UNDERSTANDING THE SELF-ASSEMBLY OF LIGNIN-BASED BIOMATERIALS

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Developing bio-renewable raw materials for manufacturing and technology has become a focus of research, with special interest in the field of biomaterials. Lignocellulosic biomass can be utilized as a raw material to produce chemicals and it is an important feedstock for renewable fuels in the production of energy. Lignocellulose is composed of mainly three biomacromolecules (cellulose, hemicellulose and lignin). Currently, most of the extracted lignin is either decanted in nearby waters or burned in energy-recovery systems. The reason why lignin is disposed of instead of being further processed is that lignin is immiscible with most polymers and its association behavior is still unknown due to its non-uniform aromatic structure with a number of methoxy, ether and ester groups. To fully utilize lignin, an improved understanding of the interfacial adhesion and interfacial tension is needed. The main motivation for this project is to find new possible ways to make lignin, a lignocellulose component, miscible with most polymers, and to understand how the molecule associates and behaves in the presence of other natural macromolecules. One of the main barriers to utilization of lignin is the
absence of significant intermolecular interactions, which cause miscibility problems resulting in phase separation, a generally undesirable characteristic for manufacturing applications, especially in the production of materials. Lignin-based polymeric blends in solution have provided a possible avenue for understanding lignin’s self-assembly behavior in solid and the variations in morphology, physical and thermal properties that come with the addition of secondary and tertiary components, and as well as foreign molecules such reduced graphene oxide (rGO).

In the first study, we focused on understanding the association behavior using high and low proportions of cellulose to test how the various functional groups may interact differentially with lignin utilizing ionic liquids as the solvent and water as the coagulation agent. A tertiary component, rGO, was introduced into the lignin-based biocomposite to modify \( \pi-\pi \) aggregations. The study looks at the effect of rGO as a function material concentration. The biocomposites were investigated using Attenuated Total Reflectance Fourier Transform Infrared spectroscopy (ATR-FTIR), Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC) and Scanning Electron Microscope (SEM) techniques. Results show that \( \pi-\pi \) aggregates are driven by the \( \pi-\pi \) interaction of the aromatic groups in lignin. The \( \pi-\pi \) aggregates undergo disaggregation by the addition of rGO on the blended biocomposite. The results showed that increasing the cellulose content in the cellulose-lignin biocomposite can increase the molecular interactions, causing an increase in the stability of the blended film and an increase in the crystallinity of the cellulose. Profound changes in the morphology was observed upon the addition of rGO. Results demonstrates that the addition of rGO into the biocomposite prevented the self-assembly of lignin.
The second study investigated the material morphological and thermal effects upon the addition of rGO as a function of material composition in a tertiary system comprised of lignin, cellulose, and xylan. The results demonstrated that the regenerated films’ structural, morphological and thermal character changed as a function of lignin-xylan concentration and upon the addition of rGO. We observed how the fibrous/spherical structure changed as results of the addition of rGO into the system. We provided evidence that shows a dramatic change in the glass transition temperature and degradation temperature.

The two studies provided evidence to suggest that the addition of rGO prevented the self-assembly of lignin by reducing π-π aggregations and reducing the cellulose percent crystallinity. In addition, it suggested that by increasing interfacial adhesion while mitigating interfacial tension increase the utility of lignin. The increase in the interfacial adhesion between the lignin backbone hydroxyl groups and the matrix with its abundant hydroxyl and ether functional groups which are available for hydrogen bonding, impacts it’s the suitability and, consequently, the its utilization as a value-added biomaterial.
It is my genuine gratefulness to dedicate this work to my parents for supporting and encouraging me to believe in myself. To my brother Meshari and my sisters who are always motivating me and being beside me through all my educational studies. Also, I dedicate my study to Saudi Arabian Culture Mission (SACM) for accepting and trusting me in this scholarship.
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Table of Contents

Title ........................................................................................................................................... i

Abstract...................................................................................................................................... ii

Dedication .................................................................................................................................... v

Acknowledgement ......................................................................................................................... vi

Chapter 1: Introduction .................................................................................................................

Lignocellulosic materials ............................................................................................................. 1
Lignin ........................................................................................................................................... 2
Cellulose ....................................................................................................................................... 5
Xylan ............................................................................................................................................ 6
Graphene oxide ............................................................................................................................ 8
Ionic liquid AMIMCl .................................................................................................................... 9

Chapter 2: Understanding the changes in lignin-self-assembly as a result of its interaction with cellulose and reduced graphene oxide ............................................................

Introduction ............................................................................................................................... 12
Material and Methods ............................................................................................................... 17
Film Regeneration ...................................................................................................................... 17
Characterization Methods .......................................................................................................... 18
Results and Discussion ............................................................................................................... 19
Structural Analysis (IR) ............................................................................................................. 19
Chapter 3: Understanding the self-assembly of lignin-based biomaterials in a tertiary system

Introduction .................................................................................................................. 32
Material and Methods .................................................................................................. 37
Film Regeneration ....................................................................................................... 38
Characterization Methods ............................................................................................ 38
Results and Discussion ............................................................................................... 40
Structural Analysis (IR) ............................................................................................... 40
Morphology Analysis (SEM) ....................................................................................... 44
Thermal Analysis (TGA) ............................................................................................. 45
Thermal Analysis (DSC) ............................................................................................. 48
Conclusion .................................................................................................................... 50

Chapter 4: summary ..................................................................................................... 52

References ..................................................................................................................... 55

List of figures .................................................................................................................. 5

Figure 1. Lignin monomer structures .......................................................................... 3
Figure 2. Repeating units of cellulose chains ............................................................. 6
Figure 3. Schematic of a basic xylan structure ............................................................ 7
Figure 4. Chemical structure of 1-allyl-3-methylimidazolium chloride .................. 10

Figure 5. ATR-FTIR spectra of material components. (A) Lignin-cellulose without rGO films. (B) with rGO .................................................................................................................. 22

Figure 6. SEM images (A) lignin-cellulose blends without (B) and with rGO ............ 25

Figure 7. DSC curves of (A) blended lignin-cellulose films without rGO (B) and with rGO ................................................................................................................................. 27

Figure 8. TGA percent weight decomposition analysis for (A) lignin-cellulose without rGO blended films, (C) TGA derivative percent weight decomposition analysis, (B) lignin-cellulose with rGO blended films and (D) derivative percent weight decomposition analysis ..................................................................................................................... 29

Figure 9. FTIR spectra of (A) material components of lignocellulosic films without rGO and (B) of material components of lignocellulosic films with rGO ......................... 42

Figure 10. SEM images: (A) lignocellulosic blended films and (B) lignocellulosic blended films with rGO .............................................................................................................. 45

Figure 11. TGA percent weight decomposition analysis for (A) lignocellulosic blended films and (B) lignocellulosic blended films with rGO. TGA derivative percent weight decomposition analysis for (C) lignocellulosic blended films and (D) lignocellulosic blended films with rGO ................................................................................................................. 46

Figure 12. (A). DSC curves of blended lignocellulosic films (A) without rGO and (B) with rGO ................................................................................................................................. 49
List of tables ........................................................................................................................................21

Table 1. Experimental conditions of regenerated film concentrations of lignin and cellulose .......................................................................................................................................21

Table 2. TGA decomposition temperatures of blended films with and without rGO components and experimental conditions ........................................................................................................30

Table 3. Experimental conditions of regenerated film concentrations of lignin, cellulose, xylan ........................................................................................................................................40

Table 4. TGA decomposition temperatures of blended films with and without rGO components and experimental conditions ........................................................................................................47
Chapter 1: Introduction

The exploitation of natural biomaterials has gained increasing attention in recent years. Biomaterials are essentially plant-based materials whose appeal has grown due to the increasing demand for environmental protection and the demand of sustainable technologies. Emerging applications for biomaterials include a wide range of packaging and industrial chemicals, medical implant devices, and drug delivery systems. The study of biomaterials includes aspects of medicine, biology, chemistry, engineering, environmental science and materials science.¹

Biomaterials are classified into two main areas: natural and synthetic materials. Natural materials have been the subject of increasing attention over the past two decades due to their wide use in medicine to replace the function of degenerated tissues or organs, thus helping to improve the quality of life for patients. In addition, due to their abundance and low cost, polymers produced by plants could be utilized as renewable raw material to produce new custom-made polymers and biofuels. Natural polymers are becoming more widely used and desirable than synthetic polymers, which could provide an improved interactions, increased functionality and more renewability.²

Bio-based products can compete with petroleum products due to the richness of their chemical building blocks. Bio-based polymers, such as lignocellulosic, have varieties of carbohydrate molecules that can be found in plants, such as crops, grasses, and algae, or in the lipids, oils and fatty acids produced from oil crops. Lignocellulosic biomass is the most abundant biomass source and consists of three different components: cellulose (40–50%), hemicellulose (20–30%), and lignin (20–30%).³ Each has high carbon, oxygen and
hydrogen content which makes them useful for chemical and fuel applications. Lignocellulosic biomass can produce biofuels that can overcome significant economic challenges because they are highly abundant and have low cost and sustainability. The crosslinking bonds, via ester or ether group linkages, between the polysaccharides cellulose and hemicellulose and the lignin make this structure very complex. Recently, numerous research studies have focused on studying the structural and physicochemical of lignocellulose-based mixtures of homopolymers.

