Cellulose is a natural abundant polymer used in a variety of applications. Its use however, is hampered by its poor solubility in various solvents. This is primarily due to the hydrogen bonds between the hydroxyl groups on the anhydoglucose chain. In view of that, various cellulose derivatives have been synthesized to aid dissolution and this impacts a variety of solubility characteristics. Cellulose acetates (CA) are cellulose esters that are partially substituted at the C-2, 3 and 6-positions of the anhydroglucopyranose residue. Their solubility in various solvents depends on the degree of substitution (DS) of the acetyl groups. For instance, CA is soluble in water at low DS of between 0.5-1. But it is insoluble in aqueous solutions at higher degree of substitution (DS > 1). CA is employed in various applications such as textile manufacture, tool handles, specialty papers, cigarette filters and is a polymer of choice in majority of reverse osmosis membrane preparation. These applications often exploit semi- to concentrated cellulose acetate solutions in appropriate solvents. Such systems can be induced to form aggregated structures such as gels which can be initiated by the addition of a non-solvent. Thus, depending on the solvent and non-solvent adopted, the cellulose acetate mixed solvent system can be tailored to exhibit sol-gel characteristics utilizing the inherent intra- and intermolecular interactions present in solution. However, such systems and the interactions influencing their behavior is not very well understood. In this regard, the main objectives of our study are as follows – to develop a
ternary mixed solvent system comprising of cellulose acetate, N,N dimethylacetamide and water and manipulate the system to form aggregated structures leading to phase separated gel network. The tools employed in this project to investigate and characterized the macroscopic properties as well as the microstructural changes are rheology, scanning electron microscopy (SEM) and laser scanning confocal microscopy (LSCM).

The first part of this study involves addition of water-N,N dimethylacetamide solutions in different ratios to bulk 20% cellulose acetate in N,N dimethylacetamide solutions with emphasis on increasing water content in the system. Using rheology as the main analytical tool, the steady state viscosity was found to increase with water content increase. Above water concentrations of 19%, there is a solution to gel transition, which also showed enhancement in dynamic viscoelastic properties with water content increment. The SEM micrographs showed similar patterns with gels having lower water content exhibiting larger voids in comparison to gels with higher water content at same cellulose acetate concentration. Using LSCM, we obtained microstructural formation with more open networks at lower water content, whiles a more compact homogenous structure was exhibited for higher water content gel samples.

In the second part of this study, addition of cellulose acetate to different ratios of N,N dimethylacetamide/water solutions are investigated. At low water content, the system showed steady state viscosity increase with water content as was observed in the first part of this thesis. Typically beyond 19% water concentration, the systems phase
separates into two layers consisting of a clear solution on top of a viscous bottom layer. This is in contrast to the first part of the study where we observed a uniform rigid material. Heating the two-phase system to 100°C and cooling back to room temperature led to the formation of a one-phase physical gel matrix. With increasing water content, the elastic and viscous moduli of the gels increased at constant cellulose concentration.

Finally, we investigate the gel properties with emphasis on yield stress when mechanical stress is applied to the gels. In addition, the gel-sol transition for the gels are investigated by subjecting them to temperature variations.
Personal Biography

Collins Appaw was born in the city of Accra, which is located in Ghana, West Africa. His desire in pursuing a career in Chemical Engineering is primarily due to his interest in math and chemistry. His interest in research led him to pursue a Master program in Chemical Engineering at North Carolina A & T State University after completing his Bachelor of Science degree from the Department of Chemical Engineering, University of Science and Technology (UST) Ghana. After completing his Master degree, he immediately joined North Carolina State University to begin work on his doctoral research in the Fall of 2000. He plans to work in an industrial setting beginning 2005.
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CHAPTER 1

INTRODUCTION AND OVERVIEW

Abstract

In this chapter, we offer the reader a brief introduction to the characteristics of cellulose and cellulose derivatives (cellulosics), in particular to cellulose acetate, the cellulosic studied in this dissertation. The natural abundance and biodegradability of cellulose together with its ability to provide unique (solution and end-use) properties through derivatization have made cellulosic polymers attractive for usage in a wide range of applications including textile fibers, molding powder sheets, optical membranes among others. This thesis involves the development and characterization of a ternary system consisting of a cellulose acetate, a solvent ($N,N$-dimethylacetamide) and a non-solvent (water). We examine the rheology and microstructure of the system as a function of composition and processing parameters such as temperature. A variety of experimental techniques are employed to gain a fundamental understanding of how the mode of interactions impact cellulose acetate in the mixed solvent systems.
1.1 Introduction

Polymers and biopolymers are used in numerous applications with the most abundant biopolymer being cellulose.\(^1\) We see an emergence in polymeric materials replacing traditional materials (e.g. metals) in many areas of applications in everyday products. This range from car body parts to everyday items such as cooking utensils. These polymers are natural or synthetic products, which science and research have studied to investigate their applicability in various applications.

Cellulose is the most abundant natural polymer (Figure 1) that obtained its name from Payen in 1842.\(^2\) The cellulose structure shows a chain-like extended linear macromolecule of anhydro-D-glucopyranose units linked at the 1 and 4 positions by glycosidic bonds.\(^2\) The use of cellulose together with its derivatives has wide spread applications including fibers, films, plastics, coatings, suspension agents, composites.\(^3\) With the advent of synthetic polymer their use has somewhat dwindled, but some applications still adopt cellulose derivatives as the raw materials of choice. In addition, various studies are still been conducted to look for and expand their usage in existing and new technologies. The inherent problem that faces users of cellulose is the general insoluble nature in most common solvents.\(^4\) There is therefore the need to modify the structure of cellulose to improve solubility which has led to the synthesis of various cellulose derivatives.\(^5\)

Cellulose derivatives (cellulosics) comes in all forms and structures depending on the functional group(s) used to substitute the hydroxyl groups on the cellulose chain.\(^6\)\(^-\)\(^10\) The derivatized cellulose molecule can be partially or fully substituted and this can go a long way in influencing solution and end-use behavior. To understand the
behavior of cellulosics calls obviously for intensive research efforts in various disciplines. Knowledge of molecular level interactions will aid researchers to manipulate their properties and impart specific properties to the cellulosic system. Aqueous soluble cellulosics such as methylcellulose are used as food-thickening agents etc. Other classes of cellulosics including cellulose acetate and cellulose nitrate are used as cigarette filters and adhesives respectively. In spite of its potential for numerous applications though, both cellulose and its derivatives are being relegated to the background in preference to other polymeric materials. Thus, it is imperative to tap into and exploit the potential for using cellulosics in existing technologies and develop new applications for putting them to use. In view of that, we choose cellulose acetate as the primary polymer to study.

Cellulose acetate is a derivative of cellulose, which exhibits different solubility pattern depending on the degree of substitution of the hydroxyl units, which are replaced with $O$-acetyl groups. A typical cellulose acetate structure is shown in Figure 2 which has three acetyl groups on the chain and such units are termed as cellulose triacetate. The presence of acetyl and hydroxyl groups on the chain causes cellulose acetate to show interesting properties in various solvents. Therefore, the dissolution of cellulose acetate can be influenced depending on the affinity of a solvent for a specific functional group. For example, the rheology of cellulose acetate in different solvents is postulated to be affected by specific interactions such as hydrogen bonding in solution. The use of cellulose acetate usually involves concentrated solutions but unfortunately research in this area is few and far between. A possible explanation may be due to the viscous nature of relatively high cellulose acetate solutions making system
characterization difficult since most techniques such as traditional dynamic light scattering work best in dilute solutions. Therefore, to gain a concise understanding, which may lead to better predictions of cellulose acetate under such conditions, it is imperative to study semi- to high concentration levels. Thus, our ternary system comprising of cellulose acetate, N,N dimethylacetamide and water is studied at fairly high cellulose acetate concentrations. Phase separation and sol-gel transition is an important feature of our work since these characteristics are of considerable interest for application purposes. An example in this regard is the pharmaceutical industry, which is interested in phase separation characteristics in microencapsulation. We employ rheological techniques as our primary tool to investigate the macroscopic properties of our system. It must be emphasized that, rheology can also be used to predict the microstructural properties of various systems. Rheology has also been determined as the most direct and reliable method to determine sol-gel transition. Quite a number of cellulose gel and membrane system use scanning electron microscopy (SEM) to investigate microstructural changes. In view of this we adopted both SEM and a relatively new technique called laser scanning confocal microscopy (LSCM) to complement our rheological analysis. Our hope is the use of these techniques enabled us gain a fundamental understanding of how the mode of interactions impact cellulose acetate in mixed solvent systems.
1.2 Goals of Project

The main objective for this thesis is to examine the structure and property relationship between cellulose acetate and mixed solvents comprising $N,N$-dimethylacetamide and water. The role of how polymer-cosolvent composition and processing parameters (e.g. temperature, cosolvent mixture) have on polymer solution properties inducing sol-gel transition in the system is examined. Furthermore, how such changes can affect the polymer conformation and interaction leading to aggregated structures (see Figure 3), and eventual phase-separation.

Several critical questions and issues need to be addressed in this project. They include:

- *How does polymer solvent interactions affect solution rheology and microstructure?*
- *Under what conditions can cellulose acetate form aggregation leading to phase-separated gels?*
- *How does process parameters (e.g., temperature) and sample preparation method influence rheology and microstructure?*

The specific step-by-step goals are as followings:

1. **Develop a ternary system comprising of cellulose acetate, solvent and non-solvent**

   The presence of hydroxyl and acetyl groups in partially substituted cellulose acetate molecule enable the polymer architecture to be influenced by cosolvents with different solubility character. This prompted us to adopt two solvents, which are miscible with each other but having different solubility behavior for cellulose acetate. $N, N$-dimethylacetamide is a good solvent for cellulose acetate and was chosen based on the
fact that, it can dissolve cellulose acetate to appreciable high concentrations. Also, other considerations included, high boiling point, low toxicity levels. Water the non-solvent for this study was chosen primarily because of its strong hydrogen bonding characteristics and obvious wide spread availability.

2. Examine the influence of cosolvent and cellulose acetate concentration pertaining to phase separation and sol-gel transition

The influence of non-solvent and how they can cause solutions of cellulose acetate to phase separate and eventually form elastic gel-like materials has been an important focus of this study. Phase separation in cellulose acetate system typically occurs when the solvent quality deteriorates. In this regard, we studied the effect of changing solvent quality by using different ratios of the cosolvents and progressively increase water content in the system. This process was also important to decipher the modes of hydrogen bond associations and dissociations in the system.

1.3 Overview of Thesis

In chapter 2, we provide a review of cellulose and cellulose derivatives. The chapter attempts to provide an investigative study of the various mechanism and mode of interactions exhibited by cellulosic systems. Details of the experimental methods adopted in our study are presented in chapter 3. Rheological methods are introduced and the basic concepts pertaining to the use of scanning electron microscopy (SEM) and laser scanning confocal microscopy (LSCM) to investigate the microstructure of the gel system are briefly outlined.
Chapter 4 deals with the rheological investigation of solutions and sol-gel mechanism of cellulose acetate, \(N,N\) dimethylacetamide solutions by the addition of different water concentrations (dissolution method 1). SEM studies are also performed to characterize and explain the gel system as a result of water content changes in the gels. In chapter 5, we examine a different route for solubilizing cellulose acetate in the cosolvents, which involves the addition of cellulose acetate to \(N, N\) dimethylacetamide/water solutions (dissolution method 2). This is in contrast to the solutions prepared in chapter 4 where we added water to cellulose acetate/\(N,N\) dimethylacetamide solutions. Rheology and SEM were used to investigate the solutions and phase separated two-phase system formed by this alternative addition process. In chapter 6, we study the behavior of gels formed from both dissolution methods with respect to their response to stress and temperature changes In addition we depict the microstructural properties of the gels using LSCM. Finally, we conclude the thesis with a summary of our findings and recommendations for future work in chapter 7.
References


Figure 1. Chemical structure of cellulose.
Figure 2. Schematic representation of a fully derivatized cellulose acetate chain.
Figure 3. (a) Polymer in solution and (b) Aggregated network structure
CHAPTER 2

BACKGROUND AND LITERATURE REVIEW

Abstract

Cellulose is the principal constituent of higher plants (40-50%) and is also the main component of various kinds of natural fibers. In as much as cellulose has many commercial uses, cellulose is hindered by the inability to be dissolved by most solvents. There is therefore, the need to modify the cellulose structure by derivatization methods to partially or fully replace the hydroxyl groups on the cellulose chain with various other functional groups. This process yields cellulose derivatives, which exhibit better solubility characteristics and thus provide a wider range of usage. In this regard, we present a summary of cellulose and its derivatives and how their solution patterns are affected by different solvents. We then briefly discuss the factors contributing to gel formation in some cellulose derivatives and how the microstructure is affected by gelation. After which we shift the discussions to cellulose acetate, the cellulosic being investigated in this thesis with respect to solution and gelation characteristics in a variety of solvents.
2.1 Introduction to Cellulose and Cellulosics

Cellulose is the most abundant naturally occurring biopolymer. Various natural fibers such as cotton and higher plants have cellulose as their main constituent. Cellulose consists of long chains of anhydro-D-glucopyranose units (AGU) with each cellulose molecule having three hydroxyl groups per AGU, with the exception of the terminal ends. Cellulose is insoluble in water and most common solvents. The poor solubility is attributed primarily to the strong intramolecular and intermolecular hydrogen bonding between the individual chains. In spite of its poor solubility characteristics, cellulose is used in a wide range of applications including composites, netting, upholstery, coatings, packing, paper, etc. Chemical modification of cellulose is performed to improve processability and to produce cellulose derivatives (cellulosics) which can be tailored for specific industrial applications as well to enable cellulosics to be characterized in the laboratory. Cellulose derivitization typically involves esterification or etherification of the hydroxyl groups on the cellulose chain. Cellulosics are in general strong, reproducible, recyclable and biocompatible, being used in various biomedical applications such as blood purification membranes and the like. Thus, through derivatization, cellulosics have opened a window of opportunity and have broadened the use of cellulosics. (Cellulosics have been around for ~100 years! And actually used more as “plastics” before petroleum plastics came around)

Cellulose esters constitute the largest sector of commercially important cellulose derivatives. Of these, both organic esters such as cellulose acetates and cellulose acetate butyrates as well as inorganic esters such as cellulose nitrate and cellulose phosphate are widely produced. Together with cellulose xanthates, the cellulosic intermediate in
Rayon production, cellulose esters comprise more than 90% of the production capacity in the chemical processing of cellulose. The manufacturing of cellulose esters typically involves the reaction of cellulose with the corresponding organic / inorganic acid and a strong acid catalyst and depending on the substituent and degree of substitution are used as textile fibers, coatings, cigarette filters, membranes, celluloid etc. ³

By contrast, cellulose ethers are manufactured through alkali reactions,⁵ are typically water soluble and widely used to modify the rheological properties in industrial applications such as paint, oil recovery, food and cosmetics.⁶ Some of the most common cellulose ethers are methyl cellulose, hydroxyethyl cellulose and carboxymethyl cellulose (CMC), with CMC dominating by far.

The utilization of cellulose and cellulose derivatives require a comprehensive understanding of the physical and chemical properties and behavior of the various derivatives. In view of that, more research is needed to better understand at the molecular level the various interactions and mechanisms influencing their properties and behavior.

Solution characteristics of cellulose derivatives

Cellulose derivatives exhibit different solution properties depending on the solvent system and the functional group(s) used to substitute the hydroxyl group(s) on cellulose chain. Cellulose esters such as cellulose nitrate and cellulose acetate dissolve in a wide range of solvents.²⁰ For instance, cellulose acetates exhibit solubility characteristics in both aqueous and common organic solvents, such as chloroform (CH₂Cl₂), acetone and DMF depending on the DS. Likewise, cellulose ethers such as
methyl cellulose and other hydrophobically modified cellulosics are soluble in aqueous solutions as well as some organic solvents depending on the degree of substitution (DS) and preparation method.\textsuperscript{7-16} Similarly, factors such as temperature, concentration, shear rate and degree of substitution have been found to affect the molecular structure of hydroxypropyl cellulose (HPC) solutions.\textsuperscript{17} HPC gels have been shown to exhibit greater elasticity with increased propylene glycol (PG) content in mixtures of water and ethanol.\textsuperscript{18} It has been observed that for aqueous carboxymethyl cellulose (CMC) solutions factors such as molar mass and concentration of the dissolved CMC are the major factors affecting its rheological properties.\textsuperscript{19} In low CMC concentration solutions Newtonian behavior was observed, while pseudoplastic, thixotropic and viscoelastic behavior was exhibited at high concentrations.\textsuperscript{20} It has been shown that in sodium CMC solutions crystalline regions act as binding or crosslinking sites and depending on the solvent or salt type lead to the formation of swollen gels or aggregates in solution.\textsuperscript{21}

\textit{Gelation of cellulose ethers and esters}

The inception of gelation is initiated by large macromolecular associations forming clusters, which lead to an infinite homogenous cluster extending through entire volume of the system.\textsuperscript{22} Solution to gel transitions have been observed in various cellulose derivatives, forming mostly physical gel systems. It is widely accepted that a physical polymer gels is initiated by physical aggregation leading to the formation of a three-dimensional network.\textsuperscript{22} The transitions from solutions to gels have been studied using various techniques including rheological methods.\textsuperscript{5, 7-8} Rheology has been
determined to be the most direct method to determine sol-gel transitions in polymeric systems. Not only can rheology be used to investigate the gelation mechanism, it also provides important characterization properties which invariably assist in assigning specific applications for polymers. This technique has been applied to various cellulosic systems to precisely determine and control gel formation. Phase separation behavior is often exhibited by cellulosic systems. It has been shown that phase separation and gelation are two characteristics which are closely related. Gelation in cellulosic systems typically exhibits phase separation characteristics prior to gelation. Phase separation in cellulosic solvent systems, are dependent on the concentrations of specific derivative and solvents used. This phenomena typically occurs when solvent quality deteriorates or changes in the polymer-solvent interactions occur due to external factors such as temperature, non-solvent addition etc. These rearrangement of the intra- and intermolecular interactions in solution due the above-mentioned factors may account for gel formation in such cellulosics systems. A variety of water-soluble cellulosics exhibit a unique thermoreversible gelation process. The unique feature of these systems is the induction of a three-dimensional network and gel formation with increasing temperature, then the return to an isotropic solution when cooled. Such thermoreversible behavior is observed for methyl cellulose solutions and has been attributed by some researchers to hydrophobic interactions in solution. Manipulation of methyl cellulose gelation has been accomplished through the addition of salting-in and salting-out salts. Sodium chloride, a typical salting-out salt has been shown to aid gelation, while sodium iodide (salting-in salt) inhibited gel formation. Likewise, the
use of ionic surfactants have been shown to greatly affect gel network strength in other aqueous cellulose derivative systems.\textsuperscript{25}

