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RHEOLOGY OF 1-BUYTL-3-METHYLIMIDAZOLIUM CHLORIDE CELLULOSE SOLUTIONS

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Joy Louise Watson
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Dedication

This thesis is dedicated to my parents, sister, brother-in-law, grandparents, Kathryn, and JoAnnice for their constant love and support, and for always believing in me. It is also dedicated to my many teachers who have helped me along the way.

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Abstract

Cellulose is the most common organic polymer on earth. It is a natural, biodegradable polymer that can be obtained from any number of renewable sources. Wood, a major source of cellulose, contains cellulose, lignin, and hemicelluloses. It can be used to make regenerated cellulosic fibers such as rayon whose manufacturing process involves chemicals which are toxic to humans and the environment. Ionic liquids (ILs) are a class of environmentally benign solvents some of which dissolve cellulose.

Cellulose can be dissolved in 1-butyl-3-methylimidazolium chloride ([C_4mim]Cl), an IL. Solutions of [C_4mim]Cl and cellulose with various concentrations were prepared and tested for their rheological characteristics. At high concentrations, low temperatures, and high angular velocities, the IL solutions of cellulose feature a viscoelastic character. Diluted solutions or concentrated ones at low angular velocities behave as viscous liquids.

IL/cellulosic solutions of different degrees of polymerization were prepared and tested for their rheological characteristics. The solutions with lower degrees of polymerization behaved as viscous liquids at all temperatures tested. The solutions with higher degrees of polymerization displayed viscoelastic properties at lower temperatures and the solution with the highest degree of polymerization showed viscoelastic properties at all temperatures tested.

Solutions were prepared manually and mechanically. Mechanically prepared solutions exhibited viscoelastic properties, but one of the manually prepared solutions did not. Limited amounts of lignin and xylose, a typical hemicellulose monomer, were added to some solutions to simulate the composition of wood pulp. These additives increased the complex viscosity of the solutions, and they displayed viscoelastic properties.

The activation energies for shear flow of different solutions were determined from the shift factors with respect to temperature and were higher than those for some polymeric melts. IL cellulose solutions have rheological characteristics similar to some melt blowing grade polypropylene melts or lyocell solutions of comparable concentration, suggesting feasible processing procedures, such as spinning or melt blowing, for the manufacture of fiber or nonwoven products.

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Nomenclature

A	area of the plate covered by material
a_T	Temperature shift factor
F	Force
f	frequency of oscillations
ΔE_a	activation energy of flow
G*	complex modulus
G'	storage modulus
G''	loss modulus
H	distance between two parallel plates
L	center line length of die
n	power-law index
ΔP	change in pressure
R	universal gas constant
T_o	reference temperature
t	Time
V	velocity
v_o	entrance velocity

δ	mechanical loss angle
δ	phase angle in radians
γ	shear strain
γ_o	strain amplitude
η'	viscous response
η^*	complex viscosity
η''	elastic response
η_o	zero shear rate viscosity
η_s	shear viscosity

λ	time constant
τ	shear stress
τ'	in phase or elastic component of stress
τ''	out of phase or viscous component of stress
τ_o	amplitude of shear stress
ω	Angular velocity
$\dot{\gamma}$	shear rate
η_r^*	reduced complex viscosity
ω_r	reduced angular velocity

$[C_4mim]Cl$	1-butyl-3-methylimidazolium chloride
IL	Ionic Liquid
NMMO	N-methylmorpholine-oxide
VOC	volatile organic compound

1. Introduction and Objectives

1.1 Introduction

Polymers make up many of today's industrial and consumer items, including plastics and textiles. Most polymers for manufactured products are considered non-renewable, because they are derived from petroleum [1]. With the increasing cost of crude oil and growing environmental concerns, there is interest in alternative "green" polymer feedstocks [2]. Polymers do not have to have a petroleum base. Cellulose is a natural, biodegradable polymer that can be obtained from any number of renewable sources. It is therefore gaining attention as new methods are discovered for processing it into products to replace those from non-renewable sources.

Cellulose is the most common organic polymer. It is renewable and considered an almost inexhaustible resource. It, along with lignin and hemicelluloses, are found in plants and trees. In order to separate the cellulose from the lignin and hemicelluloses, the pulping process is necessary, which involves energy and toxic materials such as concentrated sodium hydroxide. By-products of the pulping process are also considered hazardous to the environment and humans.

Cellulose is the main constituent in cotton [3], the most widely used natural fiber. Cotton fabrics are popular because of their comfort, aesthetics, and biodegradability. They do, however, have low wrinkle recovery and poor dimensional stability. Rayon, a regenerated cellulosic fiber found in many apparel and home furnishing items during the 20th century, has the same disadvantages. In addition, the manufacturing process for rayon involves chemicals that are toxic to humans and the environment. A new regenerated cellulosic fiber, lyocell, was developed and produced commercially in the 1980s. Lyocell fabrics exhibit the aesthetic qualities of rayon and add the comfort of cotton, but they are stronger, more wrinkle resistant, and are manufactured using an environmentally benign solvent, N-methylmorpholine oxide (NMMO).

Another class of environmentally benign solvents for cellulose is ionic liquids (ILs) [4]. ILs have a negligible vapor pressure thus eliminating the emission of volatile organic compounds (VOCs) into the atmosphere [5]. In addition ILs can be designed for a specific process, since there are potentially countless of different anion/cation combinations [6]. Recent studies have found that cellulose can be dissolved in various ILs [7] including 1-butyl-3-methylimidazolium chloride ([C_4mim]Cl) (Figure 1.1) [1]. It is speculated that the chloride ions break the extensive hydrogen bonding of cellulose, enabling dissolution even at relatively high cellulose concentrations [7].

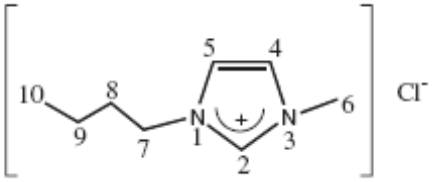


Figure 1.1: 1-Butyl-3-methylimidazolium Chloride [8]

In order to explore applications for these solutions, their rheological behavior must be determined under typical polymer processing conditions. The solvent-spun fiber lyocell is produced by the dry-jet wet spinning process [9], which should be amenable for IL/cellulose solutions as well. To determine their applicability and processability, the rheological behavior of these solutions should be first determined. In addition solutions with lignin and xylose added should have their rheological behavior characterized because these additives are found in wood, a major source of cellulose. If appropriate conditions are found, perhaps the pulping process could be modified or eliminated, making the polymer processing more environmentally benign.

1.2 Objectives

The objectives of this study were to:

1. Determine the effects of concentration and temperature on the rheological behavior of [C_4mim]Cl/cellulose solutions by measuring the:
    - Complex viscosity
    - Loss and storage moduli
    - Cross-over point of the loss and storage moduli
    - Shift factors for shifting with respect to temperature and concentration
2. Examine the effects of the degree of polymerization of cellulose on [C_4mim]Cl/cellulose solution rheology.
3. Examine the effects of preparation method on the [C_4mim]Cl/cellulose solutions (manual stirring vs. high shearing mixing).
4. Determine the effects of lignin and xylose additives on rheological behavior by measuring the:
    - Complex viscosity
    - Loss and storage moduli
    - Cross-over point of the loss and storage moduli

- Shifting factors for shifting with respect to temperature and concentration

2. Background and Literature Review

2.1 Cellulose

Cellulose has shaped human culture since the ancient Egyptians [3]. The structural unit of cellulose was determined to be $C_6H_{10}O_5$ by the French chemist Anselme Payen. He described cellulose as

> "Resistant fibrous solid that remains behind after treatment of various plant tissues with acids and ammonia, and after subsequent extraction with water, alcohol, and ether. "[3]

Cellulose is a linear chain, carbohydrate polymer as seen in Figure 2.1 [3]. It is insoluble in water or dilute alkali and acids at room temperature [10].