Lignin is a natural polymer found in wood and the second-most abundant polymer present in lignocellulosic material. It is an inexpensive, irregular cross-linked biopolymer that has an aromatic and phenolic skeleton. Lignin has building blocks of heteropolymers consisting of three hydroxyl cinnamoyl alcohol monomers: p-coumaryl, coniferyl, and sinapyl monomers of the aromatic ring at the ortho, meta, and para positions as shown in Figure 1. Hardwood lignin has more sinapyl, while softwood lignin has more coniferyl alcohols. Coniferyl alcohols have approximately 90% of the softwood lignin, whereas nearly equal amount of coniferyl alcohol and sinapyl alcohol associate in hardwood lignin. However, the additional of methoxide groups on the aromatic rings in hardwood will prevent the formation of 5-5 or dibenzodioxocin linkages, and then will cause the hardwood lignin to form linear structures. The aromaticity and electron-donating groups help to increase the hydrophobicity of the cell wall, which enhances the physical properties of the material. Lignin structure is dependent on wood species and processing conditions. It is found in the secondary cell wall, which acts to strengthen the plant walls, provides structural rigidity, and organizes the transport of water through the tissue due to its hydrophobic nature. It is produced as a
byproduct of the cellulosic ethanol and paper industries and as a waste product from chemical pulping processes (e.g., Kraft Alkali).\textsuperscript{4}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{lignin Structures.png}
\caption{Lignin monomer structures.}
\end{figure}

Lignin has varying amounts and compositions among cell types and individual cell wall layers that result in different physical properties including cell wall strength and hydrophobicity. The secondary cell wall has the highest lignin content because it occupies a larger portion of the wall.\textsuperscript{11} However, the unique amorphous structure of lignin as an aromatic polymer makes it the most important source of a variety of bio-based chemicals. Furthermore, lignin has a complex matrix that has a number of methoxy groups and in which cellulose microfibrils are attached to the network of cross-linking hemicellulose polysaccharides.\textsuperscript{12-13} However, despite the unquestionable advances in the chemistry of lignin, some problems still need to be investigated in this field. The first issue is that lignin
is difficult to analyze due to its heterogeneous linkages such as ester, ether, hydroxyl, and methoxy linkages. The second problem is that lignin is not regularly distributed in plant tissue due to the composition and structure of the lignin-carbohydrate complexes. The third problem is that lignin tends to aggregate in most solvents, and this aggregation impacts the isolation of lignin from plants. This could be due to the absence of significant intermolecular interactions, which cause miscibility problems resulting in phase separation. Even though lignin has a low molecular weight, it still aggregates in most solvents at low concentrations. These aggregates follow some patterns in terms of their size, molecular weight, monolignol composition, ionic strength, and temperature. The aggregation problem is the result of two major reasons: one is the intermolecular interaction of hydrogen bonding for lignin aggregate because of van der Waals attraction, and the other is the $\pi-\pi$ stacking of aromatic groups on their association with solution.

Lignin is known to contain abundant alcoholic hydroxyl groups, ether and carbonyl groups, and also a certain amount of methoxy groups that are available for intramolecular hydrogen bonds between lignin and carbohydrates. Disrupting and regenerating those intermolecular interactions will impact the suitability and utilization of lignin as a useful addition to the biomaterial. One strategy for increasing the usefulness of lignin is to blend it with another compatible natural macromolecule. The most suitable choice is cellulose.

Cellulose is the most abundant natural material on earth and is the main constituent of plants, present in a wide variety of living species such as bacteria, fungi, algae, and even animals. It has been used in areas such as biomedical research, fuel production, and 3D printing. It is a linear homopolysaccharide found in the cell walls of plants found in nature in the form of cellulose I ($I_\alpha$ or $I_\beta$) and consists of both crystalline and amorphous regions.
It is constituted of repeating β-D-glucopyranosyl units joined by 1→4-glycosidic linkages that stabilize by forming strong intramolecular and intermolecular hydrogen bonds between hydroxyl groups and the oxygens of adjacent molecules which control the orientation of crystallinity and the physical properties of cellulose as shown in Figure 2. However, these hydrogen bonds can be broken chemically in a strong aqueous acid or at high temperature.²⁰

Cellulose-based materials have a high degree of crystallinity and very low water solubility due to the strong interaction of the hydrogen bonds between polysaccharide chains. It is a fibrous, tough polymer whose molecular weight depends on its source as well as the extraction conditions for purification.²⁰ Cellulose as a polysaccharide polymer has the capability of forming strong intramolecular and intermolecular hydrogen bonds via its β (1-4) glycosidic bonds which provide some possible interactions with lignin.²¹ Therefore, we used cellulose as an adhesion agent to increase hydrogen bond interactions. However, to control the cellulose adhesion influence in our study, we used hemicellulose (Xylan) as a compatibilizer.

Figure 2. Repeating units of cellulose chains.
Xylan is the most common hemicellulose, and it is considered to be the second most abundant biopolymer in plants. Groups of hemicelluloses are present along with cellulose in almost all plant cell walls and polysaccharides as well as lignin. Xylan constitutes 25-35% of the biomass of woody tissues and can be present in various other plants such as grasses, algae, and herbs.

Hemicellulose is a natural composite that has an excellent material property with random, amorphous structure and little strength. It features polysaccharides in various amounts in different structures depending on whether the natural source contains glucose, xylose, galactose, glucuronic acid, galacturonic acid, and so forth. The xylan backbone has a glucan backbone of 1,4-\textbeta-D-xylopyranose with branched chains of 4-oxymethylglucuronic acid as shown in Figure 3, which gives a strong interaction with cellulose. In fact, xylan can add levels of disruption to cellulose crystalline structures, especially in the formation of microfibrils. There is an increasing interest in the application potential of xylan as a polymer. Here in, we use xylan as compatablizer to modify adhesion capabilities of cellulose.
In our investigation, to prevent the self-assembly of lignin as a function of polysaccharide content, we use the blended polymer system, a method that increases molecular interactions and ease of processing. One strategy for increasing the applicability of lignin is to blend it with other substances. For example, graphene oxide (GO) has shown an ability to blend with other polymers such as lignocellulose. Sajab et al. shows the fabrication of aerogel from cellulose with GO in an aqueous solution. The cellulose and GO interacted with each other via intermolecular hydrogen bonding that allowed a homogeneous alignment connection. Moreover, the interaction between the cellulose and GO prevents the GO layers from over-stacking and keeps the layers’ surface sites active for interaction with other substance. As a result, the combination of cellulose and GO shows rapid adsorption due to the richness by hydrophilic groups in GO surface which can be useful in wastewater treatment applications. Wang et al. used a blended film
combining lignin with graphene oxide and found that the lignin interacts with the GO’s membrane by means of the hydrophilic groups in the GO sheets, which enhance the material stability. Lignin forms hydrogen bonds with the hydroxyl groups of GO and can prevent π–π stacking between its sheets.

Graphene is a nanomaterial made of a single thin layer of sp2 bonded carbon atoms in a tight 2D honeycomb lattice with repeating units of hexagons. It is a crystalline material that can be considered a large aromatic molecule with a flat polycyclic aromatic hydrocarbon. Significantly, graphene has similar properties as rubber in both stiffness and elasticity because the carbon atoms in graphene have flat planes that make it flex easily without breaking the molecule. Due to graphene’s toughness properties, it is possible to mix it with other polymers. Adding graphene to polymer will give three-dimensional graphene with polymer composites. The resulting materials have unique mechanical and chemical properties that offer endless applications in medical, engineering, and environmental materials and much more and have received considerable attention in the past few years.

A single layer of graphene possesses a unique combination of electrical, mechanical, optical, and thermal properties. Several graphene preparation methods have been proposed, but one of the most promising is the reduction of graphene oxide (GO), which consists of oxidized graphene sheets. Graphene oxide has oxygen present in epoxide and hydroxyl groups, in addition to carbonyl and carboxyl groups located at the edge of GO rings, which determine its acid, base, and hydrophilicity properties. The functionalities of these oxygen groups provide sufficient sites for linking to macromolecules and polymers. However, when GO functionalized and reduced with
hydroxide groups can emerged as an ideal candidate. The reduced graphene oxide (rGO) sheets have a low solubility in water and most organic solvents. In addition, rGO has high \(\pi-\pi\) stacking tendency between its layers and hydrophobic interactions that make it capable of immobilizing large molecules.\(^{30}\) In our investigation, we use rGO as intermediator to immobilize the lignin molecule between the layers of carbon atoms and hydroxyl groups to prevent the lignin from wrap around itself.