Unlike cellulose ethers, reports involving gel formation of cellulose esters are rather limited and may be due in part to their general decline in such applications. Notwithstanding gelation has been observed in a variety of cellulose ester systems.\textsuperscript{32-33} Gels prepared from cellulose esters usually find applications such as filters and binding agents.\textsuperscript{34} Separation of metals in aqueous solutions have been performed using cellulose nitrate gel matrixes,\textsuperscript{34} while cellulose phosphate gels have been synthesized to be used in orthopedic applications especially for bone regeneration.\textsuperscript{35}

2.2 Physical, Chemical and Solution Properties of Cellulose Acetate

Cellulose acetates (CA) are one of the most widely produced cellulose esters. It is an acetylated cellulosic in which the hydroxyl groups along the cellulose chain are fully or partially acetylated in a statistical manner.\textsuperscript{36-42} All of the industrial processes practiced today are aimed at the manufacture of a fully substituted cellulose triacetate (DS> 2.9, or an acetyl content of 44.8%) as the primary product.\textsuperscript{42} This is either isolated and processed as is or partially desubstituted to “secondary acetate” with a DS of between 1.8 and 2.5 (predominately near 2.4).\textsuperscript{42} A heterogeneous process to produce a uniform diacetate is not currently available. The majority of CA is produced using a solution process, although fiber acetylation is also practiced. Typically cotton linters or softwood sulfite or prehydrolyzed sulfite pulps are used as the raw material. In solution acetylation either glacial acetic acid alone or in combination with methylene chloride is employed as a solvent for the CTA formed, and the reaction is catalyzed using sulfuric
acid. In secondary acetate production, the CTA is not isolated rather being immediately converted to the diacetate by the addition of water, dilute acetic acid or NaOH. This process affectively decomposes the intermediate sulfate ester groups in the chain and decrease the DS while still maintaining the cellulose acetate in solution. The manufacture of CA differs in the solvent used for the acetylation and process conditions adopted.\textsuperscript{41} Acetic acid process by far represents the route for producing the largest amount of cellulose acetate for commercial purposes. With development of new solvents for cellulose, new path for acetylation processes are still being investigated since acetylation require dissolution of cellulose.\textsuperscript{42}

The solution properties of cellulose acetates have been well studied and have been shown to be influenced by the average degree of substitution and the distribution of substituents along the chain.\textsuperscript{40} The structural properties of CA affect the rheology of the cellulose acetate-solvent system. Cellulose acetates which have degree of substitution (DS) of between 0.5 to 1 are soluble in water.\textsuperscript{43-44} This phenomena is attributed to disruption of the intra- and intermolecular hydrogen bonding within the cellulose system upon the introduction of the small number of acetyl groups.\textsuperscript{44} With increasing DS, cellulose acetates becomes insoluble in water but show good solubility in a variety of organic solvents, such as tetrahydrofuran (THF), acetone, $N,N$ dimethylacetamide (DMAc) with cellulose acetates having high DS being insoluble in aqueous solution. Similarly, depending on the DS, concentration and solvent cellulose acetates exhibit a variety of solution properties. Boerstoel \textit{et al.} found that over a DS range of 0.23 to 2.89, cellulose acetate was soluble in phosphoric acid and exhibited liquid crystalline properties.\textsuperscript{45} Using dilute solutions of cellulose diacetate (CDA) in
mixed solvents it has been reported that basic solvents (e.g. acetone) interact primarily with the hydroxyl groups on the cellulose chain, while acidic solvents (e.g. formic acid) primarily solvate the acetyl groups.  Therefore, the use of specific solvents can induce structural changes in solution depending on the amount of acetyl and hydroxyl groups on partially substituted CA chains. This in some cases lead to phase separation and/or gelation in a variety of CA solvent systems. Matsuyama et al. used supercritical CO₂ to cause phase separation and was observed to occur instantaneously when CO₂ was added to cellulose acetate in acetone, methyl acetate, 1,3-dioxolane and 2-butanone solutions respectively. CA samples with different molecular weight and degree of substitution have been showed to form gels in dimethyl phthalate. Increase in degree of substitution of CA and polymer concentration in the system, causes an increase in the dynamic moduli.

2.3 Applications and New Emerging Uses of Cellulose Acetate

The use of CA dates back to the early 1900s when the first photographic film was produced by the Dreyfus brothers. Properties including good toughness, deep gloss and a “natural” feel have made CA attractive for a number of applications. It also has the advantage of possessing low toxicity. CA is used in a variety of industrial applications such as textile manufacture, tool handles, speciality papers, cigarette filters (major constituent in the U.S. for producing cigarette filter tow), among others. Factors such as transparency, smoothness and color have allowed CA to be used in handles for toothbrushes, umbrellas and screwdrivers. Spectacle frames have been made from sheets of cellulose acetate, but this practice has been replaced to some extent with other
synthetic thermoplastic materials. CA is increasing being utilized in the manufacturing of separation and filtration media in such applications as electrophoresis and reverse osmosis membranes (ROM).\textsuperscript{50-51} As well, CA has shown good promise in the area of drug delivery and research is underway to determine its effectiveness and applicability.

2.4 Gelation Behavior of Cellulose Acetate

Previous work on the gelation mechanism of cellulose acetate has shown interesting behavior with respect to the sol-gel transition. CA gels exhibit thermal reversible properties, which depend on factors such as CA concentration, acetyl content and the type of solvent. Unlike other cellulose esters which gel when heated, CA solutions do not exhibit such gel characteristics. In most CA/solvent systems gelation occurs after the CA solution is heated to a specific temperature and subsequently cooled. Such behavior has been reported for CA/benzyl alcohol solutions.\textsuperscript{52-53} Heating benzyl alcohol solutions of CA to 60-80°C led to gelation when the system was cooled to 25°C. It is postulated that gel formation is induced by the existence of strong intermolecular associations in the system.\textsuperscript{52}

In polymeric systems physical gel formation can arise as a result of phase separation. Depending on the system phase separation leads to polymer aggregation and the formation of large macromolecular assemblies.\textsuperscript{22} In some CA/solvent systems the addition of a non-solvent (e.g. water) can induce gelation in which phase separation characteristics are exhibited prior to gel formation. Phase separation is typified by the observation of a gradual to extreme cloudiness in the system and is dependent on the
concentration of polymer and cosolvents used. Such phase separation induced CA
gelation is used in the production of wet phase inversion membranes.\textsuperscript{54} Here water is
the nonsolvent of choice owing to its nontoxic nature, widespread availability and
strong hydrogen-bonding characteristics. However, the application of other non-
solvents such as alcohol-water mixtures have been studied.\textsuperscript{55,56}
References


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CHAPTER 3

EXPERIMENTAL METHODS

Abstract

This focus of this chapter is to provide a brief description of the experimental techniques used in this thesis. A general background and the theoretical principles behind the experimental techniques used to probe our system, which includes rheology, scanning electron microscopy (SEM) and laser scanning confocal microscopy (LSCM) are elaborated in this chapter. These characterization techniques provide us information at both macroscopic and microscopic level on the solutions and gels formed in our study.
3.1 RHEOLOGICAL CHARACTERIZATION

Rheology is defined as the science involved in the study of flow and deformation of materials.\(^1\) It is a powerful tool that can be used to characterize a wide range of materials ranging from solutions, melts, gels, particulate systems among others. It can also be used to provide information and characterize microstructure of many materials.\(^2\) Rheological measurements can be performed either in steady or dynamic modes.\(^3,4\) These two measurement techniques are discussed and for more detailed information some useful text on rheology can be obtained from the following sources.\(^3,5-7\)

Steady shear rheology

The steady shear measurements is performed by subjecting a sample to a steady shear at a constant shear rate (\(\dot{\gamma}\)) resulting in a generation of a shear stress (\(\tau\)). The corresponding shear stress (\(\tau\)) on the sample is measured using a torque transducer. The viscosity (\(\eta\)) is measured as function of the steady shear rate\(^2(\dot{\gamma})\) and is defined as:

\[
\eta = \frac{\tau}{\dot{\gamma}}
\]

Solutions of cellulose derivatives typically exhibit a zero shear viscosity, \(\eta_0\), which is typified by constant viscosity (Newtonian region) at low shear rates and a decrease in viscosity (shear thinning) at high shear rates. Some polymeric systems have been shown to exhibit a shear thickening behavior with increasing viscosity with shear rate increase. The viscosity plots depicting different behaviors are shown in Figure 1.
**Dynamic rheology**

This technique also called dynamic oscillatory flow involves the application of a sinusoidally varying strain $\gamma = \gamma_o \sin(\omega t)$ in the linear viscoelastic (LVE) regime. The symbol $\omega$ is the frequency of oscillations and $\gamma_o$ is the strain amplitude.

The shear stress generated is also sinusoidal in nature given by the expression:

$$\tau = \tau_o \sin(\omega t + \delta)$$

Expanding the above expression results in two components for the stress, one in phase and one out of phase with the strain:

$$\tau = \tau_o \cos(\delta) \sin(\omega t) + \tau_o \sin(\delta) \cos(\omega t)$$

The elastic or storage modulus, $G'$, is related to the stress component in phase with the strain and is defined as:

$$G' = \frac{\tau_o \cos(\delta)}{\gamma_o}$$

While the viscous or loss modulus $G''$ is related to the stress component out of phase with the strain and is given by:

$$G'' = \frac{\tau_o \sin(\delta)}{\gamma_o}$$

$G'$ provides information on the energy stored by the sample, while $G''$ is related to the energy dissipated by the sample. Thus, for a perfect elastic system, $\delta = 0$ and $G'$ assumes a finite value while $G'' = 0$. Alternatively, for a purely viscous system, $\delta = 90^\circ$ with $G''$ having a finite value with $G' = 0$. Most materials (e.g. polymer melts) exhibit both elastic and viscous properties and are referred to as viscoelastic materials. Therefore, for viscoelastic materials, both $G'$ and $G''$ will have non-zero values. Plots of $G'$ and $G''$ as a function of frequency provides information regarding the structure of the
material under scrutiny. A schematic representation of the frequency dependence of $G'$ and $G''$ for polymer solution (melts) and gels is shown in Figure 2. For a liquid sample $G'$ and $G''$ have slopes close to 2 and 1 respectively at low frequencies. The point of intersection of $G'$ and $G''$ (overlap frequency) provides information on the relaxation time. For an elastic gel network, both moduli exhibit frequency independent behavior with $G'$ significantly larger than $G''$. For dynamic frequency analysis to be valid, the experiments have to be conducted in the LVE region. Dynamic strain sweep experiments have to be performed to determine the LVE. This test involves variation of strain amplitude while maintaining a constant frequency. The region corresponding to the stress varying linearly with strain for the sample being investigated is termed the linear viscoelastic (LVE) regime. One of main advantage of dynamic oscillatory experiments is that it probes material without disrupting the microstructure. Dynamic rheology has been used to characterize cellulose derivative systems providing important information such as the sol-gel transition.9

3.2 CLOUD POINT STUDY

This technique employs the use of a laser set-up to investigate the on-set and progress of phase separation in our system. Cloud point measurements are performed using an Edmunds JDS uniphase helium-neon laser light source operating at a maximum voltage output of 5mV. The procedure involves transferring sample into a cuvette and placing it in the path of the laser source. The output reading is then recorded on an Edmunds PD200 laser meter. A schematic diagram is shown in Figure 3. A
similar helium-neon system was used to measure the cloud point in a study of hydroxypropylcellulose in mixed solvents of glycerol and water.\textsuperscript{10}

3.3 SCANNING ELECTRON MICROSCOPY

Scanning electron microscopy (SEM) has the capability of allowing high depth-of-field image, fracture surfaces and microstructural details of different samples. Interested readers who want further review of an in-depth information on SEM can consult the following text.\textsuperscript{11} The electron gun generates beam of electrons in a vacuum, which is focused onto the sample by the objective lens.\textsuperscript{12} The beam is scanned over the sample in series of lines and frames called raster by scan coils located in the microscope. When the electron beam strikes the specimen, two types of electron scattering termed elastic and inelastic scattering occur. This is due to interactions between the primary beam electrons and atoms of the sample.

Elastic scattered electron is observed when the beam passes close to or impedes with the nucleus of atom present in the material been investigated. Back scattered electrons may result from elastic scattering and may generate secondary electrons which causes noise in the final image.

Secondary electrons are generated during inelastic scattering when some beam electrons collide with atoms. They typically have energies ranging 0 to many kev and are used to generally generate three-dimensional images. An aluminum coating over a scintillator material (Everhart-Thornley detector) is struck by the secondary electrons generating a burst of light that strikes a photocade surface. The photoelectrons are conducted to a photomultiplier where the number of electrons are increased. A small
amount of voltage generated by the photomultiplier enters a preamplifier-amplifier unit, which amplifies the weak signal to make detection possible. A schematic of a typical SEM equipment set-up is shown in Figure 4. Numerous cellulose derivative gel systems have been investigated using SEM.\textsuperscript{13-15}

3.4 **LASER SCANNING CONFOCAL MICROSCOPY**

Laser scanning confocal microscopy (LSCM) is a technique that has been employed for various studies including determination of cellulose fibril orientation\textsuperscript{16} and fibril angle\textsuperscript{17} in wood fibres. Characterization of some cellulose derived membranes and gels have adopted LSCM as a tool to determine their morphologies.\textsuperscript{18-19} It has an advantage of minimal sample preparation as compared to other techniques scanning and transmission electron microscopy.\textsuperscript{18} The principle of LSCM is derived from conventional light microscope but in this case a laser in place of a light source is used. In addition, it has sensitive photomultiplier detectors and a computer set-up, which is used control various aspects of this technique.\textsuperscript{20} It has the advantage of following structural changes, which is an important factor in this project. LSCM has been established as an important tool for obtaining high-resolution images and three-dimensional images of variety of specimens. A schematic diagram of a LSCM is shown in Figure 5. The operation involves an x-y deflection mechanism, where the laser beam is turned into a scanning beam. It is then focused onto a small spot by an objective lens on a fluorescent specimen. The objective lens is used to capture a mixture of reflected and emitted fluorescent light. The diachronic mirror deviates the reflected light while the emitted fluorescent light passes in the direction of the photomultiplier. In front of
the photodetector is a confocal aperture, which serves to obstruct the so-called out-of-focus information. This is especially important when dealing with thick specimens.

A 2-D image can be generated from a partial volume of sample centered at the focal plane. In addition, a series of images can be obtained at successive planes by alternating the focal plane in the z-direction. Using computer graphics, 3-D reconstructed images can be obtained which enable users to visualize structural details in a thin slice of a sample. Specimen to be imaged with a LSCM must be labeled with a fluorescent probe. Major factors to be considered when selecting a fluorescence dye are excitation/emission wavelengths of the probe, laser lines (wavelength of emission) available and the filter sets used.⁴
REFERENCES


Figure 1. Viscosity as a function of shear rate depicting different material responses: Shear thickening, Newtonian, Shear thinning.
Figure 2. Elastic ($G'$) and viscous ($G''$) moduli as a function of angular frequency showing a typical dynamic rheological response of polymer solutions and elastic gels.
**Figure 3.** Schematic diagram of the laser setup showing a laser source, cuvette and a detector for recording the response.
Figure 4. Schematic representation of a typical scanning electron microscopy (SEM) showing basic components of the apparatus.
Figure 5. Schematic of a typical laser scanning confocal microscopy setup.
CHAPTER 4

Effect of Water Composition on Rheological Properties in Ternary Cellulose Acetate Solutions

Chapter 4 is essentially a manuscript by Collins Appaw, Richard D. Gilbert, John F. Kadla and Saad A. Khan, prepared for submission to Biomacromolecules.
Effect of Water Composition on Rheological Properties in Ternary Cellulose Acetate Solutions

Collins Appaw†, Richard D. Gilbert‡, and Saad A. Khan†,*

Departments of †Chemical and Biomolecular Engineering and ‡Wood & Paper Science, North Carolina State University, Raleigh, North Carolina 27695

John F. Kadla*

Advanced Biomaterials Chemistry, University of British Columbia,
Vancouver, BC V6T 1R9 Canada

Abstract

The effect of increasing water composition on the rheological and microstructural behavior in a ternary system of cellulose acetate (CA), N,N-dimethylacetamide (DMAC) and water is examined. In addition, cloud point studies are conducted to determine the on-set of phase separation in this system. Increasing water content resulted in enhanced steady shear viscosity and dynamic viscoelastic properties at room temperature (25°C), which may be due to intensification of intermolecular hydrogen bonds in solution. The system forms homogenous solutions at low water content with formation of uniform turbid/cloudy system as water content is increased. At relatively high water contents (typically >19wt %) for CA concentrations presented in this paper, a sol-gel transition is observed with the formation of semi-solid system, which exhibits gel-like characteristics. The sol-gel transition is primarily dependent on water content and to some extent on CA concentration. Competitive hydrogen bond interactions between CA and cosolvents in solution can be used to explain the sol-gel transition.

* Corresponding authors: Saad A. Khan; Phone: 919 515-4519; Fax: 919-515-3465; e-mail khan@eos.ncsu.edu. John F. Kadla; Phone: 604 827-5254; Fax: 604-822-9104; e-mail: john.kadla@ubc.ca
Introduction

Cellulose and its derivatives are some of the most widely utilized natural materials. Cellulose is a linear homopolymer consisting of $\beta(1-4)$ linked anhydroglucopyranose units (AGU). Extensive intra- and inter-molecular hydrogen-bonding make cellulose insoluble in most common organic solvents. As a result, cellulose is typically derivatized to facilitate dissolution and processing. Cellulose acetates (CA) are cellulose esters that are partially substituted at the C-2, 3 and 6-positions of the anhydroglucopyranose residue. A typical CA structure is depicted in Figure 1 showing the replacement of the hydroxyl with acetyl groups. Other variations of CA with have some but not all of the hydroxyl groups replaced and depending on the acetyl groups on the chain is characterized by the term as degree of substitution (DS). Their solubility in various solvents depends on the DS of the acetyl groups, wherein the solubility is related to the interactions between the hydroxyl and acetyl groups distributed throughout the CA molecules and with the solvent. Cellulose acetates with a DS between 0.5 - 1 are soluble in aqueous solutions, while those with DS >1 tend to be insoluble in aqueous medium but soluble in many organic solvent systems. However, cellulose acetate molecules are never completely molecularly dispersed in solution, rather existing as complex molecular associates; the extent of which depends on the strength and amount of the intra- and inter-molecular interactions (e.g. hydrogen bonding). For example, $N,N$-dimethylacetamide (DMAc), which readily dissolves CA of DS ranging from 0.49 to 2.92 shows evidence of aggregates or associates of CA molecules even in dilute solution; the result of long-range hydrogen bond interactions between DMAc and CA.
Cellulose acetates are extensively used in filtration, membrane\textsuperscript{11-12} and encapsulation\textsuperscript{13} applications. In such systems sophisticated network structures are required. This is typically achieved through aggregation induced phase separation.\textsuperscript{14-15} In polymeric systems phase separation can be induced by solvent evaporation, temperature changes or the addition of a non-solvent.\textsuperscript{16} In non-solvent induced phase separation, the concentration of polymer, solvent and non-solvent are critical.\textsuperscript{17-18} Depending on the system and component concentrations phase separation can lead to physical gel formation.\textsuperscript{19} Gelation occurs as a result of non-solvent induced polymer aggregation and the formation of large macromolecular associates and clusters.\textsuperscript{20-21} Non-solvent phase separated gelation has been observed in several CA systems including dioxane/water\textsuperscript{22} and ethanol/water\textsuperscript{23} mixtures.