Cellulose is the most abundant organic polymer and is considered an almost endless source of raw material. It is derived from the processing of wood pulp [3], and is also found in other natural sources as well. Within wood pulp, lignin and hemicelluloses are also present. Lignin gives trees and other woody plants their stiffness, allowing them to withstand wind and gravity. It is an aromatic cross-linked polymer containing phenylpropane structural units and bound to the other components of wood. Hemicelluloses are comprised of five different sugars: glucose, mannose, galactose, xylose, and arabinose [11]. Cellulose, lignin, and hemicelluloses interact with each other thus interfering with processing [12]. Lignin and xylose will be added to the IL/cellulose solutions in this study to simulate the composition of wood.

2.2 Cellulose and Spinning Solutions

Natural cellulose from plants has been used in various textiles for thousands of years, although the regeneration of cellulose in fiber form is a fairly recent development. It was first suggested in 1664 by Robert Hooke, who mused that an artificial alternative to silk could be created from cellulose. This was finally accomplished by Count Hilaire de Chardonnet, who nitrated cellulose, dissolved it in alcohol, and extruded the solution into

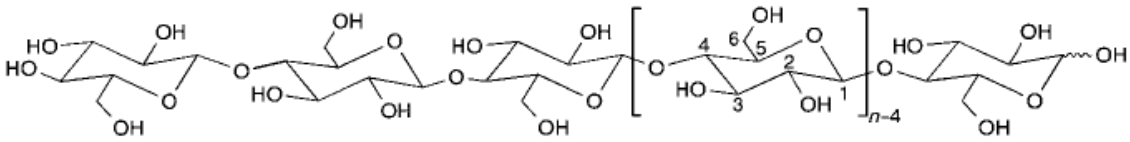


Figure 2.1: Molecular structure of cellulose [3]

water to regenerate the cellulose into fibers. The first patent for this nitrocellulose method was granted in 1884 [13]. The fibers were smooth and silk-like, but had the severe disadvantage of also being explosive and highly flammable [14].

In 1857 Schweizer was able to dissolve cellulose in a solution of copper oxide and ammonia. In 1890 Despeissis patented the process to make artificial silk fibers from this solution. Fibers produced by this method later named cuprammonium rayon, are still produced today in several countries for use in high end satins, linings, and sheer fabrics [13]. Production was discontinued in the United States some time ago because the copper is released into the effluent during the regeneration step, causing environmental concerns.

Viscose, a xanthate derivative of cellulose, was first discovered in 1892 by Cross, Bevan, and Beadle while trying to determine the chemical structure of cotton cellulose [15]. The alkaline-treated cotton cellulose was exposed to carbon disulfide (CS_2) which produced sodium cellulose xanthate. Water was then added to the compound, swelling the structure and eventually dissolving the cellulose. Purification, redissolving, and treatment of the solution with various acids, acid salts, sulfites or metallic oxides yielded regenerated cellulose which they called "viscous cellulose". At the time the regeneration of cellulose was known as a "dissociation" of the compound into cellulose, CS_2, and sodium hydroxide (NaOH). Cross, Bevan, and Beadle recognized the potential of their regenerated cellulose in the production of films, fibers, casts, molds and other products in which nitrocellulose was being used [15].

The first commercial interest in viscose fibers was for the filaments in light bulbs, a development pursued at the Incandescent Lamp Works in Zurich by C.H. Stearn and C.F. Topham. The potential for viscose as a textile fiber was recognized and a Viscose Spinning Syndicate was established. Through further research Topham developed a device that "enabled the simultaneous collection and twisting of fibers into a yarn." [16].

In 1904 Courtaulds acquired the British patent rights and in 1909 the United States patent rights to the viscose process. Courtaulds quickly became the largest and strongest firm to own the viscose patent rights. In these early commercial processes, sulfite wood pulp was the most commonly used raw material. Other cellulose forms were used by some firms in the United States but the products were inferior. The initial production process involved placing pasteboard sheets of cellulose in steeping baths with alkali or in disintegrating machines that broke up cellulosic material sprayed with alkaline liquor. In time the process was changed so that the pasteboard sheets were placed vertically in separated perforated iron plates.

Currently viscose fibers are produced by first soaking the cellulose sheets in 18% NaOH to open the polymer structure. Carbon disulfide is added to form cellulose xanthate which is then aged for a specified time and temperature to effect the controlled depolymerization of the cellulose. The shorter cellulose chains then enable the polymer

to be dissolved in NaOH, forming the viscose spinning solution. This solution is extruded into sulfuric acid in a wet spinning process to regenerate the cellulose fibers.

Rayon fibers were lustrous, smooth, and had a silk-like appearance which appealed to the consumer. However, they exhibited extensive swelling in water and had high shrinkage (even greater than cotton) and a strength which was half that of silk. [16]. Today, viscose accounts for most of the world's rayon production [14], but sulfur compounds are a by-product of the process which is known to cause environmental problems if they are not disposed of properly [16].

Cellulose acetate was first produced in 1865 by heating cotton in a closed tube with acetic anhydride to temperatures of 130°-140°C until it dissolved. The product would precipitate out when water was added to the solution. This precipitate was then washed, neutralized, and dried to form a white, amorphous powder soluble in alcohol and acetic acid [17]. Acetate was initially used for lacquers and plastic film. The first fibers were produced in 1921. Acetate is often used as linings in apparel such as suits and in non-apparel items like curtains. The largest use today is cigarette filters. One drawback of acetate is that it has low strength and abrasion resistance when compared to other manufactured fibers [17].

The lyocell process was developed in the 1980s. Lyocell solutions are cellulose dissolved in NMMO. The solution is extruded into water or a water/NMMO mixture, regenerating cellulose fibers. The fibers have a smooth cross section unlike viscose rayon fibers, which have a crenulated cross-section. Lyocell is therefore more similar to cotton in many of its characteristics [18]. Lyocell also has better strength and wrinkle resistance than other rayons. Byproducts of the lyocell process though may cause problems such as discoloration of resulting fibers, degradation of cellulose, accelerated decomposition and therefore increased consumption of NMMO and its stabilizers [19, 20].

Ionic Liquids (ILs) such as [C_4mim]Cl are gaining attention because they have the ability to dissolve cellulose and have properties that lend themselves to green engineering. Like the lyocell solvent they are non-volatile, as well as being chemically and thermally stable [7] though it is undetermined whether ILs or lyocell are more thermally stable. Solutions of [C_4mim]Cl and cellulose, like lyocell solutions, can be extruded in a dry-jet, wet-spinning processes using water to regenerate the cellulose. Experimentally produced cellulose fibers had minimal polymer degradation, a tenacity of 2.0-4.4 g/denier and breaking elongations between 4-20% [1]. Fiber properties are dependent on the spinning conditions which are yet to be optimized [1]. In order to optimize the extrusion of the [C_4mim]Cl/cellulose solutions, the shear dynamic rheology must first be determined.