In order to mix these natural polymers into a blended biomaterial film, the solid individual components must be dissolved. Some of the most popular solvents to dissolve biomacromolecules without changing its molecules weights are Ionic Liquids (ILs). Room temperature ionic liquid is considered a desirable green solvent and has been widely used and received significant attention.\(^{31}\) Ionic liquid is an organic salt that exists as a liquid solvent with low temperature and is used to dissolve natural polymers. ILs have been widely employed due to their attractive properties, such as excellent dissolution ability, chemical and thermal stability, non-flammability and immeasurably, low vapor pressure, and ease of recycling.\(^{32}\) Furthermore, ILs are used as reaction media and can be modified through changing the structure of their cations or anions, which will increase their application fields.\(^{33-34}\)

In our study, we used 1-allyl-3-methylimidazolium chloride (AMIMCL) ionic liquid because imidazolium-based ILs are shown to prevent changes in the molecular weight among other ILs as shown in Figure 4. The imidazolium ring is the cationic side which was selected because of its stability in oxidative and reductive conditions, low viscosity, and ease of synthesis. The cationic side is also responsible for certain chemical characteristics, such as melting temperature and organic solubility, whereas the anionic
side is the chloride anion which is responsible for water stability and the ILs air.\textsuperscript{35} In addition, the double bond in the AMIMCL could enhance its interaction between the biomaterials. It has been reported that AMIMCL is the most efficient solvent for lignocellulose in popular applications such as aerogels.\textsuperscript{36} The dissolution of the blended film in IL AMIMCL will help to decrease cellulose crystallinity by disrupting the intermolecular hydrogen bonds within cellulose and regenerating a new hydrogen bond between the hydroxyl groups of cellulose and the AMIMCL anion group.\textsuperscript{32-33} Moreover, AMIMCL could increase the space of the $\pi-\pi$ aggregation of the lignin rings by forming new hydrogen bonds between the anions of AMIMCL and the aromatic rings of lignin.\textsuperscript{34} It could also provide shielding for the stacking interactions between graphene sheets caused by van der Waals interactions and can help to disperse the graphene sheets uniformly.\textsuperscript{25}

![Figure 4](image.png)

**Figure 4.** Chemical structure of 1-allyl-3-methylimidazolium chloride.

In this study, we use the IL AMIMCL to dissolve the blending films. This blending polymer system will increase the molecular interactions and improve the material uniformity so that new properties of this mixture may emerge. The structural and
physicochemical properties of each compound in the blended films was confirmed by ATR-FTIR (Fourier Transform Infrared Spectroscopy), TGA (Thermal Gravimetric Analysis), DSC (Differential Scanning Calorimetry), and SEM (Scanning Electron Microscope). These techniques were used to measure the bonding interactions, morphology, and thermal stability of the regenerated films. In Chapter 2, we will study the change in the crystallization of cellulose and its adhesion capabilities with lignin and reduced graphene oxide. In Chapter 3, will add xylan to control the adhesion properties of cellulose in a mixture of lignin, cellulose, xylan and rGO.
Chapter 2:

Understanding the changes in lignin-self-assembly as a result of its interaction with cellulose and reduced graphene oxide.

Introduction

In light of industrial developments, growing energy demands, and environmental concerns, extensive efforts have been made to find sustainable resources for the fabrication of new biodegradable materials. The search for renewable resources has become a significant environmental concern. In this effort, natural polymers and raw materials have been used to replace fossil fuels. In particular, lignocellulosic biomaterial is one of the most abundant renewable resources on earth. There is significant progress has been made recently in understanding lignocellulosic biomaterials. Lignocellulosic is composed of three major substances: lignin, cellulose, and hemicellulose (xylan). Approximately 75% of lignocellulosic consists of polysaccharides.

Lignin is a promising material for the production of aromatic compounds and fuels. It is a phenolic polymer found in plants that gives strength to the plant secondary cell wall and it is the second most abundant natural biomaterial in the world after cellulose. Lignin is composed of three monomers: coniferyl, sinapyl, and p-coumaryl. These alcohols are classified by the number of methoxy groups on their phenolic ring. For example, hardwood lignin has more sinapyl, while softwood lignin has more coniferyl alcohols. Coniferyl alcohols have approximately 90% of softwood lignin, whereas almost equal portion of coniferyl alcohol and sinapyl alcohol exist in hardwood lignin. However, the
additional of methoxy groups on the aromatic rings will prevent the formation of 5-5 or
 dibenzodioxocin linkages, and then will cause the hardwood lignin to form linear
 structures.\textsuperscript{38} Furthermore, lignin molecules are thought to be made up of hundreds of these
 monomers.\textsuperscript{16} Lignin is a complex compound in which the bonds between monomers can
 form at multiple positions by many different linkages, such as ether and hydroxyl groups.
 These linkages manifest in different physical properties including cell wall strength and
 hydrophilicity.\textsuperscript{16} Despite the great properties of lignin, it is difficult to analyze due to
 heterogeneous linkages. This could be because the presence or the absence of the intra-
molecular interaction between lignin and carbohydrate components of plant tissues.\textsuperscript{14}
 Moreover, lignin tends to aggregate in most of the solvents, which cause miscibility
 problems resulting in phase separation. Even though lignin has low molecular weight, still
 aggregates in most solvents at low concentrations. The aggregation phenomenon can be
 classified into two levels of aggregation: one is the polymer molecular chains aggregate
 because of van der Waals attraction, and the other is because the $\pi-\pi$ aggregation of the
 aromatic groups in lignin.\textsuperscript{39-40}

To increase the utility of lignin, its interfacial adhesion must be increased by
 increasing the intermolecular interaction between the lignin and its matrix because lignin
 has numbers of hydroxyl and ether groups that are available for hydrogen bonding.\textsuperscript{7} This
 can be done by disrupting and preventing the lignin linkage bonds, particularly the lignin
 backbone hydroxyl groups, from wrapping around themselves.\textsuperscript{13} Disrupting those
 intermolecular interactions will enhance the suitability and usability of lignin-based
 biomaterial.\textsuperscript{13}
To take advantage of lignin linkages, it must be blends with another compatible natural biopolymer such as cellulose. Cellulose is the most abundant renewable material on earth. It is a linear homo-polymer composed of repeat units of glucose. The presence of hydroxyl groups and oxygen atoms on the pyranose rings promotes tensile strength in the cell walls, which makes it insoluble in most organic solvents. This linear polysaccharide represents the main component of plant cell walls and contains both crystalline and amorphous regions. Cellulose’s solubility in solvents is the main aspect to enhance its value-added properties for applications. Multiple glucan chains are arranged in parallel crystalline order to form cellulose microfibrils, with the glucan chains held together by hydrogen bonds and van der Waals forces. As compared to natural polymers, cellulose has both hydrophobic and hydrophilic segments in backbone or side groups, making them a good adhesive to graphene oxide. It has been used cellulose for packaging, fuel, biomedical applications, and in 3D bio-printing. It is capable of forming strong intermolecular and intramolecular hydrogen bonds via its \( \beta(1-4) \) glycosidic bonds, which provide a possible avenue for enhanced molecular interactions with lignin. The goal in utilizing these materials (lignin-cellulose) is to increase the natural interactions and take advantages of its properties. In the lignocellulose structure itself, the crystalline cellulose microfibrils are thought to be embedded in a matrix made up of lignin and hemicelluloses which are additionally encapsulated by an outer lignin layer. This network is held together by ether bonds between lignin and cellulose.

In a previous studies, we noticed that when we increased the content of lignin within lignocellulosic films, the lignin tended to wrap around itself. Thus, to prevent the self-assembly of lignin as a function of polysaccharide content, a tertiary material should be
added to the composite. Graphene is an ideal compound to increase the interaction and stabilization of lignocellulose, especially when its surface has been reduced with hydroxide groups. Graphene is made of modified graphene sheets with a number of oxygen functional groups, such as hydroxyl, epoxy, carbonyl, and carboxyl. Graphene is a one-atom thick layer and has two-dimensional sp² bonded carbon. Graphene oxide [GO] exhibits mechanical strength, conductivity, and high specific area. GO sheets possess a high adsorption capacity and have good solubility due to their abundant surface oxygen-containing groups. GO sheet surface groups provide sufficient sites for linking macromolecules and polymers and enhancing physicochemical properties, which makes them favorable for biomedical and environmental applications. It was found recently that lignin can easily bind with reduced graphene oxide (rGO) sheets by hydrogen bonding and π-π stacking. The large surface area of graphene makes it an ideal conducting matrix for anchoring nano-materials. Different thermal and chemical properties have been reported to produce single-layer graphene sheets and manipulate its properties for a variety of device applications.

To blend lignin-cellulose with rGO, we use ionic liquid (IL) to dissolve each molecule with rGO and regenerate blended film. Ionic liquids have been shown to be excellent solvents for these natural polymers, improving their process ability. ILs are also attractive due to their adjustable properties including high thermal mechanical stability, low vapor pressure, easy separation, low toxicity, and non-flammability. In this study, composite blended films were dissolved in an IL solution of different lignin-cellulose ratios. The dissolution of lignin-cellulose materials in ILs is a biomass pretreatment to decrease cellulose crystallinity and to increase the space of the π-π aggregation of the lignin
rings. In this case we chose 1-allyl-3-methylimidazoliumchloride (AMIMCL) as a solvent. The anion side chloride could form hydrogen bonds with aromatic rings of lignin and increase the space of $\pi$-$\pi$ stacking. Moreover, the mechanism of lignin-cellulose decomposition involves the disruption by the IL AMIMCL of the inter- and intramolecular hydrogen bonding network of the lignin-cellulose and regenerate a new hydrogen bonds between the anion group of AMIMCL and the hydroxyl groups. Furthermore, it has been shown that IL could provide shielding for the stacking interactions between graphene sheets caused by van der Waals interactions and can help to disperse the graphene sheets uniformly.\textsuperscript{42} Reduced graphene oxide (rGO) will be used as an intermedier to entrap the blended macromolecules between its two-dimensional flat sheets to prevent the self-assembly of lignin.

To utilize cellulose, lignin, and rGO in a diverse range of applications, it is essential to compose stable homogenous films in order to effectively modify these biopolymers. However, the characterizations of blended structures based on cellulose/lignin and cellulose/lignin with rGO in various ratios using ionic liquid AMIMCL have not yet been fully explored. The goal of this study is to characterize, understand, and compare the behavior of the biocomposite without and with rGO using AMIMCL by characterizing the modification of structures via thermal properties and topography. In this study, the formation of the blended lignin-cellulose with and without rGO films dissolved in AMIMCL was investigated using various techniques including ATR-FTIR, SEM, TGA, and DSC. Various analyses were used to elucidate if the structure and morphology of the blended films changed as a function of changes in lignin-cellulose concentration.
Material and Methods

Material.