Cellulose acetates are typically used and processed in concentrated solutions.\textsuperscript{24} However, studies involving concentrated cellulose acetate solutions are relatively few, due in part to the relatively high viscosities which make it difficult to control or characterize properties in solution.\textsuperscript{25} Furthermore, it has been observed that basic solvents interact primarily with the hydroxyl groups, while acidic solvents interact with the acetyl groups.\textsuperscript{24} Therefore, depending on the solvent system CA will exhibit varying solution properties, where the sol-gel transition and gel behavior of the resulting material will be influenced by the interactions between the CA/solvent/non-solvent.

In this paper, we aim to characterize the sol-gel transition in a semi-concentrated ternary system comprising CA, DMAc and water, specifically, the characteristics leading to gelation by non-solvent (water) addition. Using steady-shear and dynamic rheological measurements,\textsuperscript{26} the effect of non-solvent addition on viscosity and the sol-
gel transition have been studied. Steady-state viscosity ($\eta$) and elastic modulus ($G'$) measurements, both important factors in determining applicability of any polymer with respect to its usage, reveal increasing water content results in phase separation and the formation of a semi-solid system exhibiting gel-like characteristics. We present the results observed for two CA concentrations and discuss the effect of water addition on the intermolecular interactions present and the impact on polymer conformation and hydrogen bond interactions that lead to aggregation and gel-induced structures.

**Experimental**

**Materials**

The cellulose acetate (CA) used in this work was purchased from Sigma-Aldrich and it had a molecular weight of 50,000 g/mol with acetyl content of 39.7wt%. HPLC grade $N,N$-dimethylacetamide (DMAc) was also purchased from Sigma-Aldrich and together with deionized water were the cosolvents of interest. DMAc is a good solvent for CA$^6$ and dissolves CA forming homogenous solutions at appreciable high concentration levels. Deionized water was utilized as the non-solvent in our system.

**Sample Preparation**

The initial step involved preparation of a bulk 20wt% CA concentration in DMAc until a homogenous solution was achieved. The procedure adopted after that was to dilute from 20wt% to specific concentrations by the addition of calculated weight fractions of DMAc and deionized water. It must be noted that studies have been performed on various concentrations besides those presented in this paper. Different
solutions at fixed CA concentration but with varying weight fractions of water were prepared using this procedure. The samples were mixed and kept for a day at ambient conditions, after which samples were heated at 70\(^\circ\)C for ten minutes to ensure complete miscibility. Prior to heating, samples were kept under nitrogen to prevent oxidation. Samples after heating, were kept at room temperature for at least a five days prior to use to allow system to equilibrate. All stock solutions and dilutions were prepared on a weight basis.

**Rheological Measurements**

A TA Advanced Rheometer (AR 2000) was used to measure the rheological properties of the samples at ambient temperature (25\(^\circ\)C). Steady state experiments provided the viscosity of polymer samples, and is a tool that has been used in various cellulose derivatives in solution.\(^{26-27}\) The configuration used, was either a cone and plate or parallel plate geometry depending on solution viscosity. Shear rates ranging from 0.1 to 80s\(^{-1}\) were investigated in our system. In the dynamic experiments, a small oscillatory shear was applied to the samples and the corresponding elastic (\(G'\)) and viscous (\(G''\)) moduli measured as a function of frequency.\(^{26}\) Frequency ranges from 0.01 rad/s to 100 rad/s were conducted on samples. The shape and magnitude of the elastic and viscous moduli as a function of frequency provides a signature of the state (e.g., solution, gel) of a system.\(^{28}\) Dynamic stress sweep experiments were performed to determine the linear viscoelastic (LVE) regime prior to the frequency sweep experiments. For the gels, we carefully cut an appropriate circumference of samples and placed it on the lower geometry of the rheometer. Parallel plate geometry was used to measure dynamic viscoelastic properties of gels. The experiments were repeated with plates fitted with
220 grit sandpaper to check for slippage and results showed no evidence of such an occurrence. Experiments were repeated to ensure consistency and results were within an error of 10%.

**Cloud Point**

Cloud point studies were performed using an Edmunds JDS uniphase helium-neon laser light source operating at a maximum voltage output of 5mV. The procedure involved passing a laser source through the sample and the subsequent recording of the transmitted output intensity on an Edmunds PD200 laser meter. To undertake measurements, samples were transferred to a cuvette having an optical path length of 1 cm. For samples having high viscosities including gels, samples were scooped using a spatula and carefully transferred to the cuvette prior to measuring the intensity.

**Scanning Electron Microscopy (SEM)**

To investigate the microstructure of the gels formed, SEM (JEOL JSM-5900LV) was used with accelerating voltage of 20kV and a magnification of 5000x. The protocol was to cut small pieces of gel placed them in 3% glutaraldehyde Na acetate buffer, at pH 6.6 (4°C). The gels were rinsed with 3 changes of 0.1M sodium acetate buffer, at pH 6.6 and then dehydrated in a graded ethanol series of 30%, 50%, 70%, 95% and 100% ethanol, all at 4°C. Samples were then dried using critical point drying with CO₂. The dried samples were gently fractured sputter coated with Au/Pd and prior to scanning.
Results and Discussion

Solution Rheology

Our initial step involved examining the solution property changes induced by increasing water content to CA/DMAc solutions. Addition of water to bulk CA/DMAc solutions produced a system, which shows increasing viscosity with water content. This is illustrated in Figure 1a, we plots the viscosity profiles for a 10 wt.% CA solution for different water content. Figure 1b shows the viscosity trend for a sample containing a higher CA concentration from (15 wt%) and depicts a similar profile of increasing viscosity with water content. For both samples, we observe that at low or no water content, the viscosity exhibits a large Newtonian plateau, followed by a power-law regime. Above a certain water content the viscosity curves change exhibiting high viscosity at low shear rates and the gradual disappearance of the zero-shear viscosity plateau. The disappearance of the Newtonian plateau at low shear rates suggests development of microstructure in our sample as water content is increased. In Figure 2, an attempt is made to highlight the progressive increase in low-shear viscosity that occurs when water content is increased. We clearly observe that for any value of water content the viscosity increases by almost an order of magnitude when CA concentration increase from 10 to 15wt%. We also find that the viscosity enhancement with increasing water content shows the same trend for both CA concentration samples. In fact, an exponential increase in viscosity with water content is noticed.

Cloud point studies for transmission intensity as a function of water content were conducted using a helium-neon laser light source. A similar helium-neon system
for measuring the cloud point was used to study hydroxylpropylcellulose in mixed solvents of glycerol and water. Figure 3 shows that transmission remains constant until a critical water content, whereupon a sharp drop in intensity is observed for both 10 and 15wt% CA samples. For both curves, we observe the transition corresponding to phase separation occurring at relatively high water content. However, the cloud point seems to shift to lower water content when the sample has a higher CA concentration of 15wt%. Thus, an increase in CA concentration cause a quicker phase separating system since polymer-polymer and polymer-cosolvent interactions are more pronounced.

It is interesting to note that even in the water content range in which transmission remains constant, the viscosity shows an increase with addition of water. The increase in viscosity may be due to further hydrogen bonds being formed between CA-DMAc-water due to enhanced intermolecular interactions in solution precipitated by increasing water content. A detailed hypothesis for the viscosity pattern is that CA and DMAc form hydrogen bond links when CA dissolves to form a neat clean solution. This is may be due to primarily hydroxyl (OH) units on CA interacting with the acetyl groups on DMAc. Addition of water causes the formation of new hydrogen bonds with DMAc and to a much lesser extent CA, thereby intensifying the hydrogen bond interactions in solution. This phenomenon may account for the viscosity increase observed in our system. In addition CA concentration increment may favor additional intermolecular interactions in solution and may account for viscosity increases observed. Previous studies have suggested that in a CA/acetone system, strong interactions between solvent and polymer may involve hydrogen bonding between OH groups on cellulose acetate and carbonyl unit in acetone.
**Gelation Process**

Figure 5 shows a digital image of a 10wt.% CA system as a function of increasing water content. A gradual transition from a clear polymer solution to a cloudy system with increasing water content is observed. At low water content (up to 7.2wt%), the system forms a clear homogenous solution but a further increase to 16.2wt% water results in the emergence of cloudiness in the system reminiscent of a phase separating polymer solution. Water content increment to 21.6wt% leads to a uniform cloudy, self-supporting gel-like material. To quantify the sol-gel behavior, we plot in Figure 6a the elastic ($G'$) and viscous ($G''$) moduli as a function of frequency for two of the water compositions shown in Figure 4: 7.2 and 21.6wt.%. At the low water composition of 7.2wt%, we find $G''$ to be larger than $G'$ at low frequencies with both showing strong frequency dependence reminiscent of a polymer solution. At the highest water content of 21.6wt.%, there is transition with both moduli increasing substantially by several orders of magnitude. In addition, $G'$ is larger than $G''$ over the entire frequency range studied and both are relatively independent of frequencies, features characteristic of an three dimensional elastic gel.31-36 Figure 6b shows the dynamic frequency spectrum of a 15wt% CA sample at two different water content. At the lower water content of 6.8wt.%, the sample exhibits solution characteristics whereas at a water content of 20.4 wt.%, we observe behavior characteristic of a gel network. We also observe that the magnitude of the moduli, are higher for this higher CA concentration sample. Therefore, as CA concentrations increases, stronger gels are formed due to greater intermolecular interactions between CA and cosolvents.
To pinpoint the sol-gel transition as a function of water content, we plot a multifrequency plot of tan δ as a function of water content for two samples containing 10 and 15wt% CA (Figure 7). Determination of gel-point using this method was developed by Winter and Chambon and is appropriately termed as the Winter-Chambon criterion. This procedure has been applied in a variety of polymeric systems\textsuperscript{37-41} and an application of this method is extended in our work to measure the water content where the sol-gel transition occurs. The point of intersection of the various curves at different frequencies is indicative of the gel-point.\textsuperscript{40-41} Data for Figure 7 were obtained from plots similar to that in Figure 6 (dynamic frequency plots) performed at different water contents. For both samples we find the tan δ curves at different frequencies to converge for a specific water content. However, unlike conventional gelation in which these curves diverge after intersecting, our system shows the curves to remain together and independent of frequency following the convergence. Assuming the initial point of convergence to be the gel point, we find gelation to occur at a lower content (20 versus 23 wt.%) for the more concentrated CA system. Thus, even though water content increment is the key to induce sol-gel properties in our system, polymer concentration also plays a role, albeit minor, in influencing gelation.

We examine in Figure 8 the systematic variation of $G'$ as a function of water content. We find that $G'$ increases by over 4 orders of magnitude as water content increases 0 to 25 wt% for both the 10 and 15wt% CA containing samples. Interestingly, curves for both CA concentrations show the same sigmoidal shape with the one containing 15wt% CA exhibiting a higher value, inline with earlier observation of viscosity (Figure 3). As such, we observe two distinct regimes in terms of $G'$.
enhancement. As the water content increases, $G'$ initially increases slowly followed by a regime of sharp increase with formation of gel. Following gelation, $G'$ increases slowly.

Figure 9 depicts SEM micrographs of CA gels obtained under different water contents and CA concentrations. Increasing water content from 21.6 to 25.2wt% for CA concentration of 10wt% results in particulate structure with smaller voids in comparison to lower water content gels. The more uniform and homogenous microstructure having smaller voids may account for the stronger gel properties observed when water content is increased for CA concentration of 10wt%. When CA concentration is increased to 15wt%, we observe a similar structure, which are closely packed together with the voids shrinking in size with water content. The more tightly packed voids for water content of 23.8wt% provide us with a more rigid and compact gel network and may be due additional bond links formed due to water content increase. We observe that for both concentrations when water content is increase, the system portray a more continuous which have less holes in them. This may also account for the stronger gel properties when we increase water content. Thus, for both 10 and 15wt%, we observe dynamic visoelastic properties enhanced when we increase water composition at constant CA concentration.

Schematic representations of the molecular level interactions, which may be responsible for the sol-gel process are portrayed in Figure 10. The hypothesis for this process may be due to the fact that, CA is dispersed in DMAc (black dots) initially forming hydrogen bond linkages with each other. Initial addition of small amounts of water (white dots) to CA and DMAc solution causes some DMAc to interact with water. But a greater amount of DMAc may still be interacting to a greater extent with
CA thereby rendering solution homogenous. With water content increment, a competition for DMAc between CA and water occurs. Thus, as we increase water content, CA chains resist the displacement from DMAc, with water also holding on firmly to as much DMAc available for bonding. In addition some water may be weakly bonded to “free” CA in the system. This segregation effect caused by the interactions in the system lead to CA experiencing both intra- and intermolecular interactions causing CA to disperse through entire volume of sample. These interactions may be may balanced and at equilibrium this leads to the formation of a material exhibiting gel-like properties at critical water contents. Therefore, our assumption is that, this complex interaction process causes a complete dispersion of CA and lead to aggregates of CA uniformly spread throughout the entire system.

Experiments conducted on some cellulose derivatives give indications that intermolecular interactions may be one of the important mechanisms for gel formation. An earlier study of CA behavior in solvents that selectively interact with specific functional groups on the CA chain may provide more insight to the sol-gel transition process present in our system. Its our belief that similar selective interactions between CA and cosolvents may account for the gelation process. Our theory for the transition is deduced base on the fact that, the acetyl groups on DMAc preferentially interact with OH groups on the CA molecule. The addition of a non-solvent in this case water to CA/DMAc solutions, weakens this interactive bond and shifts some DMAc molecules to interact rather with the OH groups on water. The bond breaking process gets progressively worse with water content increase and lead to intramolecular interactions between unbonded or “free” CA chains some of which have
been displaced from DMAc. This process is also accompanied by intermolecular interactions between CA units, DMAc and water. It is postulated that at equilibrium the interactions mentioned lead to uniform aggregation of CA in the entire volume and invariably gelation occur. Thus, in this system CA may be experiencing intermolecular interaction as well as intramolecular interactions as we increase the amount of water in solution. We have thus been able to formulate a protocol to convert CA in a mixed solvent system from a homogenous solution to a material with “gel-like” properties using water as a non-solvent.

**Conclusions**

In this study, we examined the effect of adding water to CA/DMAc solutions using steady and dynamic rheology. Addition of small quantities of water led to formation of weakly entangled system resulting in enhanced steady shear viscosity at room temperature. Beyond critical water contents typically >19wt% dependent on CA concentration, the system transforms and forms gel network structure. Prior to gelling, the sample phase separated depicting a cloudy/turbid solution. The sol-gel transition depends to high extent on the water content and the gelation process is found to occur at lower water content when CA concentration is increased. The dynamic viscoelastic properties were also more pronounced when CA concentration is increased. The hypothesis for the gelation process is believed to occur due to when water and CA competing for DMAc in the system. Due to initial formation of CA-DMAc bonds formed, CA resists this bond breaking process. The strong attraction of water for
DMAc, leads to “free” unbonded CA units in the system leading to gelation. Thus, we have been able to tailor a process for converting solutions of ternary systems comprising of CA/DMAc/water to gels. We hope our study will lead to better understanding the interactions present in CA mixed solvent systems paving the way for such systems to be adopted and utilized pertaining to its applications in industry.

**Acknowledgement**

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Figure Captions

Figure 1. Chemical structure of a typical cellulose acetate chain with the hydroxyl groups replaced with acetyl groups

Figure 2. Effect of different water contents on steady shear viscosity for a CA/DMAc/water system. CA concentrations are (a) 10wt% and (b) 15wt%.

Figure 3. Viscosity as a function of water content obtained at shear rate of 1s\(^{-1}\) for CA concentrations of 10 and 15wt%.

Figure 4. Transmission intensity versus amount of water for 10 and 15wt% CA concentration in DMAc/water system.

Figure 5. Transition of 10wt% CA/DMAc/water system from homogenous system to a cloudy system. Water content increment is showed from left to right.

Figure 6. Effect of low and high water contents on the viscous (G''\() and elastic (G')\) moduli for CA/DMAc/water system. CA concentrations are (a) 10wt% and (b) 15wt%.

Figure 7. Multifrequency plot of tan δ as function of water content for (a) 10wt% and (b) 15wt% CA/DMAc/water system.

Figure 8. G' versus water content at a frequency of 1 rad/sec for 10wt% and 15wt% CA/DMAc/water system.

Figure 9. SEM micrographs for CA concentration of 10 and 15wt% at two different water contents.

Figure 10. An illustrative representation of molecular level interactions present in the
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CHAPTER 5

Phase Separation and Heat-Induced Gelation Characteristics of Cellulose Acetate in a Mixed Solvent System

Chapter 5 is essentially a manuscript by Collins Appaw, Richard D. Gilbert, John F. Kadla and Saad A. Khan, prepared for submission to *Macromolecules*. 
Phase Separation and Heat-Induced Gelation Characteristics of Cellulose Acetate in a Mixed Solvent System

Collins Appaw†, Richard D. Gilbert‡, and Saad A. Khan†,*

Departments of †Chemical and Biomolecular Engineering and ‡Wood & Paper Science, North Carolina State University, Raleigh, North Carolina 27695

John F. Kadla, *,§

Advanced Biomaterials Chemistry, University of British Columbia, Vancouver, BC V6T 1R9 Canada

Abstract

The rheological behavior of cellulose acetate (CA) in mixed solvents comprising of N,N dimethylacetamide (DMAc) and water is examined at different CA concentrations and water content. Addition of a constant weight of CA to different ratios but constant weight of DMAc/water solutions results in enhancement of viscoelastic properties as the ratio of water is increased at room temperature (25°C). The system displays a unique behavior exhibiting a two-phase polymer-rich viscous mixture at the bottom of an almost clear liquid layer at relatively high water content (>19wt%) based upon the CA concentrations studied. Whiles the viscous bottom exhibit a weak “gel-like” property, the top liquid layer exhibits an almost Newtonian behavior. Heat treatment results in gelation for the two-phase system. Cloud point studies also showed the onset of phase separation characteristics as water content is increased. The phase separation and gelation characteristics can be explained based on hydrogen bond interactions being intensified between CA and cosolvents in solution.