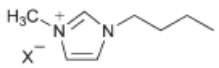
2.3 Ionic Liquids

The first ionic liquid (IL) was discovered in the mid-nineteenth century. Many early ILs were viscous oils or unwanted by-products. ILs were first used primarily as electrolytes in batteries and in electroplating metals, but today they have a wide range of applications from catalytic reactions, to electrolytes, to polymer chemistry. The first fluid-, air-, and water-stable ILs were prepared and characterized in the early 1990s [21]. Solvent characteristics are dependent on the particular IL, which can be selected for the desired properties of hydrophobicity, hydrophilicity, viscosity, conductivity, or electrochemistry.

One of the advantages of ILs is their classification as green solvents because their partial vapor pressure is negligible, which almost eliminates volatile emissions [22]. ILs are also non-flammable which is important for exothermic reactions. These two properties make them attractive when addressing health, safety, and environmental concerns. Separation techniques, like distillation or sublimation, which were not possible with low-boiling traditional solvents, can be used with these compounds [6].

ILs not only have advantages but also some disadvantages. They must be designed to be environmentally benign [5]. Most ILs are water soluble, and even though they do not pollute the air, they could enter the environment if a water spill was to occur. Garcia et al. evaluated ILs listed in Figure 2.2 and found that most were not biodegradable [23]. The closed bottle test was used in which an IL was added to an aqueous medium with aerobic waste-water microorganisms present. The depletion of dissolved oxygen was measured over time and reported as a theoretical maximum. [C_4min]Cl showed less than 5% biodegradation after a period of 28 days. The exception was 1-butyl-3-methylimidazolium octylsulfate which was 25% biodegraded after 28 days using the closed bottle test [23]. The lack of biodegradability leads to concern about build up of the ILs in the environment from industrial effluent. Also an acute toxicity test on freshwater crustaceans showed immobilization which means ILs have the potential to be harmful to other forms of aquatic life [23].

Despite the numerous disadvantages of ILs, they are a greener alternative to the traditional dissolution systems for cellulose which can involve NaOH, CS_2, sulfuric acid, and copper which are more toxic. The specific IL in this study, are ([C_4mim]Cl), is formed by the reaction of 1-methylimidazole (MIM) and 1-chlorobutane (Cl-Bu) (Figure 2.3). The synthesis typically uses excess Cl-Bu in a ratio of 1.4 mol per mol MIM in a batch reactor [24]. The focus of this research on ILs is the rheological behavior of C_4min]Cl/cellulose solutions.



3a X = Br
3b X = BF_4
3c X = PF_6
3d X = NTf_2
3e X = $N(CN)_2$
3f X = $C_8H_{17}OSO_3$

Figure 2.2: Some ILs with biodegradation tests information available [23]

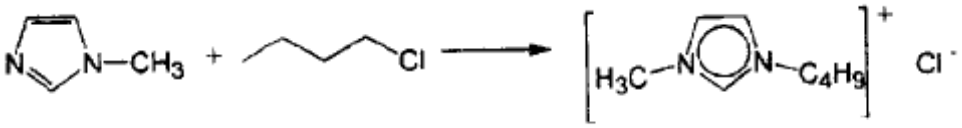


Figure 2.3: Synthesis of [C_4mim]Cl [24]

The dissolution of cellulose in an IL (N-ethylpyridinium chloride) was demonstrated by Graenacher in 1934 [7, 25]. Recent studies have shown that ILs can dissolve silk [26], wool [27], and carbohydrates [28]. Various ILs can dissolve cellulose with the highest concentration of cellulose being dissolved in [C_4min]Cl [7]. It is theorized that the cellulose is dissolved in [C_4min]Cl when hydrogen bonding occurs between the hydroxyl protons of the cellulose and the chloride ions of the IL. Similar interactions occur between the hydroxyl protons of the glucose and the chloride ion of [C_4mim]Cl [29]. Water concentrations greater than 1 wt% significantly impair the solubility of cellulose. Ethanol and acetone have the same effect as water on the solution. The dissolved cellulose can be regenerated by immersing in water [7].

2.4 Rheology

Rheology is the science of deformation and flow of materials, which include solids, liquids, or gases, under the influence of stresses [30]. It influences how materials are processed and is a clue to the molecular structure. This study concentrates on the dynamic shear rheology of [C_4mim]Cl/cellulose solutions, including the viscosity and loss and storage moduli. From this information the activation energy of flow can be determined.

2.4.1 Shear Rheology

Viscosity is the resistance to flow and is defined as the ratio of shear stress to the shear rate as seen in Equation 1. For a parallel plate rheometer, shear stress, τ, is the force, *F*, that is applied to the plate and divided by the area of the plate, *A*. The shear rate, $\dot{\gamma}$, is the velocity, *V*, divided by the gap between the plates, *h*.

$$\eta = \frac{shear\ stress}{shear\ rate} = \frac{F/A}{V/h} = \frac{\tau}{\dot{\gamma}} \tag{1}$$

By imposing a sinusoidal stress or strain on a rotational rheometer the dynamic properties can be determined. Dynamic properties are influenced by polymer molecular characteristics, temperature, frequency, stress and strain [30]. The known sinusoidal external conditions imposed on the sample are amplitude, frequency, and the fluid's response to these conditions. A perfectly elastic material, under sinusoidal stress, will develop stresses in-phase with the imposed strain. However, a Newtonian fluid subjected to the same sinusoidal strain will not be in-phase, but the stress and strain instead will exhibit a π/2 radian difference due to the time derivative, strain rate, involved [31]. The sinusoidal oscillation technique can be seen in Figure 2.4. A dynamic rotational rheometer measures shear strain (γ) and shear stress (τ) which are defined in Equations 2 and 3.

$$\gamma = \gamma_o \sin \omega t \tag{2}$$

$$\tau = \tau_0 \sin(\omega t + \delta) \tag{3}$$

Where

γ_o = amplitude of the shear strain
τ_o = amplitude of the shear stress
ω = angular velocity in radians/sec
δ = phase angle in radians
t = time in seconds

The complex stress wave can be decomposed in two waves, τ' and τ", which are defined in Figure 2.4.

$$\tau = \tau' + \tau'' = \tau_0' \sin \omega t + \tau_0'' \cos \omega t \tag{4}$$

The decomposition suggests an elastic or storage modulus (G') and a viscous or loss modulus (G") as defined in Equations 5 and 6 where ω is angular velocity in radians and f is the frequency of oscillations in reciprocal seconds.