Lignin alkali (CAS: 8068-05-1) was purchased from Sigma Aldrich. Cellulose: Avicel microcrystalline cellulose (Techware: Z26578-0) was acquired from Analtech (Newark, DE, USA). Dispersed graphene oxide (GO) in water was purchased from Aldrich. Ionic liquid: 1-allyl-3-methylimidazolium chloride (AMIMCL) was purchased from Alfa Aesar.

Film Regeneration.

The preparation of the regenerated biomass films was a modified version of the protocol seen in previous literature.\textsuperscript{13, 30} The appropriate amount of each biomass component was measured and then added together before its addition to the AMIMCL. To increase the compatibility of the GO sheets with lignin and to increase the adhesion capabilities of the cellulose, GO was reduced with 0.005 g Vitamin C in 1 ml water then heated to 50°C for 24 hours. After that, we rinsed 5 times with water in a centrifugation process to remove the rest of the Vitamin C. Then we filtrated the rGO by adding it to the cellulose filter paper and dried the mixture for 24 hours. The AMIMCL was placed in a test tube (approximately 90 w/w) and heated between 90-100°C, and biomass components (lignin and cellulose with rGO approximately 10 w/w) were added. The solution was dissolved in an oil bath with stirring. The biomass solution was transferred and spread between two glass plates and fully submerged in distilled water for 24 hours to regenerate blended film and remove as much IL as possible. Once this was completed, the films were
placed in a vacuum oven for 24 hours for drying at 50°C. Once the films were dried, they were stored in a vacuum desiccator. To analyze the solid blended films, we used various characterization equipment such as ATR-FTIR, SEM, DSC, and TGA.

**Characterization Methods**

Attenuated Total Reflectance Fourier Transform Infrared spectroscopy (ATR-FTIR) analysis was performed using a Bruker ALPHA-Platinum FTIR Spectrometer with Platinum-Diamond sample module and Bruker OPUS software version 7.2, Build: 7.2.139.1294. The spectra were collected in the wavenumber between 400-4000 cm⁻¹, resolution 4 cm⁻¹, 32 sample scans and 128 background scans. Six different locations on the film were analyzed for each sample and take the spectra average.

**Thermogravimetric analysis (TGA).**

Thermal data were obtained using Thermogravimetric Analysis (TGA), which was carried out on all samples in a nitrogen atmosphere on a TA Instruments Discovery system. The heating process was run at 10°C/min ramp to 600°C for an average sample between 5 to 6 mg. The software determines the derivative plot using peak height analysis.

Thermogravimetric analysis (TGA) was conducted in a TA Discovery system, performed on all samples in a nitrogen atmosphere. Blended film samples averaging at 6 mg were heated linearly with a 10°C/min ramp up to 650°C. Step transition analyses were performed for each sample to determine the onset of decomposition ($T_{95\%}$) and the weight-loss percentage of the sample evolution during the main decomposition step. Derivative values were calculated and peak height analyses were performed to determine the temperature at which the samples decomposed at the fastest rates ($T_{\Delta Max}$).
Differential Scanning Calorimetry (DSC).

Samples with approximately 5 mg weight were enclosed in TZero aluminum pans and run in a TA Instruments Discovery with a refrigerated cooling system (RCS) and nitrogen gas flow (25 mL min⁻¹). The standard aluminum reference was used to calibrate the heat capacity. Samples were heated from 10°C/min up to 150°C to allow the water to evaporate. They were then cooled down to -30°C and heated up again to 300°C.

Scanning Electron Microscope (SEM).

The SEM images were taken on the LEO1450EP SEM at the Rutgers University Camden campus. A small piece was mounted on carbon tape on a Denton Desk II Au-Pd sputter coater. The samples were sputter coated and run in a light-vacuum of 10 V for 60 seconds. The magnification used in this paper is a scale bar of 2000x (10.00 μm).

Results and Discussion.

The structural, thermal and morphological change.

The observable morphology of the regenerated films differed according to the blended polymer lignin-cellulose composition and rGO. Lignin-cellulose films were characterized as soft and rubbery film, while lignin-cellulose biocomposite with rGO films were rigid and breakable. Table 1 shows the composition breakdown of cellulose and lignin with extra 1% rGO used in this chapter.

Various compositions were chosen to test whether the number of interactions with lignin will increase if the number of molecules (cellulose) increases, resulting in changes in the morphology of the blended biomaterials in rGO. We expected dramatic changes in
the crystallization of cellulose and its adhesion capabilities and wanted to see how these ratios could affect the interactions between chains and the ability of the hydrogen bonding in the lignin’s hydroxyl groups to wrap around the individual cellulose sheets and whether rGO acts as a wall to prevent lignin from self-assembly in solution. Our hypothesis is that as cellulose content increases, the ability of the lignin’s phenols groups to wrap around the cellulose monomer will increase. AMIMCL, lignin, cellulose, and rGO each have a unique IR spectrum as shown in Figure 5. Although the biomass shares some overlapping bands, the major peaks of cellulose are common to all polysaccharides in the broad regions of OH (3500-3000 cm⁻¹) and C-O (around 1100 cm⁻¹). Lignin, on the other hand, shows the most unique IR expression in the peaks (700-1800 cm⁻¹), with especially strong peaks in the methoxy (1450 cm⁻¹) and aromatic (1630 cm⁻¹) groups. The major peaks at 3050, 2965, 1570, and 1165 cm⁻¹ are characteristic of AMIMCL.49 Generally, in the IR spectrum of a pure graphene sample, the peaks at around 3400 cm⁻¹ and 1720 cm⁻¹ are attributed to the OH and C-O bands, respectively. In addition, the 1577 cm⁻¹ peak is a characteristic band for C-OH flexural vibration and the 1163 cm⁻¹ stands for C-O-C vibration. The presence of a carboxylic functional group is further confirmed by the strong and broad band around 3400 cm⁻¹.
Table 1. Experimental conditions of regenerated film concentrations of lignin and cellulose.
Figure 5. ATR-FTIR spectra of material components. (A) Lignin-cellulose without rGO films. (B) with rGO.
Lignin tends to dissolve more easily in AMIMCL when compared with cellulose due to its low molecular weight. The FTIR spectrum results show the difference in the absorbance between pure components, lignin-based biomaterials, and lignin-based biomaterials with rGO (see Figure 5). These results confirm the nature of lignin’s ability to increase structural stability through its abundance of aromatic and non-polar species, which can add structural stability. In the rGO, we observed an increase in absorbance for the O-H and C-OH, indicating successful reduction of GO. As can be seen from the IR for the lignin-based biomaterials, the spectra of the blended films correspond to the predominant constituent lignin-cellulose and to rGO.

Between the two graphs (A) and (B) that are shown in Figure 5, the solid film is composed of 10, 25, 50, 75, and 90% lignin, and 90, 75, 50, 25, and 10% cellulose with 1% rGO. The given strong peaks are in -OH (3000 cm⁻¹) and C-O (1060 cm⁻¹). In Figure 5A, the interaction of lignin-cellulose indicates that increasing the concentration of cellulose can decrease the absorbance and crystallinity due to the interaction with lignin. On the other hand, increasing the concentration of lignin increases the absorbance and intensity of the blended film due to the increased interaction with cellulose. However, in Figure 5B, the lignin-cellulose with rGO component shows strong -OH bands interacting across the blend with a shift to a higher wavenumber when we increase the cellulose concentration. The solid film containing 10, 25, 50, 75, and 90% lignin-cellulose with rGO gives a complex of -OH and C-O peaks between 900-1600 cm⁻¹ which are due to the C-O-H and C=O of the COOH groups, respectively.24
Morphology Analysis (SEM)

In Figure 6, the SEM images show the topological changes in the blended biopolymer film morphology as the proportion of rGO added to the lignin-cellulose blend. The morphology and structure without and with rGO biocomposites are shown in Fig. 6 (A) and (B). As can be seen, the films with rGO have smoother surfaces than the films without it. Both the rGO and lignin-cellulose biocomposites interacted with each other via intermolecular hydrogen bonding that allowed for a homogeneous alignment/connection.\textsuperscript{24} In addition, the rGO prevents the lignin from self-assembling around itself by stacking the lignin between its layers sheets and providing interaction via hydrogen bonds in the rGO with the biocomposite. This impacts the morphology of the films presenting a more fibrous structure at its surface. It can be understood that the observed morphological changes represent changes to the structural interactions of the lignin-cellulose blend components. These insights gained from SEM images match the IR spectra pattern analysis. As the lignin content increases, the crystallinity of the fibers decreases due to the substitution of cellulose by amorphous lignin.\textsuperscript{51} Furthermore, the self-assembly of lignin can be manipulated by changing the composition of the biocomposite and by rGO interaction. These results are critical because it provides proof that the morphology of lignin could be altered by adding a tertiary components such as rGO. This results opens the door into controlling the self-assembly of lignin and its potential usability as a biomaterial.
Figure 6. SEM images (A) Lignin-cellulose blends without (B) and with rGO.

Thermal Analysis (DSC)

There were changes in the glass transition (Tg), when we increased the concentration of cellulose in the blended system. We investigated and compared the effect of high and low concentrations of blended lignin-cellulose films using rGO and the ionic liquid (AMIMCL), as well. The blended polymer technique offers distinct properties arising from the desirable characteristic of both lignin, cellulose and rGO, improving the stability and strength of the material. We can conclude from our findings that increasing the cellulose content can increase the molecular interactions between the biopolymers, causing an increase in the stability of the blended film because of an increase in crystallinity.