*Corresponding authors: Saad A. Khan; Phone: 919 515-4519; Fax: 919-515-3465; e-mail khan@eos.ncsu.edu. John F. Kadla; Phone: 604 827-5254; Fax: 604-822-9104; e-mail: john.kadla@ubc.ca
Introduction

Cellulose a renewable biodegradable natural polymer\textsuperscript{1-3} is highly insoluble in a wide range of solvents.\textsuperscript{4} The lack of solubility is attributed to the intra- and intermolecular hydrogen bond interactions between the hydroxyl units on the chains.\textsuperscript{4-6} Due to this inherent problem, various derivatives of cellulose have been prepared by substituting the hydroxyl groups with different functional groups.\textsuperscript{7} This invariably impact different solubility characteristics to cellulose derivatives. Cellulose derivatives such as cellulose ethers an example being methyl cellulose (MC) are soluble in aqueous medium.\textsuperscript{8-15} It is presumed that, at low temperatures MC is water-soluble due to water molecules presumably forming “cage-like” structures around the hydrophobic methoxyl groups.\textsuperscript{8} It is important to note that depending on degree of substitution (DS) and preparation methods, a variety of other solvents besides water can dissolve MC.\textsuperscript{15}

Cellulose acetate (CA) is a semiflexible polymer\textsuperscript{16} that has been used in the manufacture of textiles, moldings, filters for cigarettes, fibres, selective membrane, bioactive and biocompatible materials, etc. One method for preparing CA is through acetylation of cellulose by substituting the hydroxyl groups on the cellulose chain.\textsuperscript{17-19} This process yields CA with different solubility characteristics dependent on the degree of substitution of the acetyl groups. The process of direct acetylation to manufacture cellulose acetates (CAs), yield partially water-soluble CAs at same low DS.\textsuperscript{17} This is due to the fact that, nonuniform distribution of the substituents are formed as a result which is a factor inhibiting solubility of low DS water-soluble CAs.\textsuperscript{17} For CA to be soluble in water at low DS (0.5 to 1), it should be prepared only through homogenous saponification.\textsuperscript{17} Thus, CA depending on the DS can be soluble in a variety of solvents.
However, most commercial cellulose acetates are not soluble in water\textsuperscript{19} due to preparation methods and DS. The interactions between hydroxyl and acetyl groups on partially substituted CA molecule and the solvent polarity, influences its solubility\textsuperscript{20-21}. The presence of such functional groups render CA to exhibit intra- and intermolecular long-range hydrogen bond interactions dependent on solvent\textsuperscript{20}. These interactions can lead to solution to gel phenomena which is termed as gelation.

Gelation in polymer-solvents solutions can be induced by various techniques. In some instances, the process of gelation occurs when solutions are heated and subsequently cooled. Heat-induced gelation has been observed in a variety of systems ranging from food to protein samples\textsuperscript{22-24}. Heat-induced gel formation have also been observed in CA benzyl alcohol solutions\textsuperscript{25-27} typified by heating and cooling the solutions to form gels.

The gelation process can be induced by addition of a gelation medium (non-solvent) to CA/solvent system. An example is the manufacture of reverse osmosis membranes, which often employs cellulose acetate as an important raw material\textsuperscript{28-29}. The majority of porous membranes are formed by casting the homogenous polymer solution in a non-solvent. A non-solvent is a solvent that exhibits poor solubility characteristics or does not possess the capability to dissolve the polymer in question. Phase separation characteristics usually occur prior to gel/membrane formation in such ternary systems\textsuperscript{30-31}. Phase separation is mainly due to the polymer been segregated due to various interactions in solution. The polymer and cosolvent concentrations pay a vital role in phase separation formation in ternary systems\textsuperscript{32}. Phase separation accompanied by cloudiness has been observed prior to gel and/or membrane formation in some
cellulose derivative solvent systems. An earlier work we conducted on the same ternary system involved addition of water to bulk CA/N,N-dimethylacetamide solutions showed enhanced viscoelastic properties when water content was increased.\textsuperscript{33} The system exhibited phase separation prior to gelation when water content was increased depending on CA concentration. This study therefore, serves as an extension of our investigations involving ternary CA/solvent/non-solvent systems.

In this study, we take advantage of the good miscibility of \textit{N,N} dimethylacetamide with water and investigate the influence different mixtures comprising of these two solvents will have on CA. We study particularly the influence of increasing water in the system since it is a non-solvent for CA, while \textit{N,N} dimethylacetamide show good solvent properties for CA.\textsuperscript{20} Dynamic and steady-state rheology are primarily the tools used to study the solution and gels formed in our study. The important concept of rheology is the ability to predict liquid and solidlike properties since polymeric solutions typically exhibit both behaviors.\textsuperscript{34} This characterization technique has been used in a variety of cellulose based systems.\textsuperscript{8,10,33,35} It was observed that addition of CA to different compositions of DMAc/water results in a two-phase system which was formed at relatively high water contents. Heating the two-phase system resulted in a single phase gel network. In that regard, we present our results showing the effect of water content increase and its effect on intra- and intermolecular hydrogen bond interactions present in the system.
Experimental

Materials

Cellulose acetate (CA) with a molecular weight of 50,000 g/mol and acetyl content of 39.7wt% was used in this study. HPLC grade $N,N$-dimethylacetamide (DMAc) and deionized water were the cosolvents adopted for this study. DMAc was chosen as the solvent used to dissolve CA due its low toxicity and can effectively dissolve CA to high concentration levels. Both CA and DMAc were purchased from Sigma-Aldrich and used as received.

Sample Preparation

The mixed solvent system was prepared by adding CA to mixed fractions of DMAc and water. The initial dissolution step involved preparation of different ratios but constant weight of DMAc/water solutions. A constant weight of CA was then added to these solutions containing different ratios of DMAc/water. In this study, we primarily examine two representative CA concentrations, 10 and 15wt%, although other concentrations have been investigated. After addition of CA, the mixture was stirred and kept at room temperature for one day. Subsequently, to ensure an inert atmosphere, the system was purged with nitrogen and heated for 10 minutes at 70°C to solubilize samples. All solutions were prepared on a weight basis. We term this process of sample preparation dissolution method 2 to differentiate it from our earlier sample preparation technique\textsuperscript{33} (dissolution method 1) which yielded gels at relatively high water contents (dissolution method 1). In dissolution method 1, water was added to already prepared bulk solutions of CA/DMAc. The procedure involved, a progressive increase in water content with the eventual formation of a gel system at water content
19% and above. A comparison between the gelation properties of the two dissolution methods will be discussed in later sections of this discussion.

**Rheological Measurements**

A TA Advanced Rheometer (AR 2000) was used to measure the rheological properties of the samples at ambient temperature (25°C). The viscosity of the samples was obtained from the steady state experiments using a cone and plate geometry. Dynamic stress sweep experiments were performed to determine the linear viscoelastic (LVE) regime. After determining the LVE, a small oscillatory shear was applied to the samples and the corresponding elastic (G') and viscous (G'') moduli measured as a function of frequency. Frequency ranges from 0.01 rad/s to 100 rad/s were conducted on gel samples. The shape and magnitude of the elastic and viscous moduli as a function of frequency provides a signature of the state (e.g., solution, gel) of a system.\textsuperscript{36-41} Parallel plate geometry was used to measure dynamic viscoelastic properties of extremely viscous mixtures and gels. Experiments were repeated to ensure reproducibility and consistency.

**Cloud Point**

Cloud point measurements were performed using an Edmunds JDS uniphase helium-neon laser light source operating at a maximum voltage output of 5mV. Similar measurements using a helium-neon system set up has been adopted to investigate hydroxylpropylcellulose in mixed solvents of glycerol and water.\textsuperscript{42} The CA solutions in DMAc/water were transferred to a cuvette having an optical path length of 1 cm. The laser light was passed through the solutions and the transmitted output intensity measured on an Edmunds PD200 laser meter.
Scanning Electron Microscopy (SEM)

The microstructure of some gels was investigated using SEM (JEOL JSM-5900LV) with accelerating voltage of 20kV and a magnification of 5000x. The protocol was to cut a small piece of gel and place them in 3% glutaraldehyde Na acetate buffer at pH 6.6 (4°C). The gels were rinsed with 3 changes of 0.1M sodium acetate buffer at pH 6.6 and then dehydrated in a graded ethanol series of 30%, 50%, 70%, 95% and 100% ethanol, all at 4°C. Critical point drying with CO₂ was used to dry samples. The dried samples were gently fractured and sputter coated with Au/Pd before scanning, to obtain the microstructure.

Results and Discussion

Solution Behavior

The rheological and cloud point behavior are highlighted in this section regarding the addition of a constant weight of CA to N,N-dimethylacetamide (DMAc)/water cosolvents of different composition. Figure 1 shows the steady state viscosity of samples as a function of shear rate for varying composition of water at a constant CA concentration of 10wt%. The trend depicted is a Newtonian behavior with shear thinning at high shear rates. With increasing water content, there is an appearance of shear thinning at low shear rates and suggest the onset of microstructural development. The viscosity curves also shifts to higher values when water content is increased. Similar trend of increasing viscosity with water content has been observed.
for other CA concentrations studied but for simplicity it is not been presented in this report.

The transmission intensity as a function of water content of an analogous sample is portrayed in Figure 2. The intensity remains constant until a critical water content is achieved, after which a drop in intensity is observed accompanied with cloudiness in solution. The region showing constant intensity corresponds to a visually clear homogenous solution. Above the water contents presented in Figure 2, the system phase separates into a clear liquid solution on top and an opaque viscous polymer-rich mixture at the bottom. Thus, reading of the transmitted intensity of the system was rendered impossible at this juncture.

The transition from a clear homogeneous solution to a phase system with increasing water content is shown more clearly in the digital images of Figure 3. In this figure which corresponds to a 10wt.% CA in DMAc/water cosolvent with increasing water proportion, we initially observe a clear solution at a water content of 0%. At a higher water content of 16.2%, we observe onset of cloudiness. Upon further addition of water (21.6%), the system separates into a top clear and bottom opaque phase. We an intensification of the two-phase system with viscous opaque phase becoming more pronounced at a water content of 25.2%This process was slow and equilibrium between the two phases was established after about four days. It is of great interest to examine the characteristics of these two phases. We start with a discussion of the rheological behavior of the two-phase system in subsequent section. The increase in viscosity prior to phase separation as observed in Figure 1 may be due to increased hydrogen bonds in solution induced by adding water, thereby leading to greater intermolecular interactions.
between CA and cosolvents. The hypothesis for the viscosity pattern is that, water and
DMAc are completely miscible and addition of CA to the solvent system, cause both
water and to a much extent DMAc to form complex hydrogen bond interaction with
CA. We postulate the steps that hydroxyl (OH) groups on the water molecules interact
initially with the acetyl groups on DMAc. The introduction of CA lead to further partial
hydrogen bond links formed through the entire system primarily due to the OH and
acetyl groups present on the anhydroglycose chain of CA. This phenomenon may
account for the viscosity increase observed in our system. Interestingly, an investigation
conducted in dilute systems of cellulose diacetate/acetone/formamide solutions
suggested that, even though cellulose diacetate is not soluble in formamide, it swells in
formamide which is indicative of some form of interaction present. This highlights our
assertion that, water and CA interact partially in solution even though water is a non-
solvent.

Rheology of Phase-Separated System

Figure 4 shows viscosity pattern of the upper clear and lower opaque layer of a
two-phase system. Results for two representative samples of different water content are
shown. We find both samples to exhibit a Newtonian viscosity suggesting this layer to
be predominantly composed of water and DMAc. The viscosity pattern for the viscous
layer depicted in Figure 4b shows a shear thinning profile for all ranges of shear rate
studied. We also find the magnitude of the viscosity for this lower layer to be higher
than that of the top layer by several orders. Figure 4b also reveals that increasing water
content from 21.6 to 25.2% results in a slight increase in the viscosity as well as a
steeper slope at low shear rates. The absence of a low-shear plateau suggests the presence of microstructure whereas the increase in slope at 25.2% suggest an enhancement of this at the higher water content. It is interesting to note that while the viscosity increases with water content for the bottom layer, the reverse is observed for the upper liquid. These trends are consistent and suggest that at the higher water content of 25.2%, the bottom layer contains relatively more water than the sample at 21.6 water resulting in a higher viscosity. Consequently, the top layer contains relatively more DMAc than water for the higher (25.2%) water content sample resulting in a lower viscosity as DMAc has a lower viscosity than water.

We probe further the bottom opaque layer through dynamic rheology with Figure 5 exhibiting the elastic ($G'$) and viscous ($G''$) moduli as a function of frequency. We find $G'$ to be higher than $G''$ over all the frequencies studied. In addition, the moduli are weakly dependent on frequency. These features are characteristics of a gel network, albeit it may be termed a weak one by some authors. An increase in water content from 21.6 to 25.2% increases the moduli by almost an order of magnitude results in enhanced dynamic viscoelastic properties. Both $G'$ and $G''$ increased slightly over the frequency range studied which is reminiscent of a weak gel. In addition weak gels often have the magnitude of $G'' < \text{ten times that } G'$ which is exhibited by the viscous system.

The phenomenon of the two-phase behavior at high water contents leads to the idea of a competitive interaction for DMAc since both CA and water have affinity for DMAc. Because water is completely miscible with DMAc, it is envisaged water forms stronger bonds with DMAc as compared to CA. Therefore, at low water content, both
CA and water may both interact favorably with DMAc. But as we increase the water content, some CA chains are displaced from DMAc leading to some degree of aggregation in the system. Further explanation could be due to the fact that, as water composition increases, water exhibits stronger intermolecular interaction with DMAc. With increasing water content, we tend to have a poor solvent system and CA may form rigid conformation due to intramolecular interactions prevailing over intermolecular attractions. It is anticipated that, intramolecular associations with various CA chains are therefore intensified and lead to formation of a viscous mixture at the bottom of system. Thus the two-phase system formed may be due to water exhibiting a higher hydrogen bond preference for DMAc in comparison to CA. The dense viscous system is envisaged may be a combination of predominantly CA, with some amount of DMAc and to a less extent water weakly bonded with the CA chains in solution. It must be noted that the polymer concentration for the viscous mixture when isolated from liquid layer, was computed to be approximately 16wt%.

Similar phase separated two-phase system was observed in polymer solutions up to 20% CA in dioxane/water mixture, formed upon aging of turbid solutions at room temperature. Experiments conducted on cellulose derivatives give indications that intermolecular interactions may be one of the important mechanisms for gel formation. Thus in this system CA may be experiencing a greater intramolecular interaction in comparison to intermolecular interactions as we increased the amount of water in solution.
Comparison of Gels from Dissolution Methods 1 and 2

An important issue to consider is a comparison of the gel rheology of the bottom layer with the gels produced in our earlier work using a different sample preparation protocol (referred to as Method 1). This earlier approach, described also in the experimental section, involved addition of water to prepared CA/DMAc solutions in contrast to our present approach involving addition of CA to a cosolvent of DMAc and water (coined Method 2). Method 1 led to uniform gel formation at high water content and a detailed explanation for this phenomena is provided elsewhere. Nevertheless, the dynamic moduli of the two gels are compared in Figure 6 for identical system conditions. We find that that gels formed through dissolution method 1 exhibit slightly higher elastic and viscous moduli for the two representative water contents of 21.6% and 25.2%. This is counterintuitive as one would expect G’ of gels from dissolution method 2 to be higher as the effective CA concentration in the bottom layer for dissolution method 2 is higher than the corresponding gel from dissolution method 1. Since our results cannot be explained on the basis of concentration effects, we can suggest other possibilities. First, the gel from the bottom layer of the two phase system may have relatively lower water content. Second, the gel microstructures in the two cases may be different. The observed phenomenon may thus be due to the complete dispersion of CA after gelation in dissolution method 1, which provides better gel properties. In contrast, in dissolution method 2, the aggregation of CA clusters with small amounts of cosolvent weakly attached produces a system with weaker gel characteristics. Further work needs to be done to elucidate the exact nature of the
interactions. We refrain from delving into this further as it beyond the scope of this work.

**After effect of Heat Treatment**

The two-phase system formed at high water contents were subjected to temperature increment spanning from 60 to 100°C for 30 minutes and cooled back to room temperature. This procedure was performed to investigate if temperature could induce the system to exhibit a heat-induced gelation process and form a single-phase gel system. Figure 7 shows digital images of the a) initial heated two phase system, b) system heated 100°C sample cooled back to ambient temperature after heating. We find that the system heated to 100°C showed a complete gelled texture with little or no solvent around the gel matrix upon cooling. In that context, our discussions will center primarily on the initial gel layer of the two-phase system, and the transformed gel matrix upon cooling to room temperature after heating to 100°C for 30minutes. Figure 8 shows the dynamic viscoelastic profile at 10wt% for two different water contents of 21.6 and 25.2 wt%. We see a slight pronounced (about double) in the viscoelastic properties with water content increment. Thus, the aggregation process leading to gelation is enhanced to some extent when water content is increased.

Figure 9a shows SEM micrographs for heat-induced gels for 10wt.% CA concentrations at two different water contents 21.6% and 25.2%. We observe a particulate microstructure with pores with both the size of the particulates and the pores showing a small decrease with increasing water content. For a CA concentration of 15wt.% (Figure 9b), the microstructure for the lower water containing system (20.4%)

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reveal similar overall features as that observed in Figure 9a. However, increase in water content to 23.8% leads to a pronounced change in microstructure and depicts a predominantly fibrular morphology.

It is envisaged that heating the two-phase system to 100°C breaks the majority of the interactive bonds formed between water and DMAc initially, thus making unbonded DMAc assessable to CA in solution facilitating their contact. Therefore the hydroxyl groups on CA and the acetyl groups on DMAc form strong intermolecular interactions. After cooling back to room temperature, water competes with CA for the DMAc. This leads bond cleavage of some CA molecules with some of these molecules exhibiting a spike in intramolecular interactions. But at the same time CA molecules also form intermolecular interactions with DMAc and to a lesser extent water. A balance of these interactions causes dispersion of CA uniformly through the entire system leading to gelation. An earlier study of a ternary system comprising of same constituents we conducted showed a similar gelation process with increasing water content at room temperature.33

Comparison of Heat-induced and Dissolution method 1 Gels

Figure 10 compares the dynamic rheological properties of gels formed using dissolution method 1 and heating of two-phase samples. Figure 10a shows almost identical dynamic viscoelastic properties for 10wt% CA concentration containing the same amount of water (21.6%). A different pattern is however observed at the higher water content of 25.2% (Figure 10b) with the G’ and G” of the heat-induced gels showing a significantly lower value in comparison to the gels prepared using dissolution
method 1. This was also evident qualitatively from the texture and visual observation of the gels. At high water contents, the observed phenomenon may be due to the complete dispersion of CA after gelation in dissolution method 1, which provides better gel properties. On the other hand, the heat-induced gelation process, the aggregation of CA clusters with small amounts of cosolvent weakly attached produces a system with weaker gel characteristics.