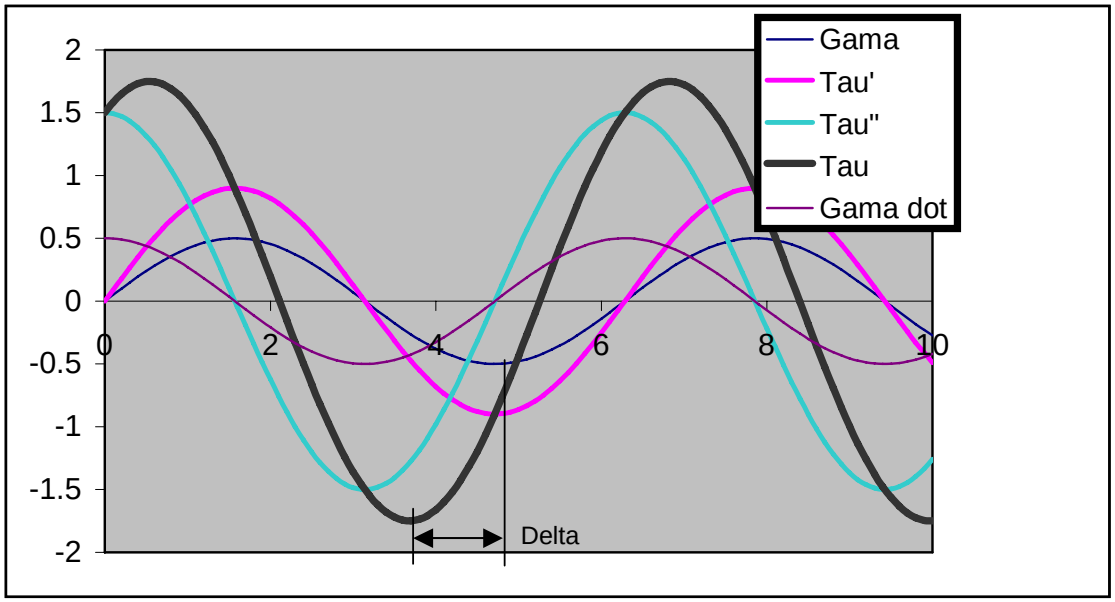


Figure 2.4: Sinusoidal oscillations technique. The stress is shifted by a phase angle delta; τ' is the component in-phase strain rate or elastic component of the stress; τ" is the out-of-phase (π/2) or viscous component of the stress; τ" is in-phase with the rate of strain wave. The shear rate is represented by $\dot{\gamma}$, and the shear strain is represented by γ.

$$G' = \frac{\tau_0'}{\gamma_0} = \eta'' \omega \tag{5}$$

$$G'' = \frac{\tau_0''}{\dot{\gamma}_0} = \eta' \omega \tag{6}$$

The complex viscosity has two components, η' defined as the viscous response, and η" defined as the elastic response. These components are discussed further in Equation 11. The angular frequency (angular velocity), ω, is defined as

$$\omega = 2\pi f \tag{7}$$

Materials exhibiting purely viscous deformation do not return to their original positions once the force is removed. A fluid is viscous when the complex viscosity is equal to the viscous response, $\eta^* = \eta'$, and the elastic response is equal to zero, $\eta''=0$. In this case the loss modulus is equal to the complex modulus, $G^*=G''$, and the storage modulus is equal to zero, $G'=0$. A fluid is purely elastic when the complex viscosity is equal to the elastic response, $\eta^* = \eta''$, and the viscous response is equal to zero, $\eta'=0$. In this case the storage modulus, defined in Equation 8 is equal to the complex modulus, $G^*=G'$, and the loss modulus is equal to zero, $G''=0$. An elastic deformation is no permanent deformation occurs once the force causing the initial deformation is removed.

$$G^* = G' + iG'' \tag{8}$$

Most non-Newtonian fluids, including polymer melts and concentrated solutions, have a combination of elastic and viscous flows, otherwise known as viscoelastic properties. In the viscoelastic region the point where the loss and storage moduli are equal ($G'=G''$) is the reciprocal of the average relaxation time for the material [32]. The relaxation time is the time it takes for the material with imposed orientation to return to a defined portion of its previous state.

The viscoelastic region of a material is that in which the phase angle and loss and storage moduli are independent of amplitudes of the specific strain in harmonic oscillations [33] [34]. The linear algebra for this phenomenon can be seen in Equations 9 and 10 for two independent parameters, x and y, z is the complex parameter and not a coordinate direction.

$$|z| = |x + iy| \equiv \sqrt{x^2 + y^2} \tag{9}$$

$$|G^*| \equiv \sqrt{G'^2 + G''^2} \tag{10}$$

Complex viscosity can also be defined by two vector components as seen in Equation 11. It is considered a linear viscoelastic property [30] [33].

$$\eta^* = \sqrt{(\eta')^2 + (\eta'')^2} = \sqrt{\left(\frac{G''}{\omega}\right)^2 + \left(\frac{G'}{\omega}\right)^2} \quad = \frac{|G^*|}{\omega} \tag{11}$$

Shear thinning is a common type of non-Newtonian behavior. It occurs when the viscosity decreases as the shear rate increases. The opposite behavior, when the viscosity increases with the shear rate, is shear thickening. The empirical power law constitutive equation demonstrates the dependence of viscosity on the shear rate, as seen in Equation 12.

$$\eta = k\dot{\gamma}^{n-1} \tag{12}$$

The symbol *n* is the power law index where n>1 implies shear thickening behavior, n=1 for a Newtonian flow, and n<1 implies shear thinning behavior [30].

Along with the shear rheology, the elongational rheology is also important in determining the characteristics of a material. It is especially important in processing operations where a rapid change in shape occurs in fiber spinning or bubble blowing processes [35]. The elongational rheology can be measured in a capillary rheometer when the capillary die is replaced by a hyperbolically convergent die [36, 37]. Pressure is applied to the material by a piston or ram which forces the material through a die from which the shear stress in the capillary is determined. The change in pressure between the entrance and exit area of the die allows the elongational viscosity to be calculated.

2.4.2 Types of Rheometers

The rheology of materials can be measured by many different methods including capillary, parallel plate, and cone and plate rheometers [30]. Shear deformation is the basis for most rheometers. They measure a force, pressure drop or torque which can determine the shear stress. An example of simple shear is the deformation that occurs when material is placed between two flat parallel plates. One plate is translated a distance of ΔU while the distance between the two plates remains constant (h). The measure of deformation generated is the shear strain (Figure 2.5).

A capillary rheometer is typically used for determining the viscosities of materials at the high shear rates commonly used in polymer processing. Parallel plate along with cone and plate rheometers are limited to lower shear rates and are often used when materials are strain sensitive where the material is in phase separated blends or liquid crystals [38]. The parallel plate method of determining viscosity is used when a small quantity of material is available or for materials that are adversely affected by a severe contraction at the inlet of the capillary flow [38]. Parallel plate rheometers (Figure 2.6) can be used in either a steady shear or oscillatory shear mode. In both modes one of the plates is driven while the gap between the plates remains constant. In steady shear mode the driven plate rotates at a predetermined rotational velocity whereas in the oscillatory or dynamic mode the plate is driven at a controlled frequency for a small strain. From the dynamic shear measurements the torque, shear viscosity, loss modulus, and storage modulus can be calculated. Cone and plate rheometers eliminate the problem of radial dependence of the shear rate and shear strain in torsional parallel disk rheometers, but it is difficult to load highly viscous samples [38].