DSC measures the temperature and heat flow during transition (change) in the material as a function of time and temperature in a controlled atmosphere. Figure 7 shows the blended lignin-cellulose films. By increasing the concentration of cellulose to 10, 25,
50, 75, and 90%, the Tg was clear when the cellulose value was low as a result of the amorphous regions of the lignin. The glass transition temperature Tg can be obtain only from amorphous polymers, crystalline polymers, and cross-linking polymers. Other changes that occurred include sharp endothermic and exothermic peaks. The endothermic peaks show the loss of water and crystalline melt in a heating run from lower to higher temperatures followed by the exothermic peak which shows the weight loss of samples and cold crystallization.\textsuperscript{52} The crystallization temperature (Tc) can take place because the sample had been rapidly cooled and frozen into a non-equilibrium state. Upon heating above the Tg, an exothermic crystallization dip may occur. As the polymer is heated, its molecules can move and crystallize at the equilibrium state, while the temperature at the apex of the peak is the point where the polymer is completely melted. Because energy is added to the polymer to make it melt, this process is called endothermic transition. Both exothermic and endothermic reactions occur due to the crystal growth of cellulose. Nevertheless, even crystalline polymers will have some amorphous portions, which is why the same sample of a polymer can have both a glass transition temperature and a melting temperature.\textsuperscript{53}

When we alternated the composition of cellulose with lignin 90C:10L and 10C:90L with and without the addition of rGO, it was obvious that the film with a high concentration of cellulose (90C:10L) with rGO has strong peaks of exothermic follow by endothermic compared to the same percentage without rGO. This indicates that the addition of rGO contributed to the strong intermolecular hydrogen bonds in the lignin-cellulose blended film. In addition, as the lignin content increased, the crystallinity of the blended films decreased because of the substitution of cellulose by the amorphous regions of lignin.
Figure 7. DSC curves of (A) blended lignin-cellulose films without rGO (B) and with rGO.
Thermal Analysis TGA

In Figure 8, the thermograms are shown for pure lignin and cellulose, and the resulting lignin-cellulose blended films with and without rGO. The blended lignin-cellulose film with rGO shows a high thermal stability with a mass loss that was observed at 250°C associated with the loss of water that physically bonded with the rGO. In the case of increasing the concentration of cellulose as shown in Table 2, the thermogravimetric curve shows clearly less mass loss for the blended film with rGO in comparison with the blended film without rGO. Moreover, when we alternated the decomposition of the lignin-cellulose biocomposites with the addition of rGO, there was a large decrease in temperature for the onset of the thermal degradation of the 75C:25L film (T Onset = 267° to 240°C). On the other hand, when we decreased the composition of the cellulose to 25C:75L, there was no change in the onset temperature. However, in the Tmax of the 75C:25L film there was a decrease in the peak height with the addition of rGO from 281°C to 257°C, while in the 25C:75L there was not much change. There was also a large weight loss from 65% to 39.5% in the 75C:25L film that has more cellulose when we added the rGO. In general, the main observation of the curves in Figure 8 is that the decomposition of the blended films with rGO occurs at a lower temperature than the decomposition of the lignin-cellulose component, which is due to the chain disruption causing stability changes. However, the addition of rGO shifts the degradation onset to slightly lower temperatures. rGO is a good thermal conductor, as a result, the heat transfer increases causing a slightly lower temperature onset. The thermal stability of the blended film decreases further as the cellulose content increases. The thermal stability of lignin itself is also affected by its
chemical composition. This is related to a decrease in cellulose crystallinity upon the addition of rGO.

**Figure 8** TGA percent weight decomposition analysis for (A) Lignin-cellulose without rGO blended films, (C) TGA derivative percent weight decomposition analysis, (B) Lignin-cellulose with rGO blended films and (D) derivative percent weight decomposition analysis.
<table>
<thead>
<tr>
<th>Sample 1</th>
<th>$T_{\text{Onset}}$ (°C)</th>
<th>$T_{\text{End}}$ (°C)</th>
<th>$T_{\Delta\text{Max}}$ (°C)</th>
<th>Wt Loss %</th>
</tr>
</thead>
<tbody>
<tr>
<td>10C:90L</td>
<td>246.597</td>
<td>354.975</td>
<td>283.717</td>
<td>53.760%</td>
</tr>
<tr>
<td>25C:75L</td>
<td>247.681</td>
<td>303.383</td>
<td>264.509</td>
<td>67.1515%</td>
</tr>
<tr>
<td>50C:50L</td>
<td>244.804</td>
<td>302.605</td>
<td>271.343</td>
<td>73.919%</td>
</tr>
<tr>
<td>75C:25L</td>
<td>267.996</td>
<td>300.348</td>
<td>281.150</td>
<td>65.648%</td>
</tr>
<tr>
<td>90C:10L</td>
<td>255.147</td>
<td>289.457</td>
<td>266.567</td>
<td>69.356%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample 2</th>
<th>$T_{\text{Onset}}$ (°C)</th>
<th>$T_{\text{End}}$ (°C)</th>
<th>$T_{\Delta\text{Max}}$ (°C)</th>
<th>Wt Loss %</th>
</tr>
</thead>
<tbody>
<tr>
<td>10C:90L:rGO</td>
<td>264.419</td>
<td>341.124</td>
<td>280.127</td>
<td>62.123%</td>
</tr>
<tr>
<td>25C:75L:rGO</td>
<td>243.468</td>
<td>309.971</td>
<td>266.898</td>
<td>67.139%</td>
</tr>
<tr>
<td>50C:50L:rGO</td>
<td>243.552</td>
<td>292.361</td>
<td>264.516</td>
<td>41.38%</td>
</tr>
<tr>
<td>75C:25L:rGO</td>
<td>240.961</td>
<td>286.897</td>
<td>257.663</td>
<td>39.532%</td>
</tr>
<tr>
<td>90C:10L:rGO</td>
<td>244.423</td>
<td>278.976</td>
<td>265.108</td>
<td>38.407%</td>
</tr>
</tbody>
</table>

**Table 2.** TGA decomposition temperatures of blended films with and without rGO components and experimental conditions.

**Conclusion**

We investigated and compared the effects of high and low concentrations of blended cellulose/lignin films using rGO and the ionic liquid 1-allyl-3-methylimidazolium chloride (AMIMCL). The importance of these biopolymers (cellulose, lignin) resides in their biological properties (biodegradability, biocompatibility, and non-toxicity). The blended polymer technique with rGO offers distinct properties arising from the desirable characteristic of both cellulose and lignin, improving the stability and strength of the
material. Also, it prevented the lignin self-assembly. We can conclude from this study that increasing the cellulose content will increase the ability of lignin’s phenols groups to wrap around the cellulose monomer, increasing the molecular interactions between the biopolymers and causing an increase in the stability and a decrease in the crystallinity of the blended film. It also causes lignin to self-assemble without control.

The significant change in IR spectra for the lignin-cellulose biocomposite indicates that increasing the concentration of cellulose can lead to a decrease in absorbance and crystallinity due to the interaction with lignin. On the other hand, increasing the concentration of lignin leads to an increase in absorbance and intensity which is related to more interaction with the cellulose. The TGA results also illustrate that thermal stability is higher for the cellulose/lignin with rGO films as compared to the cellulose/lignin films. In the SEM images, the morphology of the films with cellulose/lignin blends presents a more fibrous structure surface with heterogeneous morphology, while the films with rGO have smoother, homogeneous surfaces due to the presence of rGO. In the DSC, as the lignin content increases, the crystallinity of the blended films decreases because of the substitution of cellulose by the amorphous regions of lignin. However, the addition of rGO decreases the crystallinity of cellulose because more interaction occurs in the blended system. Understanding the effects of lignin-cellulose content with rGO on the structural and thermal stability of the blended film explained how the behavior of different blended films facilitates the development of customized blended structures for carbon fiber, ink for 3D-bioprinters, and fuel applications, among other uses. The question, now, is if this behaviors count be similar in tertiary system composed of cellulose, xylan and lignin.
Chapter 3:

Understanding the self-assembly of lignin-based biomaterials in a tertiary system.

Introduction

With the growth of demand for oil resources and petrochemical products which cause environmental pollution, it is in the worldwide interest to search for alternative natural resources, especially renewable biomass resources such as lignocellulosic woody biomass. The use of biologically renewable biomass with unique physical and functional properties is emerging as an important aspect of economic development as well as manufacturing opportunities that could minimize the consumption of energy and generation of waste. Lignocellulosic biomass is an important feedstock for the use of renewable resources in emerging applications for the packaging and production of fuels, chemicals, and energy.