In Figure 11, we observe the SEM images which show similar microstructural characteristics for the heat-induced and dissolution method 1 gels. The texture for the gels in dissolution method 1 assumes a more rough texture with close-packed structure compared to the heat-induced gels at 10wt% CA concentration and identical water contents. In addition, with water content increment, we observe the voids become smaller in size. This microstructural formation may allude to the stronger and rigid gel characteristics exhibited by dissolution 1 containing 2.8g (25.2%) water composition and the disparity that is reflected in the dynamic response in Figure 12b

Conclusions

In this study, we examine the effect of sample preparation protocol on CA systems in mixed solvents of DMAc and water. At relatively low water content, the solutions are homogenous and exhibit an increase in viscosity with enhanced water content in the cosolvent. It is evident that sequence of addition of CA and solvents greatly influence the phase separation mechanism in our system. By preparing solutions of CA in different ratios of DMAc and water, we produce a system, which phase
separates at high water contents (>19wt%) for a specific polymer concentrations. A two-phase system consisting of a dense polymer-rich gel-like bottom phase and a clear liquid upper layer are formed. Heat treatment of the two-phase system at a high temperature (~100°C) causes the formation of a uniform gel structure whereas heating it to a lower temperature causes the system to revert back to a two-phase system. By increasing water content in the system, the intramolecular interaction between CA units is increased. In addition CA forms strong and weak links with DMAc and water respectively causing gelation to occur. This pattern of hydrogen bond interactions may account for the increase in viscoelastic properties in our system.

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**Figure Captions**

**Figure 1.** Effect of different water content on the steady shear viscosity of cellulose acetate in DMAc/water cosolvent system. The total concentration of cellulose acetate is kept constant at 10wt%.

**Figure 2.** Transmission intensity versus amount of water for a constant 10wt% cellulose acetate in DMAc/water cosolvent system.

**Figure 3.** Constant 10wt% cellulose acetate in DMAc/water cosolvent system showing transition from homogenous system to a two-phase system. Water content increment is showed from left to right.

**Figure 4.** Viscosity pattern for the two-phase region for cellulose acetate in DMAc/water cosolvent system at two different water contents of 21.6 and 25.2wt%. Polymer concentration is a constant 10wt%. (a) Upper liquid and (b) Lower opaque layer.

**Figure 5.** Dynamic frequency spectrum of the elastic and viscous moduli for bottom viscous layer for cellulose acetate in DMAc/water cosolvent system at two different water contents of 21.6 and 25.2wt%. Total concentration of cellulose acetate is kept constant at 10wt%.
Figure 6. Dynamic spectrum for dissolution methods 1 and 2 for 10wt% CA concentration with water contents of (a) 21.6% and (b) 25.2%.

Figure 7. Two phase system subjected to heat treatment to 100°C after which system is cooled to room temperature.

Figure 8. Dynamic spectra for heat-induced gelation for 10wt% cellulose acetate DMAc/water cosolvent system at two different water contents of 21.6 and 25.2 wt%.

Figure 9. SEM images for heat-induced CA concentrations of (a) 10 and (b) 15wt% at two different water contents.

Figure 10. Comparison of dynamic properties of heat-induced gels and dissolution method 1 gels at 10wt% cellulose acetate concentration having water content of (a) 21.6% and (b) 25.2%.

Figure 11. SEM micrographs of heat-induced and dissolution method 1 gels for 10wt% cellulose acetate concentration having water contents of (a) 21.6% and (b) 25.2%.
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Figure 2. Transmission intensity versus amount of water for a constant 10wt% cellulose acetate in DMAc/water cosolvent system.
**Figure 3.** Constant 10wt% cellulose acetate in DMAc/water cosolvent system showing transition from homogenous system to a two-phase system. Water content increment is showed from left to right.
Figure 4. Viscosity pattern for the two-phase region for cellulose acetate inDMAc/water cosolvent system at two different water contents of 21.6 and 25.2wt%. Polymer concentration is a constant 10wt%. (a) Upper liquid and (b) Lower opaque layer.
Figure 5. Dynamic frequency spectrum of the elastic and viscous moduli for bottom viscous layer for cellulose acetate in DMAc/watercosolvent system at two different water contents of 21.6 and 25.2wt%. Total concentration of cellulose acetate is kept constant at 10wt%.
Figure 6. Dynamic spectrum for dissolution methods 1 and 2 for 10wt% CA concentration with water contents of (a) 21.6% and (b) 25.2%
Heated to 100°C

Cooled to room temperature

Figure 7. Two phase system subjected to heat treatment to 100°C. After which system is cooled to room temperature.
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Evolution of Microstructure and Rheological Properties in Cellulose acetate/N,N dimethylacetamide/Water system

Chapter 6 is essentially a manuscript by Collins Appaw, John F. Kadla and Saad A. Khan, prepared for submission to *Biomacromolecules.*
Evolution of Microstructure and Rheological Properties in Cellulose acetate/N,N dimethylacetamide/Water system

Collins Appaw and Saad A. Khan*
Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, North Carolina 27695

John F. Kadla*
Department of Wood & Paper Science, Advanced Biomaterials Chemistry, University of British Columbia, Vancouver, BC V6T 1R9 Canada

Abstract

Dynamic rheology is used to examine gelation properties induced by increasing water content in cellulose acetate (CA)/N,N dimethylacetamide (DMAc)/water system. We examine yield stress of the gels by performing stress sweep experiments by alternatively increasing water content and CA concentration both resulting in higher yield stresses. Temperature ramp and dynamic frequency experiments are also performed to determine the thermal stability of the physical gels and provide us with the gel-sol transition point (Tgs). The resulting systems exhibit “solution-like” properties beyond specific temperatures. The changes in dynamic viscoelastic properties may be caused by enhanced hydrogen interactions in the system when CA concentration and primarily water content or are increased.

*Corresponding authors: Saad A. Khan; Phone: 919 515-4519; Fax: 919-515-3465; e-mail khan@eos.ncsu.edu; John F. Kadla; Phone: 604 827-5254; Fax: 604-822-9104; e-mail: john.kadla@ubc.ca
Introduction

Cellulose derivatives exhibit variety of solution properties dependent on nature and type of functional groups used to substitute the hydroxyl groups on the anhydroglucose units in cellulose. The use of solvents which interact with specific functional groups may cause precise intermolecular linkages and can allow particular process conditions be established.\(^1\) By utilizing particular substituents some derivatives can be water-soluble or insoluble in water but soluble in some solvent systems, which can be single or combinations of different solvent mixtures. Typical derivatives, which are soluble in aqueous solutions include methyl cellulose (MC)\(^2\)-\(^{10}\), hydroxypropyl methyl cellulose (HPMC)\(^3\)-\(^4\) including other hydrophobically modified cellulose derivatives.

Cellulose acetate (CA), a derivative of cellulose is a polymer that has a semiflexible chain\(^1\)\(^{11}\) characterized by partially or fully substituting the hydroxyl (OH) groups on the C-2,3 and 6 positions with O-acetyl groups.\(^1\)\(^{12}\)-\(^1\)\(^{14}\) It exhibits different solubility behavior in various solvents dependent on the degree of substitution (DS) of the acetyl units.\(^1\)\(^{13}\)-\(^1\)\(^{14}\) For instance, cellulose acetates having a DS of between, 0.5 to 1 are soluble in water.\(^1\)\(^{15}\)-\(^1\)\(^{16}\) Uniform distribution of the substituents have been found to be essential for CA to be water-soluble.\(^1\)\(^{16}\) It is suggested that, solubility in water also depends on the substitution of the OH groups at the C\(_3\) position.\(^1\)\(^{16}\) A study on dilute cellulose diacetate (CDA) in mixed solvents, indicate that solvents capable of dissolving CDA can be classified into two main groups.\(^1\)\(^{17}\) There are basic solvents (e.g. acetone) which interact primarily with hydroxyl groups on the chain and acidic solvents (e.g. formic acid) that primarily solvate the acetyl groups.\(^1\)\(^{17}\) Thus, the use of specific solvents
could impact partially substituted CA chains to exhibit different solution characteristics which can lead to interesting system properties changes such as viscosity modifications, gelation etc.

Gel and membrane formation have been observed in different cellulose derivative solvent systems.\textsuperscript{2-9, 18-21} Most cellulose derivative gel systems if not all, form physical gel network. The process of physical gelation is not well understood in comparison to chemical gelation due to the transient nature of gel network junctions.\textsuperscript{22} These network junctions holding physical gels can be created and destroyed by thermal agitation of the polymeric system.\textsuperscript{5,8} For example, aqueous systems of MC and HPMC exhibits thermoreversible gelation by forming a three-dimensional network structure.\textsuperscript{3} This unique gelation process involves formation of gels when the aqueous systems of these derivatives are heated and reversibly form solutions when cooled.\textsuperscript{2-9} The phenomena may be attributed primarily to hydrophobic interaction between molecules having methoxyl substitutes.\textsuperscript{3} Unlike MC aqueous systems, low DS (0.5 to 1) CA aqueous solutions do not gel when heated.\textsuperscript{16} Gelation in some CA/organic solvent systems have been observed\textsuperscript{19, 23,25} and has been attributed to be mainly caused by strong intermolecular contacts.\textsuperscript{19} CA containing different amounts of acetic acid in benzyl alcohol has been shown to exhibit gel formation.\textsuperscript{18-20} The gelation temperature was discovered to depend on molecular weight and quantity of combined acetic acid.\textsuperscript{18} These gels are found to exhibit structural changes dependent on solvent quality.\textsuperscript{18} 5% solutions of CA in benzyl alcohol prepared at 60-80\textdegree C formed gels when solutions are cooled to 25\textdegree C.\textsuperscript{20} CA samples with different molecular weight and degree of substitution containing combined acetic acid concentrations of 54\% and 60\% also lead
to gel formation in dimethyl phthalate. Increase in degree of substitution and polymer concentration in the system causes an increase in the dynamic moduli.

The process of gelation can also be induced by the addition of a non-solvent to a CA/solvent system or by adding CA to a mixture of solvent/non-solvent. This gelation process may involve phase separation prior to gelling. It is dependent on not only on the polymer characteristic, but also on specific polymer/solvent and polymer/polymer interactions. A previous study we conducted which involves addition of water to CA/DMAc solutions shows gelation occurring at relatively high water contents (>18wt%) for CA concentrations investigated. The system phase separated which was determined by cloud point studies prior to gelling. Ternary systems of CA/solvent/water have been found to exhibit gelation using solvents comprising of acetone, dioxane and tetrahydrofuran (THF). The gelation process in a study conducted on CA/dioxane/water system was found to be very slow, a phenomenon observed in our previous study. It must be stated that, investigations in gel formation in CA systems are few and far between. Possibly due to the complexity involved and/or the relatively high concentrations of polymer which may be needed for gelation to occur.

We seek to take advantage of the good solvent properties of N,N dimethylacetamide (DMAc) for CA and the subsequent addition of a non-solvent (water) to induce gelation in our system. In our previous work on same system, we established protocols needed to covert solutions to gels. By tuning the polymer concentration and using appropriate combination of both solvents, we determine conditions pertaining to physical gel formation. This paper examines the dynamic
rheological properties of the gels formed by adding relatively high water content to CA/DMAc solutions. Rheological methods have been used to characterize various cellulose and cellulose derivatives in aqueous and organic solvent systems.\textsuperscript{2,4,6-7,24,27} It provides important information on gel properties such changes in dynamic viscoelastic properties and is the most direct method for determining sol-gel transition.\textsuperscript{28} Therefore rheology can also be used to study the evolution and changes during the transition from solution to gel network and vice versa. The main focus of this paper is to examine from the standpoints the effect of CA concentration and solvent quality on the gel network structure. We initially investigate the changes in dynamic viscoelastic properties by varying CA concentration and water content. The nonlinear viscoelastic behavior is also examined to determine mechanical strength and fracture properties of these gels. This is a technique that has been used in studying a considerably wide range of materials.\textsuperscript{29-31} Investigations in nonlinear viscoelastic characteristics of cellulosic fiber gels showed the gel suspensions to exhibit nonlinear behavior at strains above 1\%.\textsuperscript{29} Finally, we examine the gels with respect to their thermal stability, which provide us with the gel to sol transition temperature (T_{gs}). Heating the gels and its effect on the dynamic viscoelastic properties changes enabled us to determine the gel to sol transition point.

**Experimental**

**Materials**

Cellulose acetate (CA) with a molecular weight of 50,000 g/mol and acetyl content of 39.7wt\% was used. HPLC grade N,N dimethylacetamide (DMAc) and
deionized water were the cosolvents used for this study. DMAc is a good solvent for CA and dissolves CA to appreciable high concentrations. Both CA and DMAc were purchased from Sigma-Aldrich and used as received.

**Sample Preparation**

Bulk CA concentrations in DMAc were prepared at a constant CA concentration of 20wt%. The procedure was to add calculated weight fractions of DMAc to the aliquots of the 20wt% stock solutions. Sample were mixed and kept for a day at ambient conditions. Specific amounts of deionized water was then added to the resulting solutions, after which samples were heated at 70°C for 10 minutes to ensure complete miscibility. The relatively high water contents (>19wt%) used in this study ensured that all samples analyzed were gels. Prior to heating, samples were maintained under nitrogen atmosphere to prevent oxidation of CA solutions. Samples after heating were kept at room temperature for at least five days prior to use to allow system to equilibrate. All stock solutions and dilutions were prepared on a weight basis.

**Rheological Measurements**

A TA Advanced Rheometer (AR 2000) was used to measure the dynamic rheological behavior of the samples at various temperatures. In these experiments, an oscillatory shear was applied to the samples and the corresponding elastic ($G'$) and viscous ($G''$) moduli measured as a function of either frequency or stress amplitude. Initial experiments at a constant frequency but increasing stress amplitude were performed to determine the linear viscoelastic (LVE) for the frequency sweep experiments. The stress sweep experiments also provided information on the yield stress/strain of the gels$^{30-31}$, as discussed later in the paper. Subsequently experiments
were conducted as a function of frequency at a low strain/stress level within the LVE regime. The magnitude and shape of corresponding elastic \( (G') \) and viscous \( (G'') \) moduli measured as a function of frequency provides a signature of the state of a system (e.g., gel or liquid).\(^{31-33}\) To determine the gel to sol transition as a function of increasing temperature, two types of experiments were conducted, temperature ramp and frequency sweep at different temperatures. Experiments were performed at different temperatures between 25\(^\circ\)C and 100\(^\circ\)C. Temperature ramp experiments were conducted at a heating rate of 1\(^\circ\)C/min and frequency of 1 rad/s to obtain the temperature range where gel-sol transitions occur. Dynamic frequency sweep experiments at different temperatures were also performed and changes in viscoelastic properties used to estimate gel-sol transition. For all the experiments, the disk shaped gels were carefully cut and carefully placed on the lower plate of parallel plate geometry (20cm diameter or radius) [did you check for slip using sandpaper or different gaps?]. For temperatures greater than 25\(^\circ\)C, the samples were coated around the circumference with polydimethylsiloxane (PDMS) oil to prevent solvent evaporation.

**Confocal Scanning Laser Microscopy (CSLM)**

In the CSLM experiments, a confocal laser scanning system (Leica TCS SP) connected to an inverted microscope (Leica DM IBRE) was used to scan the gels. Confocal microscopic analysis have previously been adopted to characterize membranes of mixed cellulose esters (cellulose nitrate/cellulose acetate).\(^{35-36}\) Prior to preparing our gels, our solutions were tagged with calcofluor white which is a cellulose-selective fluorescent dye.\(^{34}\) Measurements were performed with 100x numerical aperture 1.4 oil immersion objective. Optical sectioning was performed as a function of
the depth of the gels along the z-axis. The excitation source we used was a UV laser (350 nm, 361 nm; it might excite at both wavelengths simultaneously). The spatial resolution of the images was 512x512 pixel. The image analysis was done using Adobe Photoshop 7.0 (Adobe Systems Inc.).

**Results and Discussion**

**Rheology and Microstructure**

We first investigate changes in the dynamic viscoelastic properties at 25°C for two conditions: constant CA concentration with varying water content and constant water content with changing CA concentration. Figure 1a shows frequency spectrum of the elastic ($G'$) and viscous ($G''$) moduli of 10wt% CA samples in DMAc/water containing different water content. Figure 1b reveals similar data for samples with 15wt.% CA. For the sake of clarity, $G''$ results are shown only for one representative sample. We observe $G'$ to be relatively flat and greater than $G''$ (this is true for all samples although data for only one is shown), features indicative of a gel network.37-41 In addition, we observe $G'$ to increase with increasing CA content or water.

The effects of water content and CA concentration are depicted more clearly in Figure 2. Figure 2 shows $G'$ (at a fixed frequency of 1 rad/s) as a function of water content for a CA concentration of 10 and 15wt%. With successive increase in water content, $G'$ shifts to higher values, with an overall increase greater than an order of magnitude. We observe over a five-fold increase in $G'$ as CA concentration is varied from 7.5wt% to 15wt%. The increasing trend in $G'$ observed in Figure 2 suggests
formation of a progressively stronger network with either an increase in water content or CA concentration.

Direct evidence of a sample spanning gel network is observed from confocal micrographs shown in Figure 3 obtained under different water content for two different CA concentrations. In Figure 3a, at low CA concentration (10wt.%) and water content (21.6%), we observe a very open network. The microstructure also seems somewhat aggregated. At a higher water content (23.2%) but at the same CA concentration, we find the network to be less open and the microstructure more uniform. In Figure 3b at a higher CA concentration (15%), we see a significantly different microstructure. A denser network with a fine and uniform structure is observed. Incorporation of additional water to this system accentuates these features. The increased network connectivity with enhanced CA or water content is consistent with the higher $G'$ observed in rheological experiments.

To explain the phenomenon of increase in $G'$, we must revisit our earlier work where we established conditions needed for sol-gel formation. In the previous study, we found that at low water contents, the system forms a clear solution. We envisage that at low water contents, water does not possess the capacity to break a lot of the interactive bonds formed between CA and DMAc. Gelation occurs when critical water content is attained dependent on CA concentration, beyond which competitive interaction for DMAc between water and CA becomes more or less balanced. Thus some of the bonds formed between CA and DMAc are broken off and a lot more DMAc become accessible to water. CA therefore exhibits an increase in intramolecular interaction between different chains whiles “holding” onto as much DMAc as possible.
It is speculated that the system involves CA and water forming strong bonds with DMAc, with partial weak links also formed between CA and water. This leads to aggregates of CA spanning uniformly through the entire system. In view of the explanation provided, the trend in Figures 1a & b may be due to water content increase promoting the intramolecular interaction between CA units forming stronger aggregates leading to the formation of a more rigid gel network. Similarly, increase in CA concentration may lead to significant intermolecular interactions being formed between CA, DMAc and water promoting aggregation of CA, which causes stronger gel formation. Tactile and visual observations respectively showed gels exhibiting harder texture and more whitish appearance with increase in CA concentration and water content.