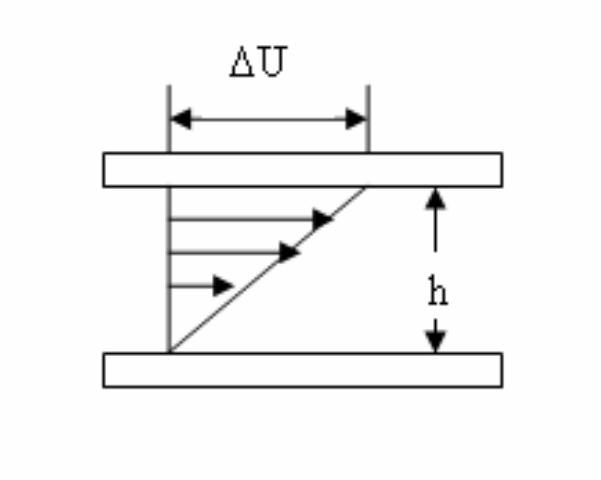


Figure 2.5 Deformation of shear flow

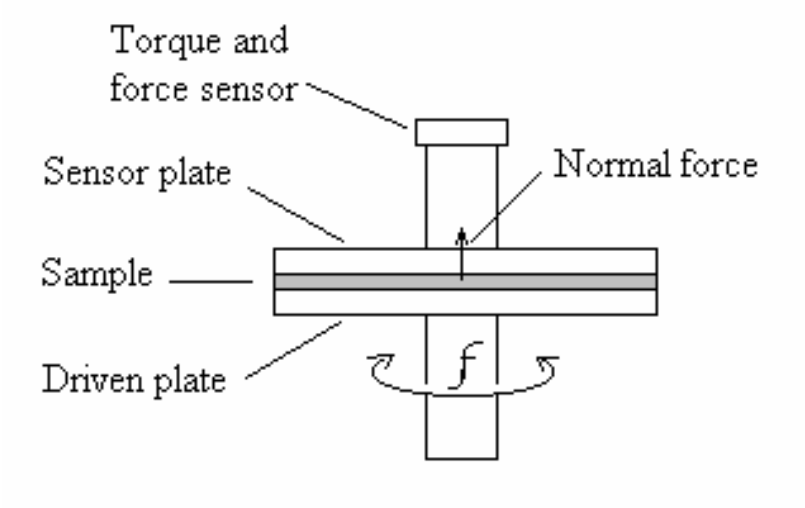


Figure 2.6: Parallel plate rheometer

2.5 Rheology of Polymeric Melts and Solutions

Temperature and molecular weight are two important factors in determining the rheology of a polymer. Characterizing the rheology of polymers is necessary in order to optimize the production process, and to determine what type of processing may be suitable for new polymeric solutions as they are discovered.

At sufficiently low temperatures, polymers are hard glassy materials and become flexible materials and even a viscous liquid at sufficiently high temperatures. During transition between a hard glass-like material to a viscous liquid the polymer becomes a rubbery material. The temperature at which the material changes from a hard glass material to a rubbery material is called the glass transition temperature. At temperatures below the glass transition temperature the polymer molecules can only move in the vibrational motion of the atoms or in short cooperative motion. At temperatures immediately above the glass transition temperature, molecules are able to uncoil; therefore, recoverable deformation can occur. At these temperature though the molecules do not easily flow. At higher temperatures polymers become a viscous liquid [39]. The temperature of a polymer must be controlled so that the polymer flows easily, but does not waste excess energy or degrade.

To quantify the effect of temperature, shear viscosity curves are obtained at different temperatures. The shear viscosity curves can then be shifted using calculated shift factors to a reference temperature curve which produces a master curve [40]. The activation energy for flow can be determined from the shift factors. Equation 13 defines the shift factors

$$a_T = \frac{\eta_0(T)T_0}{\eta_0(T_0)T} \tag{13}$$

where $\eta_0(T)$ and $\eta_0(T_0)$ are zero-shear-rate viscosities of the polymer melt or concentrated solution at temperature T and reference temperature T_0. The shift factor (a_T) is the ratio of relaxation time at two different temperatures [41]. The relaxation time is the reciprocal of the loss and storage moduli cross-over point with respect to the shear rheology. As the temperature of the polymer increases the cross-over point shifts to a higher angular frequency, and the shift factor will decrease with the increasing temperature.

Master curves are created by plotting the reduced complex viscosity, η_r^*, vs. reduced angular velocity, ω_r. The reduced variables are calculated using Equations 14 and 15 [42].

$$\eta_r^* = \eta^*(\omega,T)\frac{\eta_0(T_0)}{\eta_0(T)} = \eta^*(\omega,T)\frac{T_0}{a_T T} \tag{14}$$

$$\omega_r = \omega a_T \tag{15}$$

By fitting the experimental data to the Carreau model, a four parameter model with a continuous first derivative, given in Equation 16, the zero-shear rate viscosities of polymer melts and concentrated solutions at various concentrations and temperatures, can be determined where λ is a time constant and n is the power-law exponent [42].

$$\eta = \eta_0 \left[1 + (\lambda\dot{\gamma})^2\right]^{(n-1)/2} \tag{16}$$

An alternative to the Carreau model is the Cross model presented in Equation 17.

$$\eta = \frac{\eta_o}{1 + (\lambda\dot{\gamma})^{1-n}} \tag{17}$$

The difference between the Carreau model and the Cross model is that generally the Carreau model under predicts the viscosity while the Cross model over predicts the viscosity [43]. The temperature dependence of a_T is often found to be an Arrhenius dependence of the following form

$$a_T = \exp\left[\frac{\Delta E_a}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \tag{18}$$

where ΔE_a is the activation energy of flow and R is the gas law constant [38].

The degree of polymerization is another factor that influences viscosity. Polymers are made up of repeating units and the number of units within the polymer is its degree of polymerization (DP). If the polymer's viscosity is a function of temperature its viscosity can be calculated from the structure of the repeat unit and its DP as seen in Equation 19 [39]. At the same temperature, polymers of lower molecular weights will have a lower viscosity assuming that their repeat units are similar. The lower the molecular weight and viscosity the easier it is to shape the polymer, but it also has poorer service properties; therefore, a balance must be obtained between the service properties and the ease of processing [44].

$$\eta_o = K M_W^{3.4} \tag{19}$$

3. Materials and Methods

3.1 Materials

The IL ([C_4min]Cl) was purchased from Fluka Chemie. Three cellulose dissolving pulps, with DPs of 670, 1720, and 3900, were provided by Buckeye Technologies, Memphis, TN. The organosolv lignin was purchased from the Aldrich group. The xylose and propylgallate were purchased from ACROS Organics.

3.2 Solution Preparation

3.2.1 Manual Preparation

Cellulose/[C_4mim]Cl solutions were prepared by heating the IL, which is a solid at room temperature, to 90°C to obtain the liquid form. The dissolving pulp, propylgallate (1 wt% versus dried dissolving pulp), and additives, if any, were then added. The solution was stirred until it formed fine filaments when the stirrer was extracted (i.e. the viscoelastic properties were evident). The propylgallate is added to increase the thermal stability of the solution [20]. If the solution became too cool, and therefore difficult to stir before fine filaments were seen, the solution was placed in an oven at 90°C for 5-10 minutes and then stirred again. The heating and stirring continued until the filaments could be observed. After the filaments became visible, the sample bottles were capped loosely and allowed to cool to room temperature. Once they reached room temperature the sample bottles were capped tightly and stored at room temperature for one week prior to testing.

3.2.2 Mechanical Preparation

Cellulose/[C_4mim]Cl solutions were prepared by heating a portion of the IL in a C. W. Brabender Type-6 mixer (C. W. Brabender Instruments, Inc.) to 90°-100°C while stirring at 50-60 rpm. The cellulose and propylgallate (1 wt% versus dried dissolving pulp) were then added before the IL was fully dissolved to prevent the IL from leaking out of the Brabender. The remaining IL and cellulose were added slowly in order to prevent the cellulose from forming clumps. The solution continued to mix until it formed fine filaments (i.e., the viscoelastic properties were evident). The sample was then removed from the Brabender and placed in a clean capped container. The sample bottles were then stored at room temperature for one week prior to testing.