Lignocellulosic biomass is a natural composite which consists of three major substances: lignin, cellulose, and hemicellulose (xylan). It has been recognized as the most abundant renewable resource. About 75% of lignocellulosic biomass components consist of polysaccharides which are present in the cell walls of woody plants. The goal in using these compounds is to increase the natural interactions of lignocellulosic biomass with other materials. In the natural structure of the lignocellulosic material, cellulose is embedded in a matrix of hemicelluloses, and the network between the cellulose-hemicellulose is further encapsulated by an outer lignin layer. This network occurs mostly through extensive hydrogen bonding between all three components. There is also a
covalent bonding among the components, such as an ester bonding between lignin and hemicellulose and an ether bonding between cellulose and lignin.\textsuperscript{57-58}

Lignin is one of the three major components of lignocellulosic biomass. It is a three-dimensional amorphous polymer consisting of aromatic methoxy phenyl-propane structure. In plant secondary cell walls, lignin fills the spaces between hemicellulose and cellulose, where it acts as a resin that holds the lignocellulosic matrix together.\textsuperscript{13} In addition, lignin has a cross linking, random, irregular structure in which the bonds between monomers can form at multiple positions by many different linkages, such as ether and hydrogen bonds.\textsuperscript{59} These linkages contribute different physical properties including cell wall strength and hydrophilicity.\textsuperscript{16} As it is a natural polymer with a complex homogenous structural characterization, we should understand both the structure and the function of lignin. It consists of three monolignol monomers as building blocks: p-coumaryl, coniferyl, and sinapyl alcohols. These alcohol monomers are categorized by the number of methoxy groups on their phenolic ring.\textsuperscript{33} The molecular weight, composition, and amount of lignin differ from plant to plant, decreasing in the order of softwoods > hardwoods > grasses.\textsuperscript{9}

Despite its potential, it is still a major challenge to convert lignin into a valuable material because lignin has evolved complex structural and chemical mechanisms which make it difficult to analyze due to its heterogeneous linkages.\textsuperscript{60} This could be related to the presence or absence of the inter or intra-molecular interaction between lignin and carbohydrate components.\textsuperscript{14} As a result, it is practically impossible to dissolve lignin in common solvent systems, which cause the aggregation and miscibility problems resulting in phase separation. Even though lignin has a low molecular weight, it still aggregates in
most solvents at high concentrations. The aggregation (self-assembly) is governed by the non-bonded orbital \( \pi-\pi \) interaction among the aromatic groups or because of the van der Waals attraction.\(^{39}\)

To increase the usefulness of lignin in environmental applications, we have to understand the lignin structure and its self-assembly in tertiary system. Lignin has hydroxyl and ether groups that are available for hydrogen bonding, which could help to increase the intermolecular interaction between its matrix by disrupting the hydroxyl groups in the backbone and preventing these bonds from wrapping around themselves.\(^{7}\) Disrupting those intermolecular interaction bonds will increase the usability of lignin’s structure.

Because of the availability of the lignin’s linkages, we could blend it with another compatible natural polysaccharide such as cellulose. Cellulose is a natural biopolymer found in the cell walls of plants. It is considered to be the most abundant material in the world and it found in nature as cellulose I (I\(_\alpha\) or I\(_\beta\)).\(^{61}\) It is a linear homo-polysaccharide composed of repeating (\(\beta 1-4\)) D-glucose units and stabilized by van der Waals forces and hydrogen bonds between hydroxyl groups and oxygens of adjacent molecules. It is capable of forming strong intermolecular and intramolecular hydrogen bonds via its \(\beta (1-4)\) glycosidic bonds, which provides a possible avenue for enhancing its molecular interactions with lignin.\(^{62}\) In this project, cellulose will be used as an adhesion agent. Because cellulose contains both crystalline and amorphous regions, so the crystalline structure of cellulose and its extensive hydrogen network could hinder the dissolution of cellulose in conventional solvents. Thus, we add xylan as a compatibilizer polymer to control the cellulose crystallinity and its adhesion influence.
Xylan is another natural polymer and a biomass component of the lignocellulosic material. In the xylan backbone, the glucan of 1,4-“-Dxylopyranose, holds branched chains of 4-oxymethylglucuronic acid, which has a strong interaction with cellulose. Xylan could add levels of disruption to the cellulose crystalline structures, especially in the formation of microfibrils.

However, the extensive network of inter- and intra-molecular hydrogen and dispersive bonds of the lignocellulosic biomass could impede their dissolution in most solvents. Therefore, efficient solvents and specialized processes are needed to produce regenerated cellulose fibers. To dissolve all the lignocellulosic mixture together, we use ionic liquid to dissolve lignocellulosic materials and regenerate a blended film. Ionic liquids (IL) are one of the most popular solvents for natural polymers and have been shown to be able to powerfully dissolve cellulose for film synthesis without breaking its molecular weight. ILs have unique properties, such as low vapor pressure, high thermal mechanical stability, low toxicity, and non-flammability. We chose 1-allyl-3-methylimidazoliumchloride (AMIMCl) as a solvent because it can disrupt the inter-molecular hydrogen bonds within the lignocellulosic biomass and then regenerate new hydrogen bonds between the anion group of AMIMCl and the hydroxyl groups of lignocellulosic blended mixture. The IL AMIMCL could help to decrease the cellulose’s crystallinity and increase the space of the \( \pi-\pi \) aggregation of the lignin’s aromatic rings.

In this study, we use alternating composite ratios of lignin and xylan no greater than 35% while the cellulose level is held constant around 45% in the blended films. These ratios ranges were chosen in order to simulate the proportions that found in natural plant species. We have noticed that when we use a higher concentration of lignin in the blended
film, the lignin becomes aggregate in the mixture because there is no enough cellulose to wrap around it. Thus, to prevent the self-assembly of lignin, another intermediator should be added to the mixture, such as graphene.

Graphene is an ideal compound to increase the interaction and stabilization of lignocellulosic biomass, especially when its surface has been reduced with hydroxide groups such as Vitamin C.\textsuperscript{24,30} Graphene sheets are modified by the powerful oxidation of graphite with a number of oxygen functional groups, such as hydroxyl, epoxy, carbonyl, and carboxyl.\textsuperscript{24} Graphene is a one-atom thick layer of carbon with a large aromatic molecule and has two-dimensional layers and sp\textsuperscript{2} bonded. Graphene oxide (GO) has many unusual properties, including high mechanical strength, efficiency in conducting heat, and thermal transport properties.\textsuperscript{29} GO has been investigated for its varied properties such as high adsorption capacity and good solubility due to its abundant surface oxygen-containing groups. GO sheet surface groups provide sufficient sites for linking macromolecules, polymers and enhancing physicochemical properties, which makes them favorable for biomedical and environmental applications.\textsuperscript{42}

It was found recently that lignocellulosic materials can easily bind with reduced graphene oxide (rGO) sheets by hydrogen bonding and π-π stacking.\textsuperscript{24} The large surface area of GO makes it an ideal conducting matrix for trapping lignocellulosic components, especially lignin, between its 2D sheets. GO single-layer sheets could produce different thermal and chemical properties for variety applications.\textsuperscript{47} Reduced graphene oxide (rGO) will be used here as an intermediator to immobilize the lignocellulosic biomass between its two-dimensional flat sheets and prevent the self-assembly of lignin.
To utilize cellulose, lignin, xylan and rGO in different kinds of applications, it is essential to compose stable homogenous films in order to effectively modify these biopolymers. Changing the ratio of the lignocellulosic biofilms with the addition of rGO can result in structural modifications which affect the thermal stability and topography of these films. However, the characterizations of blended structures based on lignocellulosic biomass (lignin, cellulose, xylan) and lignocellulosic film with rGO in various ratios using IL AMIMCL have not yet been fully explored. Our investigation focuses on comparing the behavior of each blend of lignocellulosic biomaterial individually and with rGO using AMIMCL. In this study, the formation of the blended lignocellulosic film with and without rGO dissolved in AMIMCL was investigated using various techniques including ATR-FTIR, SEM, TGA, and DSC. Various analyses were used to explain if the structure and morphology of the blended films changed as a function of changes in lignocellulosic concentration. We observed profound morphological and thermal changes with the introduction of rGO in the matrix.

Material and Methods

Material.

Lignin alkali (CAS: 8068-05-1) was purchased from Sigma Aldrich. Avicel microcrystalline cellulose (Techware: Z26578-0) was acquired from Analtech (Newark, DE, USA). Xylan was obtained from beechwood (CAS:9014-63-5). Dispersed graphene oxide (GO) in water was purchased from Aldrich. Ionic liquid 1-allyl-3-methylimidazolium chloride (AMIMCL) was purchased from Alfa Aesar.
Film Regeneration.

The regenerated biomass films were prepared using a modified version of the protocol seen in previous literature. The appropriate amount of each biomass component was measured and then added together before its addition to the AMIMCL. To increase the compatibility of the GO sheets with the lignin and to increase the adhesion capabilities of the cellulose, GO was reduced with 0.005 g Vitamin C in 1 ml water and then heated to 50°C for 24 hours. After that, we rinsed 5 times with water in a centrifugation process to remove the rest of the Vitamin C. Then we filtrated the rGO by pouring it through cellulose filter paper and dried the mixture for 24 hours. The AMIMCL was placed in a test tube (approximately 90 w/w) and heated to between 90-100°C, at which point the biomass components (lignin, xylan, cellulose with rGO approximately 10 w/w) were added. The solution was dissolved in an oil bath by stirring. The biomass solution was transferred and spread between two glass plates and fully submerged in distilled water for 24 hours to regenerate the blended film and remove as much IL as possible. Once this was completed, the films were placed in a vacuum oven for 24 hours for drying at 50°C. Once the films were dried, they were stored in a vacuum desiccator.

Characterization Methods

Attenuated Total Reflectance Fourier Transform Infrared spectroscopy (ATR-FTIR) analysis was performed using a Bruker ALPHA-Platinum FTIR Spectrometer with Platinum-Diamond sample module and Bruker OPUS software version 7.2, Build: 7.2.139.1294. The spectra were collected in the wavenumber between 400-4000 cm⁻¹,
resolution 4 cm⁻¹, 32 sample scans and 128 background scans. Six different locations on the film were analyzed for each sample and the spectra average was taken.