**Yield Behavior**

Several approaches have been described in the literature on measuring the “yield stress” of complex materials, and references and brief descriptions of some these approaches can be found in a recent study from our group. In this work we undertake one such approach for measuring yield stress to examine relative magnitude and trends of different systems. Gels having different CA concentrations and water contents were subjected to increasing oscillatory shear stress values to determine the yield behavior at room temperature. An example is displayed in Figure 4a where stress sweep are conducted for different CA concentrations at a constant water content of 21.6%. Figure 4b shows similar experiments performed at constant CA concentration of 15wt% with varying water contents of 20.4 and 23.8%. Both \( G' \) and \( G'' \) at low stress are relatively
independent of applied stress, which indicates materials are in the linear viscoelastic regime. However, with increasing stress, there is a breakdown of the interactive bonds in the materials and we see a gradual decrease in $G'$. Beyond a critical stress value ($\tau_c$), the structure ruptures and/or yields leading to a sharp drop in $G'$. To obtain the yield stress, two asymptotic lines are drawn through the initial and post-breakdown $G'$ values (as shown in Figure 4a and 4b). Interestingly, $G''$ shows a gradual increase and a maximum at the onset where $G'$ begins to decline. This process may be caused by viscous properties being enhanced as the bonds get broken with gradual stress elevation.

Since essentially the gel formation is attributed to intramolecular interaction between CA units, with additional links formed between DMAc and water. At the initial stages of gel rupture, some of the bonds between the CA units may be broken leading to “free” CA units being formed at some sections in the gel. Thus, there is an introduction of some viscous components, which may account for the initial increase in $G''$. Eventually after $G'$ and $G''$ crossover and the critical stress is exceeded, we observe a sharp decline in both dynamic properties after which the material completely breaks down.

For all the gels studied, we see the nonlinear and yield behavior shift to higher values with increasing CA concentration and/or water content (Figure 4a and 4b). Figure 5 shows the effect of these two variables on yield stress more clearly. We find that the yield stress increases substantially, and in some cases by an order of magnitude, when water content or CA concentration is increased. The shift in the onset of non-linearity and yield stress to higher values can be attributed to the formation of stronger network as CA concentration or water content is increased, thereby requiring a greater stress to disrupt the microstructure.
Effects of Temperature

Since our system forms physical gels, the networks junctions should be disrupted by the application of thermal energy.\textsuperscript{5,8} In this regard, we examined the transition of our gels to liquids by subjecting them to temperature increments from room temperature upwards. Figure 6 is a digital image showing the transition of a gel to solution at temperatures of 25 and 80°C for 10wt% CA concentration containing 21.6% water fraction. We see a transition and a change in the gel characteristics from a completely opaque at 25°C to a system that shows an almost clear solution at 80°C. This pictorial transition correlates well with rheological experiments, which showed gel-sol properties at approximate conditions. Similar images were observed for varying water content and CA concentrations. The dependence of $G'$ and $G''$ on temperature\textsuperscript{43} provides good indications of the transition from solution to gel and vice versa. As such, we conducted two types of experiments to examine the gel-sol transition: temperature ramp and isothermal dynamic frequency experiments at different temperatures. Figure 7a shows temperature ramp experiments conducted at 1°C/min for CA concentrations of 10wt% at two different water contents of 19.8 and 21.6%. The first region was characterized by a relatively low dependence on temperature for both $G'$ and $G''$, showing viscoelastic behavior of a gel network. However, beyond 40°C, there is a rapid decrease in $G'$ and $G''$ until a crossover point at about 73°C and 81°C for 19.8 and 21.6% water compositions respectively is observed. Following the crossover, $G''$ exceeds $G'$. We term this crossover point the gel-sol transition temperature. The trend for a 15wt.% system follow a similar pattern with the only difference being the
crossover of $G'$ and $G''$ which occur at higher temperatures of about 79°C and 90°C for 19.8 and 21.6% water compositions respectively. Obviously, one could argue that a better way to obtain this transition point would have been to use the Winter-Chambon approach.\textsuperscript{22,37,44-45} In fact, we attempted to obtain the gel-sol temperature by plotting the loss tangent ($\tan \delta$) measured at various frequencies as a function of temperature.\textsuperscript{22,37,45} But the procedure was aborted because there were no precise convergence at a set temperature. The inability of the Winter Chambon criteria to hold has been observed for other systems as well and can be attributed to absence of self-similarity, heterogeneity.\textsuperscript{46}

To ascertain the validity of the temperature ramp experiments, dynamic frequency experiments over a wide range of temperatures were performed. Figure 8a exhibits the dynamic frequency spectrum of $G'$ and $G''$ for a 10wt% CA sample concentration at different temperatures. For clarity, we plot only three temperatures to show the transition from gel to solution. At room temperature the system shows relatively frequency independent dynamic properties. As the temperature is increased to 60°C, both $G'$ and $G''$ drop substantially. However, $G'$ is still larger than $G''$ and both moduli are frequency independent at low frequencies, suggesting that a gel network still persists. As the temperature is elevated to 80°C, both moduli are frequency dependent and there is a crossover between $G''$ and $G'$. These features indicate the system is behaving solution-like. A similar plot is depicted in Figure 8b for CA concentration of 15wt%. The sequence of gel-sol transition is similar to that Figures 7a & b with the difference being the transition to a solution-type behavior, which is observed above 85°C for the higher CA concentration system. To check how our gel-sol transition temperature obtained from temperature ramp experiments compare with results
obtained from the frequency spectrum at different temperature, we plot in Figure 9
G’ and G’’ (at \( \omega = 1 \) of Figure 8) as a function of temperature. We observe a decrease in
both dynamic moduli until approximately \( 77^\circ C \) when G’’ crosses over and exceeds G’.
This transition temperature, which is slightly lower than \( 82^\circ C \) obtained from the
temperature ramp experiment (Figure 8a), is expected as the sample is equilibrated at
each temperature in this case. In the temperature ramp experiment, the sample does not
have sufficient time to equilibrate at each temperature. This pushes the transition to
manifest itself at a higher temperature. This trend is observed in Figure 9b for 15wt.%
sample where the crossover of G’ and G’’ occur \( 85^\circ C \) which is lower in comparison to
temperature ramp experiment which had the G’’ crossing G’ at \( 90^\circ C \). In any event, the
results are quite close and depict the same trend.

A semi-logarithmic plot of G’ versus reciprocal temperature for a 10 and 15wt.%
system containing 21.6% and 20.4% water respectively is shown in Figure 10. From the
Arrhenius plot, the apparent activation energy calculated from the slope is found to be
approximately 113 kJmol\(^{-1}\) for 10wt.% sample, while the apparent activation energy is
approximately 92 kJmol\(^{-1}\) for the 15wt.% system. Thus, using the apparent activation
energy and the pre-exponential factor, G’ at different temperatures can be estimated.
Similar Arrhenius plots can be used to estimate G’ at different CA concentration and
water contents.
Conclusions

This study presents a detailed examination of the effects of CA concentration and water on the rheological behavior of CA gels in mixed solvents of water and DMAc. Linear, and non-linear rheological behavior together with direct observation of microstructure through confocal microscopy are illustrated. In this study, gel formation induced by addition of relatively high water content 19% and above in CA/DMAc solutions have been described using rheological methods. The elastic (G’) and viscous moduli (G”) have been found to increase with increasing water content and CA concentration. This increase in elastic character has been attributed to CA units undergoing a progressively increase in intramolecular interactions whiles forming relatively strong and weak intermolecular interactions with DMAc and water respectively. The yield stress followed a similar pattern with gels exhibiting greater yield stresses with water content and CA concentration increase, which can be attributed to similar reasoning as stated earlier. Confocal images showed a system exhibiting a more closely knit structure with water content and CA concentration increase. The increased homogenous closely packed network with enhanced CA or water content is consistent with higher dynamic viscoelastic properties observed in rheological experiments.

The gel-sol transition temperature (Tgs) for all gels were between 70°C to 90°C, with Tgs showing a progressive increase with CA concentration at comparable water content. The Tgs has been found to also shift to high values with increasing water content at constant CA concentration. This trend emphasizes the earlier explanation of stronger gel network formed with increase in water content and CA concentration, thus
increasing the Tgs. The results show that, the gel strength and for that matter the rheology of the gels are highly dependent on water content and CA concentration and both properties play important roles in determining how gels respond to stress and temperature variation.

Acknowledgement

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References


(16) Bochek, A.M., Kalyuzhnaya, L.M., Interaction of water with cellulose and cellulose acetates as influenced by the hydrogen bond system and hydrophilic-


Figure Caption

Figure 1. Dynamic frequency sweep experiments for (a) CA concentration of 10wt% (b) CA concentration of 15wt% having different water contents.

Figure 2. $G'$ as a function of water content for CA concentration of 10 and 15wt% Data were obtained at frequency of 1 rad/s.

Figure 3. CSLM images for CA concentration of (a) 10wt% and (b) 15wt% at two different water contents.

Figure 4. Stress sweep experiments conducted for (a) different CA concentrations at constant water content of 21.6wt.% (b) constant CA concentration of 15wt% with varying water contents.

Figure 5. Yield stress as a function of water content for varying CA concentration.

Figure 6. Digital image showing transition of a gel to solution at two different temperatures for 10wt% CA concentration with water content of 21.6%.

Figure 7. Temperature ramp experiments conducted at 1°C/min (a) for 10wt% CA (b) 15wt% CA concentration at different water contents.
Figure 8. Dynamic frequency sweep experiment for (a) 10wt.% CA and (b) 15wt.% CA concentration at different temperatures.

Figure 9. Dependence of G' and G" on temperature for (a) 10wt% CA system having water content of 21.6wt.% (b) 15wt.% CA system having water content of 20.4wt%. Data obtained at a frequency of 1 rad/s.

Figure 10. Arrhenius plot for (a) 10wt% CA concentration having water content of 21.6% (b) 15wt% CA concentration having water content of 20.4%.
Figure 1. Dynamic frequency sweep experiments for (a) CA concentration of 10wt% (b) CA concentration of 15wt% having different water contents.
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Data obtained at a frequency of 1 rad/s.
Figure 10. Arrhenius plot for (a) 10wt% CA concentration having water content of 21.6% (b) 15wt% CA concentration having water content of 20.4%.
CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS
7.1 Conclusions

In this thesis study, we have investigated various protocols pertaining to the effect of varying water content (non-solvent) on solutions of cellulose acetate (CA) and \( N,N\) dimethylacetamide (solvent). The initial challenge in this project was the selection of the appropriate solvent to dissolve CA. We chose \( N,N\) dimethylacetamide because of its high boiling point, low toxicity and the ability to dissolve CA to appreciably high concentration levels, since we were interested in studying semi- to concentrated CA solutions. The second phase involved the selection of a non-solvent which can interact in solution to generate phase-separated gel systems. In this regard, water was then chosen as the non-solvent due its strong hydrogen bonding characteristics and the obvious wide spread availability. We have shown in our investigations that solvent quality, most importantly water composition, plays a major role in influencing polymer rheology and microstructure. Our work has explored the changes in solutions and eventual transition to gel formation by increasing water content in our system. In view of these findings, some of the important conclusions that can be inferred from this dissertation are summarized in the following paragraphs.

- Both CA concentration and water content have been shown to have profound effects on solution viscosity. Increasing water content at constant CA concentration and vice versa resulted in enhanced steady state viscosity. In the same vein, increment in CA concentration depicted a similar trend of viscosity increase. This phenomenon is attributed to the enhanced intermolecular interactions between CA and cosolvents. Further explanation can be due to the
fact that additional hydrogen bond linkages in solution are formed causing some entanglements in solution, thus, causing the solution to become more viscous with increase in water content or CA concentration.

- The process of dissolving CA in the cosolvents had a strong influence on the mode of phase separation leading to gelation. Addition of water to CA/N,N dimethylacetamide (dissolution method 1) solutions led to the formation of cloudy samples at intermediate water content depending on CA concentration. Formation of gels with uniform structures was observed at high water contents above the intermediate water composition. The gels became more elastic with increase in water composition and CA concentration depicted by enhanced dynamic viscoelastic properties. In contrast, addition of CA to different ratios but constant weight of water/N,N dimethylacetamide (dissolution method 2) showed a two-phase system depicting a low viscosity liquid layer on top of a gel layer at identical high water contents in comparison to dissolution method 1. The hypothesis speculates the two different phase separated systems to occur mainly due to competitive hydrogen bond interactions in the system. It is postulated that, water competes with CA for N,N dimethylacetamide in solution and at high water contents, different mode of segregation of CA lead to different phase separated systems.

- Heating the two-phase system in dissolution method 2 above a certain temperature resulted in the formation of a uniform gel network. It is
hypothesized that the elevation in temperature breaks some of the \( N,N \) dimethylacetamide-water hydrogen bonds enabling unbonded CA units to obtain access to “free” \( N,N \) dimethylacetamide. Thus, when the system is cooled to room temperature, water has to compete for \( N,N \) dimethylacetamide with CA causing a gel system to be formed due to dispersion of CA through the entire volume of the matrix.

- Gel-sol transition which was influenced by water and CA composition was observed in the gel. Gels with high water content and/or CA concentration had the transition occurring at much higher temperatures. The yield behavior also portrayed a similar pattern where greater stress/strain was needed to disrupt the microstructure of the network. This is mainly due to the stronger gel network formed at such conditions attributed to greater level of hydrogen bond interactions. These stronger gels invariably will need an increase in external factors to break (stress application) or revert them solutions (temperature elevation) as was observed. This hypothesis was supported by examining different water contents and CA concentrations.

- Gel microstructure showed a more homogenous network with increasing water content and CA concentration. Both laser scanning confocal microscopy (LSCM) and scanning electron microscopy (SEM) depicted this trend. This was consistent with rheological studies and confirmed that gel strength was enhanced when water or CA concentration was increased.
7.2 Recommendations

This research has examined the various aspects of changing CA and cosolvent compositions in ternary systems of CA, $N,N$ dimethylacetamide and water. We have thus employed a variety of techniques to understand the rheological and microstructural properties. However, there are various areas of research which need to be explored to fully understand the molecular level interactions accounting for solution and gel characteristics observed.

Differential scanning calorimetric study of gels

Our main characterization technique was rheology. This was supplemented with scanning electron microscopy (SEM) and confocal laser scanning microscopy (CLSM) to correlate microstructure with rheology. Differential scanning calorimetry (DSC) is recommended as an additional tool to determine the thermal properties of the gel formed using a heating and cooling process.\textsuperscript{1,2} The shift and peaks of the relative thermal heat capacity will provide information on gelation process\textsuperscript{3,4} in relation to water content and concentration of CA.

Addition of other non-solvents

Since a variety of solvents interact differently with acetyl and hydroxyl groups on the CA chains\textsuperscript{5}, addition of other non-solvents to CA-$N,N$ dimethylacetamide solutions in place of water is recommended. We observed in our work enhanced steady state viscosity and a sol-gel system transition which primarily depended on water content in the system. Therefore, a class of solvents that can be explored as an initial
step in any future work, are organic alcohols. Essentially, alcohols and water share a
common characteristic in that both have a hydroxyl group attached to side group. Even
though water exhibits much stronger hydrogen bond association in solution, the addition
of alcohols may provide additional information by showing a fundamental difference in
solution properties. Because of the variety of alcohols available, it is envisioned that the
influence of the side chain attached to the hydroxyl group (e.g. methyl, ethyl etc) will
also allow investigators determine how they impact the system. In addition, solvents
such the diols which are compounds that contain two hydroxyl groups can also be
utilized. All the solvents recommended exhibit to some extent hydrogen bonding
characteristics and based on the strength of the hydrogen bonds, we can evaluate how
CA-$N,N$ dimethylacetamide bonds are affected in solution. The effect of alcohols as
non-solvents have shown different systems in relation to microstructure being formed in
a variety of CA solvent system.

Another class of solvents that will also provide some useful information is
solvents that practically exhibit no hydrogen bonding character in solution. These would
include hexane and octane among others.

*Effect of salts*

The influence of salt on the suppressing or enhancing polymer solution, phase
separation and gel properties is an important future direction, and preferably will shed
light and expand our knowledge of the hydrogen bond interactions between CA and the
cosolvents, especially water in the system. Progressive increase in the valence number
of the cation in a particular class of salt will affect the ordering of salt around the water
molecules. This will invariably affect the intermolecular hydrogen bonds already formed, and based on salt-type and concentration, phase separation and gelation can be induced to occur at low or high non-solvent content. Previous studies on CA acetonitrile solutions containing different salts have shown viscosity increase to depend on the valence number of the cation.8

To aid or suppress gelation, another approach would be to classify the salt-type into “salting-in” and “salting-out” since the mechanism of interaction in solution is different. The use of NaCl and NaI, typical salting-out and salting in salts respectively3-4, will enable us to determine the extent to which gelation is affected. For instance, NaCl exhibit strong interactions with water molecules3 and may suppress or aid gel formation.

Effect of pH

The modification of pH in solution is an interesting feature which can affect the strength of bonds in the system influencing solution and gel properties. The initial step can be the change in pH of water prior to its addition to the polymer-solvent system. Therefore, increasing or decreasing the pH can allow us to develop a pattern of altering system characteristics.
References


APPENDIX A

CELLULOSE GELS AND LIQUID CRYSTALLINE POLYMER (LCP)

Appendix is essentially a manuscript by John F. Kadla, Qizhou Dai, Collins Appaw, and Saad A. Khan, prepared for submission to Encyclopedia of Chemical Processing (EHCP).
CELLULOSE GELS AND LIQUID CRYSTALLINE POLYMER (LCP)

John F. Kadla¹, Qizhou Dai¹, Collins Appaw² and Saad Khan²

¹Advanced Biomaterials Chemistry, University of British Columbia, Vancouver, BC V6T 1R9 CANADA

²Department of Chemical Engineering, North Carolina State University, Raleigh, NC 27695 USA

KEYWORDS: Cellulose, cellulose derivatives, liquid crystal, chiroptical property, rheology, relaxation, phase separation, gelation, hydrogen bond, sol-gel

ABSTRACT

INTRODUCTION

CELLULOSE

Cellulose constitutes the most abundant, renewable polymer resource. It has been estimated [1] that the yearly photosynthesis of biomass is 170 billion tons, 40% of which consists of polysaccharides; mainly cellulose and starch. Today, with the availability of an enormous variety of synthetic polymers, cellulose and its derivatives are somewhat overshadowed. Nevertheless, cellulose occupies a unique place in the annals of high polymers. It was one of the first polymers studied starting with Anselm
Payen’s investigations [2]. “Many of the basic principles were worked out in the course of cellulose investigations” [3]. Payen first recognized cellulose as a definitive substance and coined the name cellulose. Today it is still widely investigated. Synthesis of cellulose derivatives and regeneration of cellulose, along with the physical chemistry of cellulosic solutions, including those, which are mesomorphic, constitute areas of active research. The use of cellulose and its derivatives in a diverse array of applications, such as fibers, films, plastics, coatings, suspension agents, composites, wood and paper products, continue to grow on a worldwide basis. Relatively newer uses of cellulose and cellulose derivatives include cellulosic membranes for hemodialysis and hemafiltration, [4] chiral isomer separations, [5] and calorie-free fat substitutes [6].