3.3 Solution Concentrations

Dissolving pulp of 670 DP was used to manually prepare solutions of 3, 7, 10, 12, and 15 wt% of cellulose in [C_4mim]Cl. A 3 wt% solution was also prepared with dissolving pulps of 1720 DP and 3900 DP. Additionally, solutions of DP 670 10 wt% and the DP 3900 3 wt% were prepared by the mechanical method described in Section 3.2.2. A summary of the make-up of the solutions and preparation method is given in Table 1.

3.4 Rheological Measurements

3.4.1 Equipment

Testing was performed on the Advanced Rheometric Expansion System (ARES) by TA Instruments, a parallel plate rheometer. The ARES subjects a sample to either a dynamic or steady shear strain deformation and measures the resultant torque experienced by the sample. A motor applies the shear strain while the torque is measured by the transducer.

The properties were probed over the selected strain rate range of 0.1 to 100 s^{-1}. All measurements were taken with parallel plates that were 2.5 cm diameter and 1.0 mm apart. During testing the samples were enclosed in a convection oven in order to maintain the temperature of the samples at 80, 90, 100, 110°C.

3.4.2 Shear Measurements

The linear viscoelastic region was first determined on the ARES. The region is where the shear stress, viscosity, and shear moduli of a polymeric solution or melt is only a function of the shear rate independent of time [34]. A strain of 0.1 was determined to be within the linear viscoelastic region (Figure 3.1). The sample and spatula were heated in an oven for 30 minutes before placing the solution on the parallel plates. Before the dynamic frequency test was initiated, a thin layer of viscosity standard silicon oil (20034 mPa-s at 25°C) was placed on the edges of the specimen sandwiched between the plates. The sample remained between the parallel plates for five minutes before the dynamic frequency test was initiated. Data on the frequency, dynamic viscosity, moduli, and strain were obtained and saved electronically. Multiple tests and samples were run for Objective One. Tests were not repeated for Objectives Two, Three or Four.

3.5 Shift Factors

The effect of temperature on the shear viscosity of any fluid can be better quantified by shifting the viscosity curves at different temperatures on a reference temperature

Table 1: Summary of solutions prepared

	Concentration				Degree of Polymerization	Preparation Method
	Total Additives	Cellulose	Lignin	Xylose		
Objective One	3	3	0	0	670	Manual
	7	7	0	0	670	Manual
	10	10	0	0	670	Manual
	12	12	0	0	670	Manual
	15	15	0	0	670	Manual
Objective Two	3	3	0	0	670	Manual
	3	3	0	0	1720	Manual
	3	3	0	0	3900	Manual
Objective Three	3	3	0	0	3900	Manual
	3	3	0	0	3900	Mechanical
	10	10	0	0	670	Manual
	10	10	0	0	670	Mechanical
Objective Four	10	10	0	0	670	Manual
	10	9	1	0	670	Manual
	10	9	0	1	670	Manual
	10	8	2	0	670	Manual
	10	8	0	2	670	Manual
	10	8	1	1	670	Manual
	15	14	1	0	670	Manual
	15	14	0	1	670	Manual

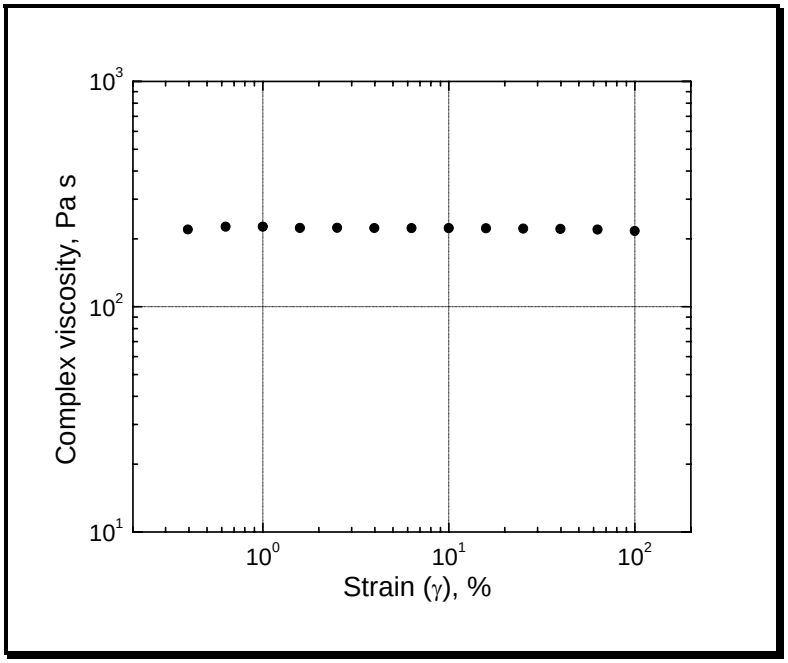


Figure 3.1: Dyamic strain sweep (10 wt% DP 670 cellulose)

viscosity curve to generate master curves and shift factors, from which activation energy for flow can be calculated.

The method of reduced variables [40] was used to develop master curves by plotting the reduced complex viscosity η_r^* vs. reduced angular velocity ω_r. The shift factors were then defined (Equation 13, page 13) so that the reduced variables could be calculated (Equation 14). The experimental data were then fitted to the Carreau Model, and the activation energy of flow (ΔE_a) was calculated using the equations discussed in the Rheology section of Chapter 2.

4. Results and Discussion

4.1 Objective One

To determine the effects of concentration and temperature on the rheological behavior of [C4mim]Cl/cellulose solutions

Viscosity curves for concentrations of 3, 7, 10, 12, and 15 wt% cellulose at various temperatures are shown in Figures 4.1-4.5. Multiple runs were performed to check the experimental errors; error bars are shown in Figure 4.5 for viscosity curves of 15 wt% solutions. For the 3 wt% solution, only curves at 80° and 90 °C are shown, the results at higher temperatures being below the lower limit of the torque range (0.02 g cm). The same was true for 7 wt% solution at 110 °C. It should be noted that the viscosity curves of the 7 wt% solution at 100°C were different from the curves at 80° and 90°C (Figure 4.2). Perhaps this was due to a change in the character of the solution that is dependent on the temperature, concentration, and DP. The viscosity curves showed shear thinning behavior at all temperatures and concentrations. Increasing the testing temperature decreased the viscosity. A quasi-Newtonian behavior was evident, mainly at low angular velocities and lower temperatures.

