexes with carboxymethyl cellulose. Polymer International, Vol. 37, pp.93-96


Jackubovics, J. P., (1987), Magnetism and magnetic materials, Institute of metals, North American publication center, Brook field , USA


Kondo , T., (1997), The assignment of IR absorption bands due to free hydroxyl groups in cellulose. Cellulose, 4, 281-292

Kongdee, A. and Bechtold, T.,(2004),The complexation of Fe(III)-ions in cellulose fibres: a fundamental property. Carbohydrate Polymers 56, 47–53

Kongdee, A. and Bechtold, T.(2009), Influence of ligand type and solution pH on heavy metal ion complexation in cellulosic fibre: model calculations and experimental results, Cellulose, 16:53–63


Mabbs, F.E. and Machin, D.J. (1973), Magnetism and transition metal complexes, Chapman and Hall Ltd, London, UK


Mathew, A., Oksman, K. and Sain, M., (2005), Mechanical Properties of Biodegradable Composites from Poly Lactic Acid (PLA) and Microcrystalline Cellulose (MCC). Journal of Applied Polymer Science, Vol. 97, 2014–2025


Néel, L., (1948). Propriétées magnétiques des ferrites; Férrimagnétisme et antiferromagnétisme, Annales de Physique (Paris) 3, 137


Oh, S. Y. et al. (2005). Crystalline structure analysis of cellulose treated with sodium hydroxide and carbon dioxide by means of X-ray diffraction and FTIR


Said, A., Samir A., Alloin, F., and Dufresne, A., (2005), Review of recent research into cellulosic whiskers, their properties and their application in nanocomposite field. Biomacromolecules, 6, 612-626

Samir, A. S., Alloin, F. and Dufrense, A., (2005), Review of recent research into cellulosic whiskers, their properties and their application in nanocomposite field, Biomacromolecules 6, 612-626


Sundar, S.T., Sain, M. M. and Oksman, K., (2010), Characterization of microcrystalline cellulose and cellulose long fiber modified by iron salt. Carbohydrate Polymer. 80,35-43

Syrkin, Y.K. and Dyatkina,M. E., (1964), Structure of molecules and chemical bonds, Dover publications, New York, USA


Catalytic air oxidation of 3,5-di-t-butylphenol by Cu( II) and Fe( III) complexed to a polyphenylene polymer containing P-di-and tri-ketone surface ligands. Journal of Molecular Catalysis A: Chemical 101 187-198

Appendix

Fig 9.1 CT Scan image of cellulose orientation in PLA polymer matrix