Cellulose is the main constituent of higher plants, including wood, cotton, flax, kemp, jute, bagasse, ramie, cereal straws, etc. Industrially, the principle sources of cellulose are wood, cotton fiber and cotton linters. Cellulose is also produced by a type of acetic acid-producing bacterium, *Acetobacter xylinum*. [7] Algae such as *Valonia, Chladophora, Rhizoclonium and Microdictyon* also produce highly crystalline cellulose I. There are also several celluloses of animal origin, of which tunicin, a cell wall component of ascidians, has been extensively studied [8].

**Composition and Conformation**

In 1838, Payen first proposed the elemental composition of cellulose to be $C_6H_{10}O_5$, [2] classifying it as a carbohydrate. A number of studies [9-12] have shown cellulose is a chain-like extended linear macromolecule of β-D-glucopyranose units linked by (1, 4) glycosidic bonds in which the anhydroglucopyranose units exist in the
lowest energy $^4C_1$-chair conformation. [13] It is generally accepted that in the cellobiose repeat unit (being 10.3Å) each anhydroglucopyranose residue is displaced 180° with respect to its neighbor. Thus cellulose has a two-fold screw axis. [14]

The rigidity of cellulose chain comes from the steric repulsion between atoms on the adjacent units and intra-chain hydrogen bonding. For cellulose, the conformation of the chain depends on the rotation of the two bonds linked to each glucosidic oxygen atom. Results from conformational energy indicate that cellulose chain can have only limited number of energetically favorable conformations and all stable and metastable conformations are extended helices [15,16]. Three hydroxyl groups on each unit form a large number of inter- and intra-chain hydrogen bonds. The intra-chain hydrogen bonds, C(3)OH—O(5’) and C(6)OH—O(2’)OH, limit the rotations of adjacent rings and contribute to the rigidity of the cellulose backbone. As a result of these strong inter- and intra-chain hydrogen bonding, cellulose has poor solubility in common solvents.

CELLULOSE GELS

Solution to gel transitions has been observed in various cellulose derivatives. Most cellulose derivative gel systems if not all, form physical gel networks. The process
of physical gelation is not well understood in comparison to chemical gelation due to the transient nature of gel network junctions [17]. Gelation in cellulosic systems in some circumstances exhibits phase separation characteristics prior to gel network formation. The phenomenon of phase separation depends to a large extent on the concentrations of polymer and solvents used [18, 19].

_Gelation properties in aqueous cellulosics_

Some cellulosic systems, which are soluble in aqueous solutions exhibit unique thermoreversible gelation by forming three-dimensional gel networks [20]. The system when heated is transformed into gels and reversibly forms solutions when cooled [20-27]. Various studies have been conducted particularly on methyl cellulose (MC) to investigate the gelation mechanism. Various reasons have been proposed to explain this phenomenon and particularly for MC and there exist some level of controversy detailing the gelation mechanism [20]. It is reported that heating of MC aqueous solutions form aggregates due to the hydrophobic regions being exposed when the “cage-like” structures formed by the water molecules are broken [21]. Lizaso et al. [28] indicated that thermoreversible gels were formed in solutions of ethylcellulose in diester solvents. Gelation in a novel azobenzene functionalized hydroxypropyl methylcellulose (AZO-HPMC) have been suggested to be mainly caused by hydrophobic associations between HPMC chains [29].

_Cellulose acetate gel systems_
Cellulose acetate (CA) exhibits dual solubility characteristics depending on the DS. CA a derivative of cellulose is characterized by partially or fully substituting the hydroxyl (OH) groups on the C-2,3 and 6 positions with O-acetyl groups [30-31]. It has been observed that cellulose acetates having DS of 0.5 to 1 are soluble in aqueous solutions [33, 34]. Studies have shown that solubility in aqueous medium may depend on the uniform distribution of the substituents and substitution of the OH groups at the C₃ position [34]. On the other hand, when the DS > 1, CA tend to be insoluble in aqueous solutions but soluble in various other solvents. Boerstoel et al.[35] found that over a DS range of 0.23 to 2.89, cellulose acetate was also soluble in phosphoric acid exhibiting liquid crystalline properties. Pintaric et al. [36] mentioned in a study on dilute solutions of cellulose diacetate (CDA) in mixed solvents, that basic solvents (e.g. acetone) interact primarily with hydroxyl groups on the chain, whiles acidic solvents (e.g. formic acid) primarily solvate the acetyl groups. Therefore, the use of specific solvents can induce structural changes in solution due to the presence of both acetyl and hydroxyl groups on partially substituted CA chains.

Unlike MC aqueous systems, low DS (0.5 to 1) CA aqueous solutions do not gel when heated [34]. Gelation in some CA/organic solvent systems have been observed to be mainly caused by strong intermolecular contacts [37]. CA containing different amounts of acetic acid in benzyl alcohol has been shown to exhibit gel formation [37-39]. The gelation temperature was discovered to depend on molecular weight and quantity of combined acetic acid [37]. These gels are found to exhibit structural changes dependent on solvent quality [37]. 5% solutions of CA in benzyl alcohol prepared at 60-80°C formed gels when solutions are cooled to 25°C [39]. The gelation process can be
induced by the addition of a non-solvent. Ternary systems consisting of CA/solvent/water exhibits gelation, adopting solvents comprising of acetone, dioxane and THF [19]. A study on CA/dioxane/water system was found to gel even though the process was very slow [40]. Chauvelon et al. [41] reported weak gel-like systems being formed in water-soluble cellulose acetate sulfate (CAS) at high concentrations (above 7-8 g/l).

Rheology of cellulosic solutions and gels

Rheology has been used in quite a number of cellulosic solutions and gel systems [21, 22, 24, 41, 42, 43]. Wang and Fried [42] postulated that specific interactions such as hydrogen bonding between CA and solvents may affect rheological properties in solution. Dynamic rheology provide information on viscoelastic property changes and is the most direct method to study sol-gel transformation [44]. This technique has used in most MC gel system to investigate and probe gel properties [21, 22, 24].

Figure 1. Effect of different water contents on the steady shear viscosity of cellulose acetate in DMAc/water cosolvent system. The total concentration of cellulose acetate is kept constant at 10wt%.

Steady state viscosity measurements for the study conducted by adding CA to DMAc/water (dissolution method 1) fractions showed viscosity with increasing water content at CA concentration of 10wt% (Figure 1). At low water content the system
portray a Newtonian pattern with low shear thinning at high shear rates. But at relatively high water contents, the viscosity profiles show shear thinning being developed at low shear rates. It is postulate that the hydroxyl (OH) groups on the water molecules interacting strongly with the acetyl groups on DMAc. Therefore, the addition of CA to the solvent system, cause both water and to a much extent DMAc to form complex hydrogen bond interaction with CA in the system leading to intermolecular interaction intensification. Thus increasing the viscosity with water content increment. The system phase separates forming a two-phase region at high water contents (>19wt%). The upper layer depicts a clear solution, which exhibits Newtonian behavior whiles the polymer-rich viscous bottom show a shear-thinning behavior over the whole range of shear rate studied (Figure 2).

**Figure 2.** Viscosity pattern for the two-phase region for a constant 10wt% CA in DMAc/water system

The phenomenon of the two-phase behavior at high water contents leads to the idea of a competitive interaction for DMAc since both CA and water have affinity for DMAc. It is perceived that water and DMAc form strong hydrogen bond links due to the high composition of water. Therefore CA is hindered from gaining access to DMAc and may be weakly bonded to DMAc and possibly some water molecules. This causes CA to exhibit a greater level of intramolecular interactions, which leads to formation of a viscous mixture at the bottom of system.
Figure 3. Effect of different water contents on steady shear viscosity for a cellulose acetate/DMAc/water system. CA concentration is 10wt%.

By utilizing a different route of sample preparation, which involved addition of water to homogenous CA/DMAc solutions (dissolution method 2), the system showed similar viscosity increase with water content (Figure 3) at CA concentration of 10wt%. It is envisaged the intensification of bonds interactions was the main factor influencing the increment in viscosity. Beyond critical water content (>19wt%), the system transforms from a homogenous to a uniform cloudy rigid gel-like material. This sol-gel transition is shown in Figure 4 where $G'$ and $G''$ as a function of frequency for two different water compositions at CA concentration of 10wt%. At the low water composition, we find $G''$ to be larger than $G'$ over the frequency range with both showing dependence on frequency a behavior typically depicted by a polymer solution. But at the high water composition shown, $G'$ is larger than $G''$ indicating that elastic properties are dominant over viscous properties. Furthermore, both $G'$ and $G''$ are relatively independent of frequency indicating the formation of a gel network. Thus the system can be tuned from a solution to a gel by increase in the non-solvent composition.

Figure 4. Effect of low and high water contents on the viscous ($G''$) and elastic ($G'$) moduli for 10wt% cellulose acetate/DMAc/water system.
It is envisaged that when bulk CA/DMAc solutions are prepared, the CA form strong hydrogen bonds with DMAc in solution. As we increase the amount of water in the system, CA resist water from displacing the hydrogen bond formed initially but water due to its strong hydrogen bond characteristics can break off some of the CA-DMAc bonds. Thus we have this complex hydrogen bond formation involving CA-DMAc-water with some weak bonds formed between CA and water. This causes aggregates of CA to span entire sample leading to formation of rigid, uniform gel-like structures. Gelation process may also be described as the aggregation of particles during the growth process of these clusters, which collide to form gels [45].

CELLULOSIC LIQUID CRYSTALLINE POLYMERS (LCPs)

Formation of Liquid Crystals

Liquid crystalline phase, or mesophase, is a special state of the matter that possesses long-range order on a macroscopic scale but can flow like fluids. Generally, molecules are required to have asymmetric shapes to form liquid crystalline phases. For polymers, the mesogenic groups (moieties to form liquid crystalline phases) are linked either in the main chain with flexible segments or on the side chain attached to the flexible main chain. It is these mesogenic groups that provide the liquid crystalline properties for the polymers. Some polymers without mesogenic groups are also capable of forming liquid crystalline phases. These polymers have a rigid or semirigid backbone arising from the steric effects or intra-molecular hydrogen bonding which restrict the flexibility of the chain.
Flory first predicted that linear rod-like polymer would form ordered phases in concentrated solutions [46]. By using a lattice model, Flory’s theory predicted that the rigid polymer solution would separate into two phases - isotropic and anisotropic, at a concentration given by:

\[ V_p^* = \frac{8}{x^2} \left(1 - \frac{2}{x^2}\right) \]

where \( V_p^* \) is the critical volume fraction of the polymer, \( x \) is the axial ratio, given by \( x = \frac{l}{d} \) (rod length to diameter). The phase separation can be attributed to a favorable entropy of forming an ordered phase at high polymer concentration.

Both entropy and enthalpy are found to contribute to the stability of nematic mesophases, although for LCPs the dominant factor is the entropy term, which is controlled by the size and shape of the molecule [47, 48]. The original theory, which assumed that the polymer chains were completely rigid and rod-like, does not reflect real polymers. Even the most rigid polymers have some degree of flexibility. Besides, polydispersity, distribution of substituted side groups as well as polymer-solvent interactions will affect the flexibility of the polymer.

*Formation of Lyotropic Liquid Crystalline Phase of Cellulose*

As discussed above, due to the strong inter- and intra-chain hydrogen bonding, cellulose has poor solubility in common solvents. Solubility problems limit the formation of lyotropic liquid crystalline solutions of cellulose. Only a few solvents are known to dissolve cellulose and form the anisotropic phase.
For cellulose solution in N-methyl-morpholine-N-oxide (NMNO)/H₂O, the formation of anisotropic phase was reported [49] without determining the nature of the mesophase. Patel et al. reported the mesophase formation of cellulose in trifluoroacetic acid (TFA)/chlorinated alkane solvent system and labeled as chiral nematic [50]. However, due to the high acidity and reactivity of TFA, cellulose is degraded or derivatized. Cuculo reported the formation of mesophase of cellulose in liquid NH₃/NH₄SCN [51]. Both nematic and chiral nematic phases were observed at different cellulose concentrations. Later, Hattori and Cuculo observed the anisotropic phase formation of cellulose in hydrazine/thiocyanate salt solvent system [52] and ethylenediamine/thiocyanate salt solvent system [53]. The nature of these mesophases was not determined.

Dimethylacetamide (DMAc)/LiCl system is a stable cellulose solvent system. The dissolution of cellulose comes from cellulose complexes and hydrogen bonding [54]. However, due to the solubility limit of cellulose, a high concentration (> 15%) is unlikely to achieve [55]. The critical concentration to form mesophase (10 – 15%) depends on the salt concentration of the solvent.

Hydrolysis of natural cellulosic materials by sulfuric acid or phosphoric acid produced highly crystalline well-defined rods – cellulose nanocrystallites (or cellulose whiskers)[56]. The cellulose crystallites formed colloidal suspension in water and it was stabilized by the negative surface charge. The suspension formed ordered chiral nematic phase at a critical concentration as low as 1-2% volume fraction [57].

*Formation of Lyotropic Liquid Crystalline Phase of Cellulose Derivatives*
The hydroxyl groups on cellulose can be easily substituted to form ethers and esters, resulting in variety of cellulose derivatives. The introduction of substituents on cellulose disrupts the intra-chain hydrogen bonds and brings new steric interactions, which results in the change of rigidity of the cellulose backbone and solubility of the cellulosic polymer. In generally, cellulose derivatives have better solubility than cellulose in a larger range of common solvents.

Following the discovery of mesophases formation in aqueous solutions of hydroxypropyl cellulose (HPC) [58], a variety of other cellulose derivatives have been reported to form liquid crystals [59-61]. In general, lyotropic liquid crystalline formed by cellulose derivatives are achieved in highly concentrated solutions, ranging from 20 – 70% by weight. Due to the semi-flexible nature of cellulosics, these polymers have a critical concentration to form mesophase greater than that of rigid rods predicted by Flory’s theory. The critical concentration for phase separation has been demonstrated to depend on the nature of substituents, the degree of substitution (DS, defined as the average number of hydroxyl groups substituted on each anhydroglucopyranose unit), the distribution of substituents for partially substituted cellulose derivatives, temperature and solvents. This indicates that the stiffness of cellulose derivatives in solutions is a function of steric interactions between adjacent units, intra-chain hydrogen bonding, and intermolecular interactions of polymer-polymer and polymer-solvent.

*Intermolecular Interactions in Lyotropic Cellulosic Liquid Crystalline Solutions*
The formation of liquid crystalline phase is highly dependent on specific polymer-solvent and polymer-polymer interactions. The transition from isotropic to ordered phase of lyotropic systems of semi-rigid polymers often represents a delicate balance of polymer-polymer and polymer-solvent interactions [61]. Not all cellulose derivatives form liquid crystalline phase at high concentrations. Actually, only those with appropriate solubility in a particular solvent can form liquid crystalline solutions. In some cellulose/solvent systems, increasing the polymer concentration from the semi-dilute state, where already microgel appear, leads directly to the gel state, with no evidence of liquid crystallinity, even though the backbone of these derivatives has similar stiffness compared to those derivatives that produce mesophases. Other cellulose derivatives, due to strong polymer-polymer interactions, do not have high enough solubility in a particular solvent to achieve the concentrations necessary for mesophase formation.

The solvent effect on the stiffness of cellulose backbone is clearly demonstrated by difference in the clearing temperature of anisotropic ethylcellulose (EC) solutions in acetic acid (AA), dichloroacetic acid (DCA) and the mixture of these two [62]. The higher clearing temperature of EC/DCA mesophase indicates that EC is more rigid in DCA than in AA. The effect of polymer-solvent interactions on polymer rigidity was further shown using shear-relaxation studies. After shearing a rigid polymeric liquid crystal, a band texture (regular bright and dark lines under cross polarizers), formed in which the direction of the bands was perpendicular to the shearing direction. The band structure formed due to a periodic packing of rigid/semi-rigid polymer chains in a zigzag fashion. This orientation process is a transient phenomenon. After a period of
time the polymer chains relax and the band texture disappears. The bandwidth and the relaxation time of the bands depend on the rigidity of the polymer chain. In fact, at the same concentration, EC chains are more rigid in DCA than in acrylic acid or glacial acetic acid, resulting in wider bands and longer relaxation time [63].

**Chiroptical Properties of Cellulosic Liquid Crystals**

Most lyotropic liquid crystalline solutions of cellulose derivatives form chiral nematic (cholesteric) phase. Some can form nematic phase under certain critical conditions [61, 62, 64]. These chiral nematic mesophases possess a unique structure in which the alignment of the cellulosic molecules is at a slight angle to one another to result in a helicoidal supramolecular structure (Figure 5). The helicoidal structure is described by a pitch $p$ (or its inverse, the twist $\frac{1}{p}$) and the corresponding handedness of the twist. Pitch is the distance between two layers that have the same molecular orientation and is determined by $p = \frac{\lambda_0}{\bar{n}}$ where $\lambda_0$ is the reflection wavelength and $\bar{n}$ is the mean refractive index. The right-handed helicoidal structure is conventionally assigned to a positive pitch ($p > 0$) and left-handed helicoidal structure to a negative pitch ($p < 0$)[59, 65]. The nematic phases can be considered as a special state of chiral nematic phases with no handedness and infinite pitch. Chiral nematic phases are formed when optically active molecules are incorporated into the nematic state. Chiral nematic phases exhibit unique optical properties, such as selective reflection of incident light and optical rotation, because of their helicoidal supramolecular structure [59].

![Figure 5](image-url) Helicoidal structure of chiral nematic mesophase
The anisotropic phase of cellulose in DMAc/LiCl [61] and anisotropic cellulose nanocrystallite suspension [66] are left-handed. Cellulose in TFA/chlorinated alkane is right-handed, which may be due to the esterification reaction of TFA with cellulose [50]. Most cellulose derivatives form right-handed mesophases. Guo [67] hypothesized that the handedness of cellulosic mesophase was somewhat determined by the size of substituents, with small groups to form left-handed phase and bulky groups to form the right one. This statement was supported by the fact that methylcellulose and fully acetylated methylcellulose formed only left-handed mesophase [67] but acetylated ethylcellulose showed the reversal of handedness, from left-handed to right-handed, with increasing acetyl content [64]. However, the handedness of cellulosic mesophase is not only determined by the size of side groups. Several bulky derivatives, such as phenylacetoxy cellulose in CH$_2$Cl$_2$ [68], cellulose tris(4-chlorocarbanilate) in diethylene glycol monomethyl ether (DMME) [69] and 6-O-trityl-2,3-O-hexylcellulose in THF [70], were reported to form left-handed phase. The handedness and pitch of cellulosic mesophases result from complicated inter- and intra- molecular interactions in the solutions.