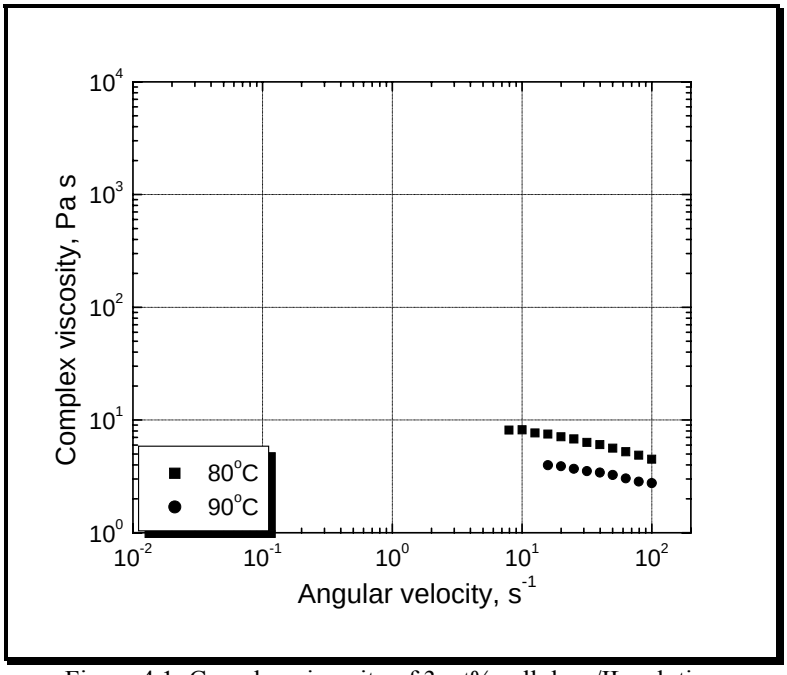


Figure 4.1: Complex viscosity of 3 wt% cellulose/IL solution

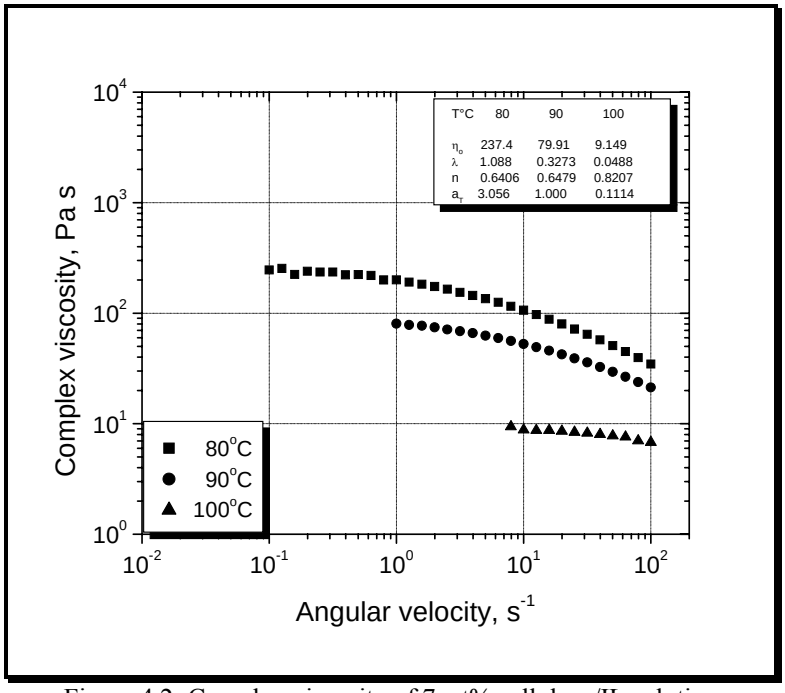


Figure 4.2: Complex viscosity of 7 wt% cellulose/IL solution

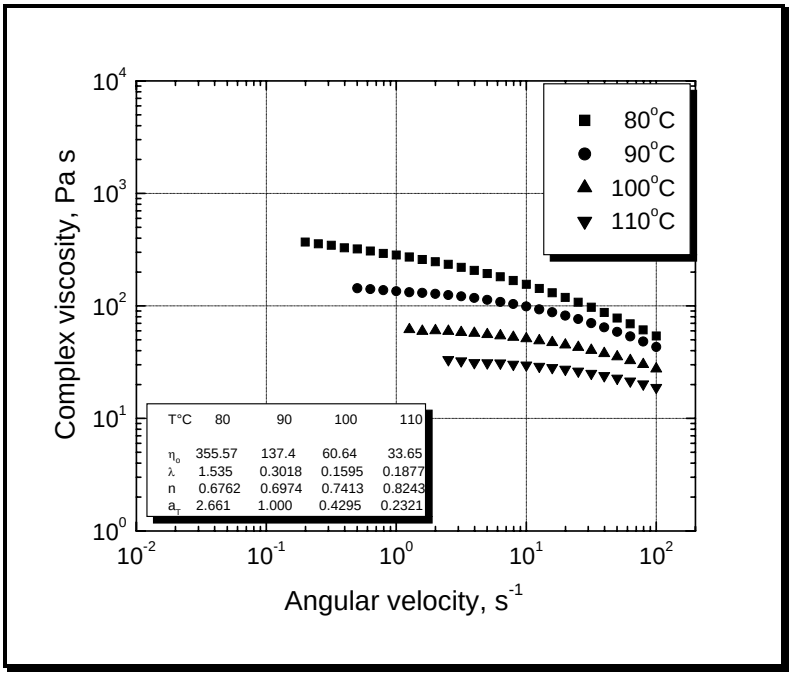


Figure 4.3: Complex viscosity of 10 wt% cellulose/IL solution

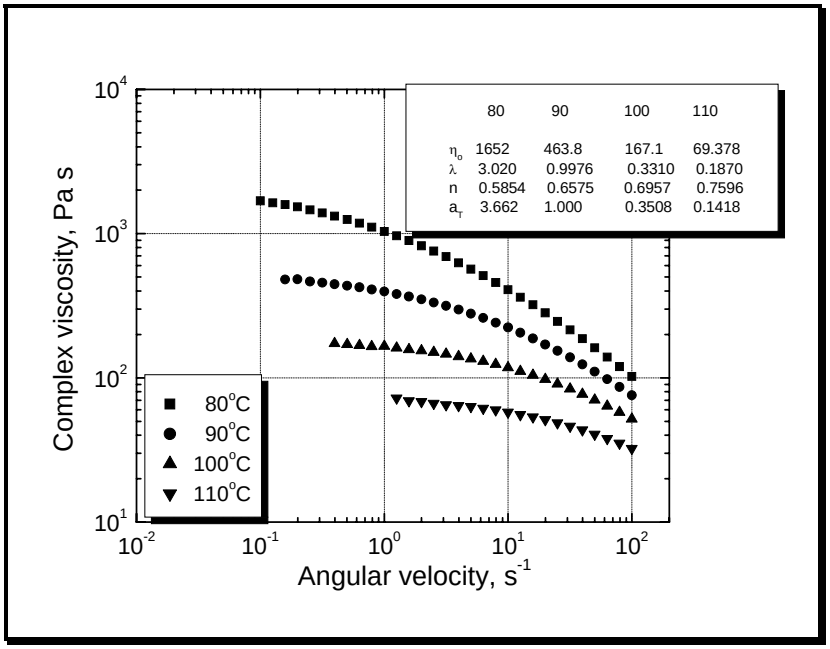


Figure 4.4: Complex viscosity of 12 wt% cellulose/IL solution

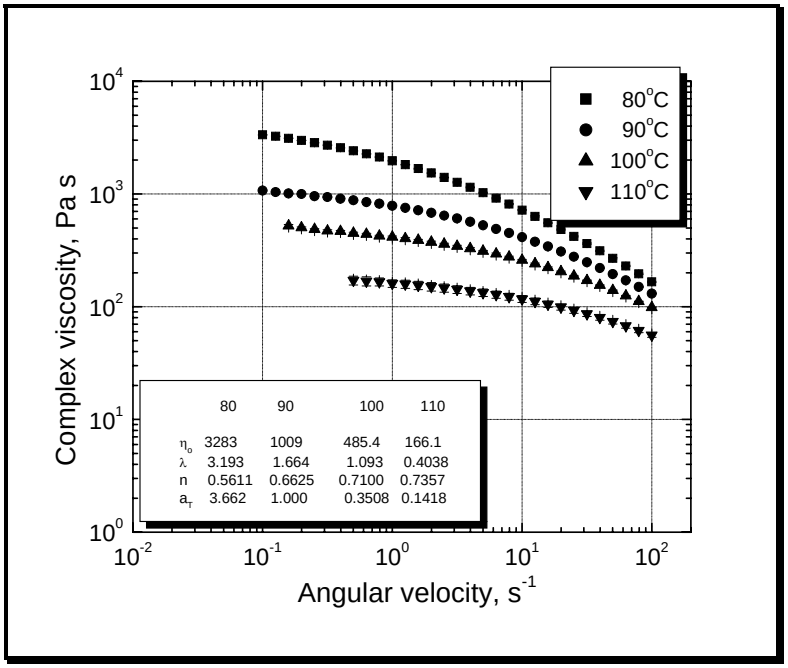


Figure 4.5: Complex viscosity of 15 wt% cellulose/IL solution

The complex viscosities of the IL solutions at 90°C were compared with those of three melt blowing grade polypropylenes (PPs) and a lyocell solution prepared from the same dissolving pulp (Figure 4.6). The viscosities of the ILs solutions were comparable to those of melt blowing grade PPs and lyocell solution throughout the range of angular velocities. This would suggest that IL solutions of cellulose could be processed by both spinning and melt or solution blowing, for manufacturing fibers or nonwoven products.

Viscoelastic properties of the IL solutions are displayed in Figures 4.7-4.12, where dynamic moduli are plotted against angular velocity. Both concentration and temperature are important parameters for a solution's viscoelasticity. At lower concentrations (3, 7 and 10 wt% at high temperatures), solutions behaved as viscous liquids; i.e. the loss modulus (G") was higher than the storage modulus (G'). At higher concentrations (Figures 4.10-4.12) and high deformation rates, the IL solutions behaved as viscoelastic liquids, with the loss and storage modulus curves crossing. The cross-over point shifted to lower angular velocities, extending the viscoelastic domain, as the concentration increased.