**Thermogravimetric analysis (TGA).**

Thermal data were obtained using Thermogravimetric Analysis (TGA), which was carried out on all samples in a nitrogen atmosphere on a TA Instruments Discovery system. The heating process was run at 10°C/min ramp to 600°C for an average sample between 5 to 6 mg. The software determines the derivative plot using peak height analysis.

Blended film samples averaging 6 mg were heated linearly with a 10°C/min ramp up to 650°C. Step transition analyses were performed for each sample to determine the onset of decomposition (T₉₅%) and the weight-loss percentage of the sample evolution during the main decomposition step. Derivative values were calculated and peak height analyses were performed to determine the temperature at which the samples decomposed at the fastest rates (Tₐ₅ₐₓ).

**Differential Scanning Calorimetry (DSC).**

Samples of approximately 5 mg weight were enclosed in TZero aluminum pans and run in a TA Instruments Discovery with a refrigerated cooling system (RCS) and nitrogen gas flow (25 mL min⁻¹). The standard aluminum reference was used to calibrate the heat capacity. Samples were heated from 10°C/min up to 150°C to allow the water to evaporate. They were then cooled down to -30°C and heated up again to 300°C.
Scanning Electron Microscope (SEM).

SEM images were taken on the LEO1450EP SEM at the Rutgers University Camden campus. A small piece of the blended film sample was mounted on carbon tape on a Denton Desk II Au-Pd sputter coater. The samples were sputter-coated and run in a light-vacuum of 10 V for 60 seconds. The magnification used in this paper is a scale bar of 2000x (10.00 µm).

Results and Discussion.

Structural, thermal and morphological changes.

FTIR was performed to measure the structural changes of the regenerated films according to the blended lignocellulose\rGO polymer. Lignocellulosic films were characterized as soft and rubbery, while lignocellulosic with rGO films were rigid and breakable, similarly to as Chapter 2 biocomposites. Table 3 shows the composition breakdown of lignin, xylan, cellulose and only 1% of rGO used in this chapter.

<table>
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<tr>
<th>Cellulose</th>
<th>Lignin</th>
<th>Xylan</th>
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<td>20%</td>
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<td>45%</td>
<td>27.5%</td>
<td>27.5%</td>
</tr>
<tr>
<td>45%</td>
<td>35%</td>
<td>20%</td>
</tr>
</tbody>
</table>

Table 3. Experimental conditions of regenerated film concentrations of lignin, cellulose, xylan.
Multiple compositions were chosen to test if the rGO would prevent the self-assembly of lignin in high concentrations of the blended system and produce alignment configuration of the lignin or not. The objective in utilizing these compounds is to increase the natural interactions of lignocellulosic biomass (cellulose, lignin, and xylan) in order to measure the possible additive influence from rGO to these interactions. Our working hypothesis is that blended systems with a high concentration of lignin will produce lignin alignment configurations that change upon the addition of rGO. We also hypothesize that the rGO will prevent self-assembly at high lignin content. We also want to determine the extent in which the molecular interactions of intra- and inter-hydrogen bonds and hydrophobic interactions will affect the association of lignin with polysaccharides, rGO, and AMIMCL.

The FTIR results show the absorbance spectra between the pure components of the lignocellulosic materials and lignin-based biomaterials without and with rGO in Figure 9. The IR spectra within the broad regions of OH (3500-3000 cm⁻¹) and C-O (around 1100 cm⁻¹) was assigned to cellulose. Xylan has a stronger peak at 1600 cm⁻¹, which is indicative of C=O stretching. On the other hand, lignin has the most unique IR peaks, with strong peaks which showed the ester and carbonyl stretching absorption in the 1700 cm⁻¹ range. Specifically, the bands at 1450 cm⁻¹ and 1630 cm⁻¹ are attributed to the methoxide and alcohol of the propane chain. Other bands occurring from 1600 to 1500 cm⁻¹ are characteristics of aromatic compounds for phenolic hydroxyl groups.¹ These results confirm the nature of lignin’s ability to increase structural stability through its abundance of aromatic and non-polar species. The major IR peaks for AMIMCL are attributed to 3050 O-H, 2965 C-H, 1570 C=C, and 1165 cm⁻¹ C-O.⁴⁹ In addition, the IR spectrum of a pure
graphene sample shows characteristic peaks at around 3400 cm\(^{-1}\) and 1720 cm\(^{-1}\) which are due to C-OH deformation and C-O stretching of COOH groups, respectively (not shown in Figure 9). The absorption bands at 1163 cm\(^{-1}\) and 1577 cm\(^{-1}\) are due to epoxy ring deformation and C-O stretching mixed with C-O-C bending.

![Figure 9](image_url)

**Figure 9:** FTIR spectra of (A) material components of lignocellulosic films without rGO and (B) of material components of lignocellulosic films with rGO.
The FTIR spectrum results in Figure 9 represent the difference in absorbance between pure components of lignocellulosic biomaterials, lignin-based biomaterials, and lignin-based biomaterials with rGO. As can be seen from the IR for the lignin-based biomaterials, the spectra of the blended films correspond to the predominant constituent lignocellulosic biomass and to rGO. Between the two graphs (A) and (B), the blended film is composed of 20%, 27.5%, and 35% lignin, alternating with 35%, 27.5%, and 20% xylan with a constant ratio 45% of cellulose with an extra 1% rGO. Holding the cellulose concentration steady allows us to see whether the changes observed are due to the alteration of xylan and lignin.

In Figure 9 (A), the blended films of lignin-based biomaterials have more intense absorbance compared with the pure component, and the spectra give sharper peaks related to the imidazolium rings of the AMIMCL at 1165 cm\(^{-1}\) trapped between chains in the structures of lignocellulosic blended films. This can be explained by the hydrogen bonding that occurs between hydroxyl groups in the lignocellulosic materials and the cation (imidazolium ring) or anion (Cl\(^-\)) groups in the AMIMCL. Generally, as lignin concentration is increased, there appears to be more intermolecular interaction between the film and AMIMCl, causing possible changes to the inter- and intra- intermolecular bonding with the cellulose and xylan as the ionic liquid diffuses out to form the blended film. However, in Figure 9 (B), the lignocellulosic biomass with rGO blended films shows broad -OH bands interacting across the blend with a shift to a higher wavenumber when we increase the lignin concentration. The lignocellulosic blended film with rGO gives a complex of -OH and C-O peaks between 900-1600 cm\(^{-1}\) which are due to the C-O-H and C=O of the COOH groups.\(^ {24}\) In addition, we observed an increase in absorbance of rGO
for the O-H and C-OH, indicating successful reduction of GO. This indicates that the biocomposites with rGO has less ionic liquids retention during coagulation.

**Morphology Analysis (SEM)**

As can be seen in Figure 10, the SEM images illustrate marked changes in film morphology according to alternate lignin-xylan proportions in the blended biopolymer film with and without the addition of 1% rGO. The morphology and structure of the lignocellulosic blended films are shown in Figure 10 (A). The lignocellulosic blended films with less lignin (20% and 27.5%) and more xylan content show a more fibrous structure on their surface. Alternatively, as we increase the lignin content to 35%, spherical patterns appear in the topology. It can be understood that the observed morphological changes represent changes to the structural interactions of the blended components of the lignocellulosic films.

The lignocellulosic blended films with rGO that are shown in Figure 10 (B). The addition of rGO to the blended films results in smoother surfaces than the films with just lignocellulosic blends. Both the rGO and lignocellulosic blends interact via intermolecular hydrogen bonding that allows the film to become homogeneous. Moreover, the rGO prevents the lignin from self-assembling by trapping the lignin between its 2D sheets and providing interaction via hydrogen bonds in the rGO with lignocellulosic blends. This very important results as it provides evidence that the rGO prevent the self-assembly of lignin in tertiary system.
Figure 10. SEM images: (A) lignocellulosic blended films and (B) lignocellulosic blended films with rGO.

**Thermal Decomposition Analysis TGA**

The thermal analysis curves show further structural modifications based on thermal stability as measured by decomposition temperatures. In Figure 11, TGA data represents the precursors of lignocellulosic biomass and the resulting lignocellulosic blended films with and without rGO. The lignocellulosic blended film with rGO shows a high thermal stability with a mass loss that was observed at around 230°C due to the evaporation of water absorbed from the rGO.
Figure 11. TGA percent weight decomposition analysis for (A) lignocellulosic blended films and (B) lignocellulosic blended films with rGO. TGA derivative percent weight decomposition analysis for (C) lignocellulosic blended films and (D) lignocellulosic blended films with rGO.

As shown in Table 4, when we alternated the composition of lignin and xylan with the addition of rGO, we observed an increase in temperature for the onset of the thermal degradation of the (45C:20L:35X) film (T onset = 245°C to 256°C). In addition, when we increased the composition of the lignin to (45C:35L:20X), the T onset increased about 10 degrees from 244 to 254°C. Moreover, in the Tmax of the (45C:35L:20X) film there was an increase in the peak height with the addition of rGO from 264°C to 278°C, while in the
(45C:20L:35X) there was not much change. However, there was a large weight loss from 97.75% to 70.76% in the (45C:35L:20X) film as a function of lignin content. When the rGO was added the decomposition temperature and the weight lost percentage became stable. Therefore, we can conclude that the rGO is well integrated within the matrix causing it to resist more thermal stress. We can observed in the SEM figures that the biocomposite with rGO are homogeneous and does not look like fibers.