The observed handedness and pitch of the helicoidal structure is sensitive to temperature, concentration, substitutions, solvent, ions as well as external field [71, 72]. The effect of temperature, concentration, molecular weight, solvent, substitution on the chiroptical properties of the helicoidal structure have been comprehensively reviewed by Zugenmaier [60, 61], Guo [59] and Gray [65]. Due to the complicated inter-
molecular interactions caused by these factors, except for molecular weight, all other factors do not seem to follow any particular patterns without exceptions.

An effective way to study the specific interactions in lyotropic liquid crystalline solutions is to utilize regioselective substitution of cellulose. Kondo [73] reported that free hydroxyls at the C3 position played an important role in determining the handedness of the EC mesophase in CH$_2$Cl$_2$. Breaking intramolecular hydrogen bonding by increasing the substitution at C3-OH position cause the cellulose backbone to become more flexible, which may account for the handedness change. Similarly, the twisting power of the mesophase of cellulose regioselective tricarbanilate derivatives was less influenced by the substitution in C6-OH, more by the C2-OH and probably most by C3-OH [74].

For chiral molecules, equal amount of L- and R- isomers will compensate the opposite twisting power and form a racemic mixture without optical activities – nematic phase, as formation of nematic phase by poly-(γ-benzyl-L-glutamate) (PBLG) and poly-(γ-benzyl-D-glutamate) (PBDG) [75]. For cellulosics, due to the existence of multiple chiral centers in each unit, the interactions among these chiral centers are complicated. With the same average degree of acetylation, pure AEC and mixture of EC and fully acetylated AEC showed different chiroptical properties in chloroform [76]. However, the inversion in handedness provides a useful routine to untwist the helicoidal structure and to form nematic phases. This “untwisting” of the helicoidal structure, characterized by an infinite pitch and the absence of macroscopic chirality, has been observed experimentally. Zugenmaier et al. found that at an appropriate ratio of two solvents in which the handedness of the individual mesophase is opposite produced a nematic-like
ordered phase [61, 62]. By introducing a random distribution of phenyl and 3-Cl-phenyl side groups into cellulose tricarbanilate, which cause opposite handedness of mesophases in the same solvent individually, a phase with a zero twist formed [62]. Guo reported that for lyotropic AEC mesophases, at a critical temperature or a degree of substitution (DS), no chiral order was observed due to the property that the reversal in handedness with increasing acetylation of AEC [65]. By mixing a certain among of EC and fully acetylated AEC polymers in the same solvent, which form left- and right-handed mesophase individually, a nematic phase may be formed [76].

**Rheology of Cellulosic Liquid Crystalline Solutions**

The microstructure and polymer-solvent interactions of lyotropic cellulosic mesophases can be derived from the rheological studies. The lyotropic PLC solution is a complicated system and a wide range of unusual rheological phenomena has been observed. Following the first observation of mesophase formation of HPC/H₂O, this system has been most widely investigated in rheology. Rheological studies in other cellulosic mesophases, e.g., cellulose [77], ethylcellulose [62, 78, 79] and cellulose tricarbanilate [61], have also been reported.

*Concentration dependence of viscosity*

Isotropic solutions show a monotonic increase in shear viscosity with the increasing concentration. The viscosity increases to a maximum when the isotropic to anisotropic transition is approached. Upon formation of anisotropic phase the viscosity begins to decrease. After which viscosity increases exponentially as the concentration
continues to increase (Figure 6). In the isotropic state, the hydrodynamic volume is large due to the random polymer orientation, which restricts the polymer diffusivity and causes an increase in viscosity. Upon anisotropic phase formation, the aligned polymer leads to a small hydrodynamic volume. The viscosity decreases since rotational diffusion is much easier with a net orientation.

**Figure 6.** Viscosity as a function of concentration for lyotropic LCPs

However, Zugenmaier found that the correlation of the viscosity maximum with the formation of the anisotropic phase was valid only when the shear rate was low (shear rate \(\rightarrow 0\))[61]. At a higher shear rate, the concentration at which the maximum of viscosity occurs shifts to a smaller value. When the shear rate is high enough to cause shear-induced orientation (pseudo-nematic phase), entanglements of the random distributed polymers are loosened. The viscosity maximum disappears and a monotonic increase of viscosity vs. concentration is observed. This indicates that the viscosity of the nematic or pseudo-nematic mesophase is less sensitive to concentration than that of the chiral nematic phase [61].

Anisotropic suspensions of cellulose nanocrystallites demonstrate similar viscosity-concentration relationship. The viscosity vs. concentration curve has a maximum, which disappears at high shear rates [80].

*Steady flow behavior*
The steady flow behavior is the most thoroughly studied rheological property. Onogi and Asada hypothesized the universal existence of three shear flow regimes [81] to describe the viscosity of PLCs: a shear thinning regime at low shear rates (Region I), a Newtonian plateau at intermediate shear rates (Region II), and another shear thinning regime at low shear rates (Region III) (Figure 7). The three-regime curve was observed in the anisotropic aqueous HPC solution [82] and HPC in acetic acid [83]. Asada proposed that some PLC systems do not show all regimes because not every regime lies in the accessible shear rate range. In fact, it appears to be unusual to be able to access all regimes for PLCs including cellulosics. Whether the three-regime flow curve is indeed universal or not is still questionable.

**Figure 7.** Three-regime steady state shear viscosity for LCPs

So far, for cellulosic mesophases with all three regimes, microstructures in all three regimes have been well documented by experiments. Region I is generally believed to reflect a defect structure, or piled polydomain texture. The texture is a supramolecular disorder of the nematic structure and is composed of nematic domains possessing little or no macroscopic orientation [82, 84]. This region is characterized by distortional elasticity associated with spatial variation in the director (average local molecular orientation) field. Region II reflects a “dispersed polydomain” structure. Region III is believed to be characterized by non-linear effects of flow on the molecular orientation. In region I and II, the flow is not strong enough to affect the molecular orientation. In Region III, the flow field is very strong that shear induced molecular
orientation becomes important. By birefringence measurement, the molecular orientation is a monotonic increasing function of steady state shear rate for anisotropic HPC/H₂O solutions [85] and HPC/m-cresol solutions [86].

The most striking phenomenon in the steady flow of PLCs is the occurrence of negative first normal stress difference (N₁) – two sign changes in N₁ as a function of shear rate. In contrast, isotropic solutions only show positive N₁ at all shear rates. Negative N₁ has been reported in HPC/H₂O system [87-89] and HPC/m-cresol system [90].

The negative N₁ results from a coupling between molecular tumbling under flow and the local molecular-orientation distribution [87]. At low shear rates, the director tumbles with the flow and N₁ will be positive. At intermediate shear rates, nonlinear viscoelastic effects are important. The director tumbling competes with the steady director alignment along the flow and director oscillates about a steady value. N₁ becomes negative. At very high shear rates, the director aligns along the flow and N₁ is positive again. It is generally believed that the shear rate at which N₁ is minimum halts director tumbling and aligns the molecules [90]. However, negative N₁ behavior disappears at very high polymer concentration due to the polymer-polymer friction interactions [87].

*Relaxation behavior*

The relaxation behavior, or the transient behavior of cellulosic liquid crystalline solutions upon the cessation of steady flow, is unique for PLCs. There are two kinds of relaxations. The bulk stresses relax quickly while the structures relax over a much
longer time. Moldenaers and Mewis suggested that two levels of structures exist [91]. Stress relaxation reflects the fast relaxation at molecule level arrangements and is independent of the previous shear rate. Structure relaxation reflects the gradual changes of the textures. This slow process is unique in that its time scale is inversely proportional to the previous shear rate. When the strain recovery (or recoil) after cessation of steady state flow is plotted against time multiplied by the previous shear rate, the curves superimpose one another [92].

It is generally believed that under high rate flow, the chiral nematic mesophase aligns along the flow direction and uncoils to form nematic structure. Upon cessation of flow, the chiral nematic phase will reform and the molecular orientation will decrease [93]. By using evolution of the dynamic moduli [94] and birefringence [95] as a function of time, the structural change can be investigated. For lyotropic HPC/H2O solutions, upon flow cessation, molecular orientation decreases to a globally isotropic condition at all rates [95] and the dynamic moduli increase to a maximum [94]. However, the final relaxed state depends on the shear history. After high shear rates, the solutions evolve towards an 'equilibrium' state with a high modulus, while after low shear rates, the solutions relax to the 'equilibrium' state with a low modulus [85]. The low-modulus state is ordered and evolves out of a state that has no macroscopic upon cessation of the flow. The high-modulus state is much less ordered, although it evolves from a rather well flow-aligned state upon cessation of the flow [96].

The formation of band texture is another type of relaxation phenomenon, as discussed in previous sections. For HPC/H2O solutions, the band texture is only observed when the molecules have been well orientated in the shear direction [87].
critical lower shear rate limit exists due to the stability of chiral nematic textures. An upper shear rate limit also exists above which no bands are formed [97]. The upper critical shear rate is associated with the flow-aligning region of molecular dynamics. Band texture formation is driven by the release of energy, which has been stored in the mesophase during shear [87]. The evolution of the band texture depends on the previous shear rate applied to mesophase. The rate of evolution of the band texture increases, remains constant or decreases according to whether the mesophase is shear at low, intermediate or high rates [98]. When the band texture appears during recoil, the appearance of band texture stops the strain recovery process until the band texture disappears, and then recovery continues. The presence of the band texture during recoil enhances the strain recovery [99].

Relaxation Behavior of Lyotropic (Acetyl)(ethyl)cellulose / Acrylic Acid Solutions with Different Chiroptical Properties

At a high shear rates the chiral nematic structure changes to a flow-induced nematic phase. However, the shear-oriented phase is easy to disrupt after removing shear force, which is due to the driving force for the liquid crystalline solution to form the more thermodynamically stable chiral nematic structure [93]. For a pseudo-nematic lyotropic solution, after oriented along the high shear rate direction, the driving force to reform helicoidal structure may be limited and the relaxation persists for very long time. So far, only few reports are available on the relations
between the relaxation behavior and chiroptical properties of the mesophases. In the case of PBG solutions containing a single optical isomer (PBLG or PBDG) or racemic mixture of these two, there is no phenomena that cholestercity has any significant effects on the relaxation [95]. This is due to the fact that the mesophases of both the optical isomers and the racemic mixture have large pitch and are nematic-like. In our recent study, relaxation behaviors upon shear force removal were investigated for lyotropic solutions of (acetyl)(ethyl)cellulose (AEC) in acrylic acid (AA) with different chiroptical properties.

Ethylcellulose (EC) and AEC can form cholesteric liquid crystalline solutions in many solvents and were found to change handedness as well as pitch with the change of degree of acetylation. In acrylic acid, EC forms left-handed mesophase. Fully acetylated AEC forms right-handed mesophase [100]. At a certain critical degree of acetylation (DA*) the pitch becomes infinite and nematic-like and untwisted structure forms. When the degree of acetylation of AEC increases across DA*, the handedness of cholesteric liquid crystalline solutions changes from left-handedness to right-handedness. The pitch of lyotropic solution of EC or fully acetylated AEC in AA is about one tenth of that of PBG solutions. Therefore, the effect of chiroptical properties on relaxation behavior is expected to be more pronounced in AEC system than in PBG system.

The values of pitch for lyotropic AEC solutions in AA (50% w/w) are in Table 1. AEC-2 is a pure AEC with medium DA. AEC-3 is the mixture of EC and fully acetated AEC, which has the same average DA as AEC-2. However, in the liquid crystalline solutions, even at the same concentration, AEC-2 and AEC-3 have different pitch and handedness. This phenomenon was also observed in lyotropic...
AEC/chloroform system [76]. The difference in chiroptical properties may come from the complex interactions of multiple chiral centers existing in each repeating unit on cellulose chain, not to form simple racemic mixtures as in PBG system.

**Table 1.** Chiroptical properties of lyotropic AEC/AA solutions with different degree of acetylation (DA)

<table>
<thead>
<tr>
<th>Steady state flow</th>
</tr>
</thead>
</table>

At the same concentration, the viscosities of AEC solutions are different. The larger the pitch, the smaller the viscosity [64]. To eliminate the influence of viscosity of LCP solutions on the relaxation behaviors, the concentrations of AEC solutions were adjusted so that all solutions had similar viscosities under shear. The steady state shear curves of AEC/AA are shown in Figure 8. It is a typical three-region curve. With the increase of shear rate, a shear-thinning is followed by a Newtonian plateau, then followed by another shear-thinning region at high shear rate. The Newtonian plateau is in the shear rate range $1 - 5 \text{ s}^{-1}$. With the increase of pitch, the curve becomes flat and the three regions are not as distinct as the one with smaller pitch. When the shear rate is between $0.5 \text{s}^{-1}$ and $6 \text{s}^{-1}$, the four AEC solutions had the same viscosity.

**Figure 8.** Viscosity as a function of shear rate of AEC/AA solutions
Stress relaxation.

Mercer and Weymann [101] proposed an equation for the time-dependent viscosity $\eta(t)$ of thixotropic suspensions:

$$(\eta(t) - \eta_f)/ (\eta_i - \eta_f) = \eta^* = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \quad (1)$$

where $\eta_i$ and $\eta_f$ are viscosities at shear rate $\gamma_i$ and $\gamma_f$, $A_1$ and $A_2$ are constants, $t$ is time, and $\tau_1$ and $\tau_2$ are relaxation times.

Based on Mercer and Weymann’s Equation, Suto et al. [102] found that the stress relaxation was a two-stage process for lyotropic EC/m-cresol solutions and proposed another equation for lyotropic liquid crystals:

$$(\sigma(t) - \sigma_f)/ (\sigma_i - \sigma_f) = \sigma^* = A_1 \exp(-t/\tau_1) \text{ when } (t < t_c)$$

$$= A_2 \exp(-t/\tau_2) \text{ when } (t > t_c) \quad (2)$$

where $t_c$ is a characteristic time. $\ln(\sigma^*)$ is the reduced shear force.

The stress relaxation behavior of some AEC/AA solutions is in Figure 9. Only one relaxation process was observed, not a two-relaxation process as Suto found. This may be due to the fact that the first stage relaxation process is too fast to be observed. Therefore, the stress relaxation behavior can be represented as:

$$(\sigma(t) - \sigma_f)/ (\sigma_i - \sigma_f) = \sigma^* = A \exp(-t / \tau) \quad (3)$$

Figure 9. Reduced shear stress $\sigma^*$ vs. time for 50% AEC-4(□) and 51.5% AEC-2(Δ)

The relaxation times of different AEC solutions can be evaluated according to equation 3 by the least-square method. The relaxation time and the chiroptical
properties of AEC solutions are listed in Table 2. The larger the pitch, the longer the time for shear force to relax. The relaxation times for AEC solutions with similar pitch but different handedness are approximately the same.

**Table 2.** Relaxation times as the function of chiroptical properties of lyotropic AEC/AA solutions

*Dynamic modulus evolution upon cessation of flow*

The development of storage and loss moduli after flow cessation is a useful tool to analyze structural relaxations on LCPs. Upon flow cessation, the flow-induced orientation is lost. The evolution of the moduli with time is due to the reformation of a chiral nematic phase that had become nematic under flow. Figure 10 shows the relaxation in complex modulus with time.

**Figure 10.** Complex modulus evolution of AEC solutions vs. time

Upon flow cessation, the larger the pitch, the slower the modulus evolved. The modulus of right-handed mesophase (AEC-4) developed faster than that of the left-handed one (AEC-1) with the similar pitch. The difference in relaxation behavior of AEC solutions may be due to the smaller driven force for the mesophases with larger pitch (nematic-like) to reform helicoidal structures of chiral nematic phases from nematic under flow.
REFERENCE


10. Spencer, C. C., Cellulosechemie, 1921, 10, 61. (C.A. 35, 1042)


Figure 1. Effect of different water contents on the steady shear viscosity of cellulose acetate in DMAc/water cosolvent system. The total concentration of cellulose acetate is kept constant at 10wt%.
Figure 2. Viscosity pattern for the two-phase region for a constant 10wt% CA in DMAc/water system.
Figure 3. Effect of different water contents on steady shear viscosity for a cellulose acetate/DMAc/water system. CA concentration is 10wt%.
Figure 4. Effect of low and high water contents on the viscous (G″) and elastic (G′) moduli for 10wt% cellulose acetate/DMAc/water system.
Figure 5. Helicoidal structure of chiral nematic mesophase
Figure 6. Viscosity as a function of concentration for lyotropic LCPs
Figure 7. Three-regime steady state shear viscosity for LCPs
Figure 8. Viscosity as a function of shear rate of AEC/AA solutions
Figure 9. Reduced shear stress $\sigma^*$ vs. time for 50% AEC-4(□) and 51.5% AEC-2(Δ)

$R^2 = 0.9711$

$R^2 = 0.9908$
Figure 10. Complex modulus evolution of AEC solutions vs. time
Table 1. Chiroptical properties of lyotropic AEC/AA solutions with different degree of acetylation (DA)

<table>
<thead>
<tr>
<th>AEC Sample</th>
<th>Sample Description</th>
<th>Degree of Acetylation</th>
<th>Pitch*</th>
</tr>
</thead>
<tbody>
<tr>
<td>AEC-1</td>
<td>Low DA</td>
<td>0.13</td>
<td>- 360nm</td>
</tr>
<tr>
<td>AEC-2</td>
<td>Medium DA</td>
<td>0.34</td>
<td>- 7.4μ</td>
</tr>
<tr>
<td>AEC-3</td>
<td>AEC/EC Mixture</td>
<td>0.34</td>
<td>+ 1.2μ</td>
</tr>
<tr>
<td>AEC-4</td>
<td>High DA</td>
<td>0.50</td>
<td>+ 370nm</td>
</tr>
</tbody>
</table>

+: right-handed; -: left-handed
Table 2. Relaxation times as the function of chiroptical properties of lyotropic AEC/AA solutions

<table>
<thead>
<tr>
<th>Sample</th>
<th>46% AEC-1</th>
<th>51.5% AEC-2</th>
<th>48% AEC-3</th>
<th>50% AEC-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pitch</td>
<td>- 500nm</td>
<td>- 5.9μ</td>
<td>+ 1.3μ</td>
<td>+ 370nm</td>
</tr>
<tr>
<td>Relax. Time (sec)</td>
<td>14.5</td>
<td>28.4</td>
<td>16.7</td>
<td>14.9</td>
</tr>
</tbody>
</table>