<table>
<thead>
<tr>
<th>Sample 1</th>
<th>( T_{\text{Onset}} ) (°C)</th>
<th>( T_{\text{End}} ) (°C)</th>
<th>( T_{\Delta \text{Max}} ) (°C)</th>
<th>Wt Loss %</th>
</tr>
</thead>
<tbody>
<tr>
<td>45C:20L:35X</td>
<td>245.448</td>
<td>299.907</td>
<td>267.393</td>
<td>79.60%</td>
</tr>
<tr>
<td>45C:27.5L:27.5X</td>
<td>245.209</td>
<td>300.687</td>
<td>270.227</td>
<td>80.84%</td>
</tr>
<tr>
<td>45C:35L:20X</td>
<td>244.286</td>
<td>297.369</td>
<td>264.747</td>
<td>97.75%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample 2</th>
<th>( T_{\text{Onset}} ) (°C)</th>
<th>( T_{\text{End}} ) (°C)</th>
<th>( T_{\Delta \text{Max}} ) (°C)</th>
<th>Wt Loss %</th>
</tr>
</thead>
<tbody>
<tr>
<td>45C:20L:35X:rGO</td>
<td>256.595</td>
<td>289.231</td>
<td>264.921</td>
<td>77.72%</td>
</tr>
<tr>
<td>45C:27.5L:27.5X:rGO</td>
<td>254.047</td>
<td>299.955</td>
<td>272.569</td>
<td>72.98%</td>
</tr>
<tr>
<td>45C:35L:20X:rGO</td>
<td>254.470</td>
<td>305.045</td>
<td>278.00</td>
<td>70.76%</td>
</tr>
</tbody>
</table>

Table 4. TGA decomposition temperatures of blended films without and with rGO components and experimental conditions.
Thermal Analysis (DSC)

Thermal stability studies on lignocellulosic biomass films with and without rGO were carried out through DSC. DSC measures the temperature and heat flow during change in the material as a function of temperature in a controlled atmosphere. In Figure 12 (A) shows that the glass transition temperature (Tg) of lignocellulosic blended films is at 120°C for all samples. With the addition of rGO the glass transition temperature is reduced to 85°C. When we raise the temperature above the Tg, an exothermic peak may occur which shows the weight loss of samples and cold crystallization. The crystallization temperature (Tc) occurs due to the rapid cooling and freezing of the lignocellulosic sample into a non-equilibrium state. As the temperature goes up, the polymer molecules can move and crystallize at the equilibrium state, while the temperature at the highest point, the peak that occur shows that the polymer is completely melted. Because energy is added to the polymer to make it melt, this process is called endothermic transition. When we alternated the composition of lignin with xylan (45C:35L:20X) and (45C:20L:35X) with and without the addition of rGO, we observed two well-defined exothermic peaks for the DSC curve in the film with a low concentration of lignin (45C:20L:35X) followed by an endothermic peak, while in (45C:35L:20X) there was only one exothermic peak. This is related to the morphological nature of the material. We suspect that the biocomposite with high composition of lignin has more amorphous regions. On the other hand, the lignocellulosic film (45C:20L:35X) with rGO has strong peaks of exothermic follow by endothermic peaks compared to the alternate percentage (45C:35L:20X) that has a decrease in its exothermic peak and is not followed by an endothermic peak.
Figure 12 (A). DSC curves of blended lignocellulosic films (A) without rGO and (B) with rGO.

In addition, we have noticed that when we use equal concentrations of lignin and xylan (45C:27.5L:27.5X), there was only one exothermic peak followed by an endothermic peak. With the addition of rGO the endothermic peak disappeared. This indicates that the
addition of rGO contributed to strong intermolecular hydrogen bonds in the lignocellulosic blended film. We can conclude from our findings that as the lignin content increased, the crystallinity of the blended films decreased because of the substitution of the cellulose by the amorphous regions of lignin. In addition, increasing the lignin content can increase the molecular interactions between the biopolymers, causing change in the stability of the blended film. This suggests that more energy is required to break down the bonds in these lignocellulosic films, yielding a more stable material. DSC analysis results support the conclusion that rGO improved the thermal characteristics of lignocellulosic films due to its good thermal conductivity.

**Conclusion**

Here, we compared the behavior of blended lignocellulosic biomass in a tertiary system with and without rGO using the ionic liquid 1-allyl-3-methylimidazolium chloride (AMIMCL). We can understand from the findings that increasing the xylan content will increase the ability of lignin’s phenol groups to wrap around the cellulose monomer and increase the molecular interactions between the biopolymers, causing change in the stability and decrease in the crystallinity of the cellulose in the blended film.

The significant change in IR spectra for the lignocellulosic blended film indicates that adding rGO can increase the intermolecular interaction with the blended films, causing possible changes to the intermolecular bonding, while the IL AMIMCL diffuses within the mixture to regenerate the blended film. These results confirm the nature of lignin’s ability to increase structural stability through its abundance of aromatic and non-polar species and the ability of rGO to imbedded itself within the matric. The TGA results also show that
thermal stability is higher when we increase the lignin content for the lignocellulosic biopolymer through the addition of rGO as compared to the lignin-based biofilms.

In the SEM images, the morphology of the films with high content of lignin has a small fibrous/spherical pattern, but the surfaces of the films with rGO are smoother with an homogeneous structure. This result provides evidence to suggest that rGO prevents the self-assembly problem of lignin. In the DSC, as the lignin content increases, the endothermic peak disappears due to the decrease in the crystallinity of the blended films. However, adding rGO results in a decrease in the glass transition temperature and in appearance of two exothermic peaks due to the effect of the rGO to interact with both lignin and xylan. This explains why the endothermic peaks disappeared. As a result, we provide evidence to suggest that by using 1% of rGO it prevent the lignin self-assembly in the blended system cause changes to the physicochemical properties and providing a new path to use lignin as added value material.
Chapter 4: Summary

Blended lignocellulosic biomaterial (cellulose, lignin, xylan) systems have been widely studied to obtain desirable properties for different applications. In this study, we were able to mimic the complex hierarchical structure of some stable natural structures, such as cell walls of plants, to acquire a stable material that can be used in environmental applications, specifically in the usability of lignin-based biomaterials in material development. Non-toxicity, biocompatibility and accessibility of these natural materials make these polymers suitable for environmental and material science applications. In our study, we prepared regenerated films made from varying proportions of lignocellulosic biomass using the ionic liquid AMIMCl. We compared the dissolution and coagulation steps with respect to two different blended systems. The first blended system, described in Chapter 2, was composed of lignin and cellulose. The second blended system, described in Chapter 3, was composed of lignin, cellulose, and xylan. Both blended systems were tested with and without the addition of rGO.

The study in Chapter 2 was conducted to compare the effects of high and low concentrations of a system composed of lignin and cellulose to study molecular interactions and physicochemical properties of blended solid films with IL AMIMCL and with or without rGO. This model system is important because they allow us to evaluate the chemical structure, morphology and thermal properties of the various compositions. We have proven that the structural characteristic of lignin-cellulose biocomposites in combination with rGO will prevent the self-assembly of lignin upon coagulation. Moreover, when we increased the cellulose content, the ability of lignin’s phenols groups to wrap around the cellulose monomer increases. In addition, increasing the molecular
interactions between the biopolymers help to increase the stability and to decrease the crystallinity of the blended film. The FTIR spectra for the lignin-cellulose film showed that increasing the concentration of lignin leads to an increase in absorbance and intensity with a decrease in the crystallinity of cellulose which is related to the interaction with the amorphous regions. On the other hand, with the addition of rGO, there were an increase in absorbance due to its ability to interact with the matrix. In the SEM images, the addition of rGO converted the morphology of the lignin-cellulose blended films from a fibrous with spherical surface to a smoother, homogeneous surface, which proves that rGO plays a role in preventing the self-assembly of lignin. We also investigated the effect of temperature on the blended film by studying the thermodynamic effect on interactions and self-assembly. The TGA results indicated that the thermal stability of lignin-cellulose biocomposite with rGO is lower than without rGO. The DSC provided evidence to suggest that the decrease in thermal stability with rGO is the results of a decrease the crystallinity of cellulose upon the addition of rGO.

In Chapter 3, our objective was to understand lignin self-assembly in various compositions with and without the addition of rGO. We were also determining the extent in which the molecular interactions (e.g., intra-and inter-hydrogen bonds and hydrophobic interactions) affect the association of lignin with polysaccharides (cellulose, xylan), rGO, and IL AMIMCl. To understand the effect of composition on the molecular interactions, we observed variations in the structural, morphological and thermal properties of the blended film as a function of component concentration. In the FTIR analysis, the spectra showed increasing peaks similarity and intermolecular bonding changes depending on the component concentration and due the addition of the rGO. The findings of SEM showed
significant differences in morphology from fibrous surface structures with increasing lignin content, while the addition of rGO makes the surface smoother and homogeneous. The thermal data obtained from TGA showed that, as the lignin content increases with the addition of rGO, the thermal stability increases due to the disruption related to the change in the structure and its interaction with xylan. In the DSC, the crystallinity of the blended films decreases as the lignin content increases, and the endothermic peak disappears. However, the addition of rGO showed a significant decrease in glass transition temperature and two exothermic peaks related to an increase in interactions with cellulose and xylan resulting in the decrease in crystallinity.

The study of self-assembly of lignin-based biomaterial with the addition of rGO provides insight into possible avenues to significantly change the material, structural, thermal and physical properties to meet the demands for lignin as materials for value added products. This study provides knowledge of the impact of changing the self-assembly of lignin which provides a new path to use lignin as a new material for the medical, environmental and material manufacturing. The ability to engineer materials at an atomic level to tune physicochemical properties with rGO and IL can be employed to develop fibers, ink for 3D-bioprinters, and medical textiles.
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