Temperature showed a different effect on the viscoelastic properties of IL solutions (Figures 4.11-4.14). At lower temperatures and low angular velocities the solutions behaved as viscous liquids, whereas at high angular velocities there was a viscoelastic domain. At 110°C the 15% solution exhibited properties of a viscous liquid over the entire range of angular velocities, (Figure 4.14). The reciprocal of the cross-over point angular velocity has units of time and is an indication of the relaxation time of the macromolecular chains from the solution, which is an important parameter for fiber forming.

The Carreau parameters are given for 7, 10, 12, 15 wt% solutions in Figures 4.2-4.5. The master curve for the complex viscosity of 15 wt% cellulose/IL solution is given in Figure 4.15. The coefficient of determination ($R^2 = 0.9938$) showed that the shifting procedure was very accurate. The temperature dependence of a_T was often found to be an Arrhenius dependence as seen in Figure 4.16. Similar master curves were generated for other solutions and activation energies, calculated from the Arrhenius plots, are presented in Table 2. As noted previously the viscosity curve of the 7 wt% solution at 100°C had a different behavior than curves of the same solution at lower concentrations which could affect the activation energy for flow; thus the activation energy was calculated with and without this curve. As indicated in Table 2 the activation energy for 7 wt% solution was affected by the viscosity curve at 100°C. These activation energies for flow of IL/DP 670 cellulose solutions are higher than those of some corresponding values of common industrial polymer melts shown in Table 3 [39].

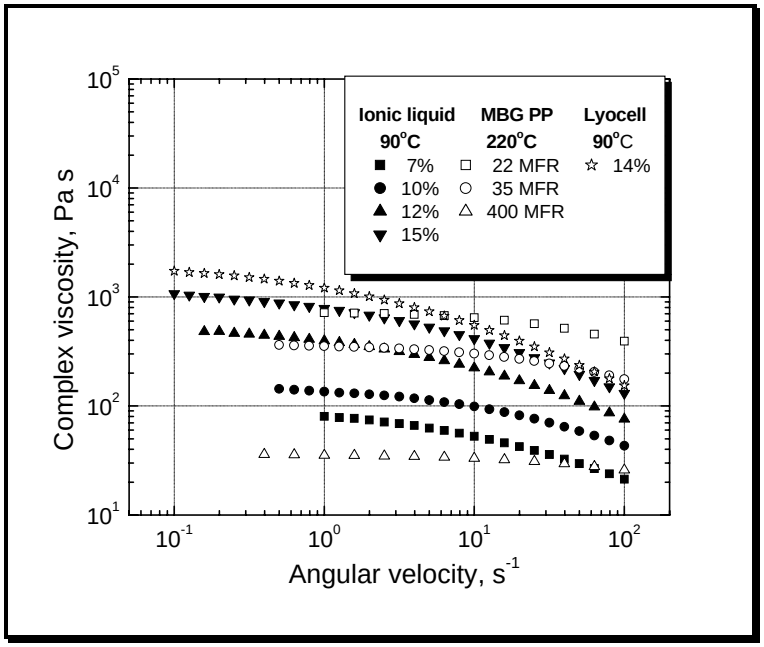


Figure 4.6: Complex viscosity of IL/cellulose solutions, melt blowing grades (MBG) of propropylene (PP) and a lyocell solution.

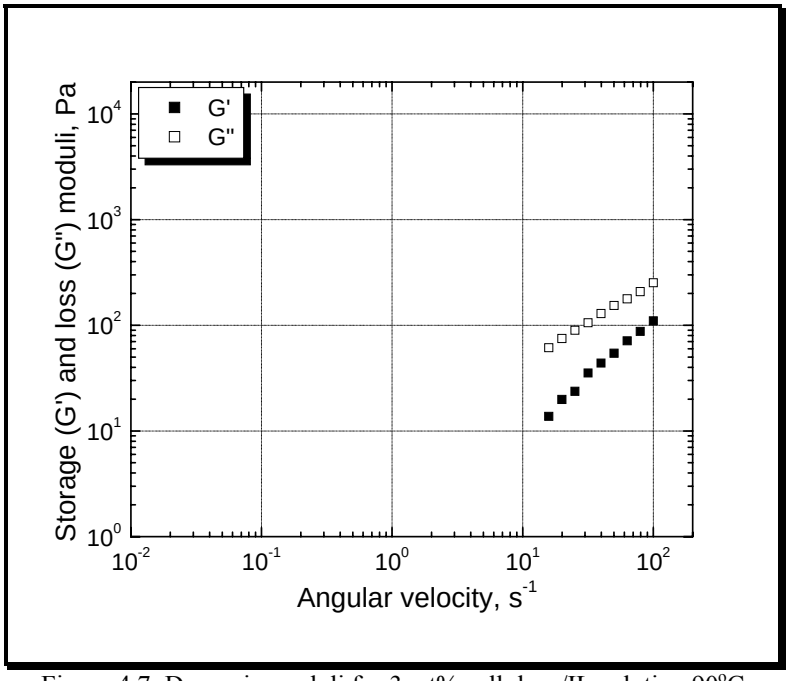


Figure 4.7: Dynamic moduli for 3 wt% cellulose/IL solution 90°C

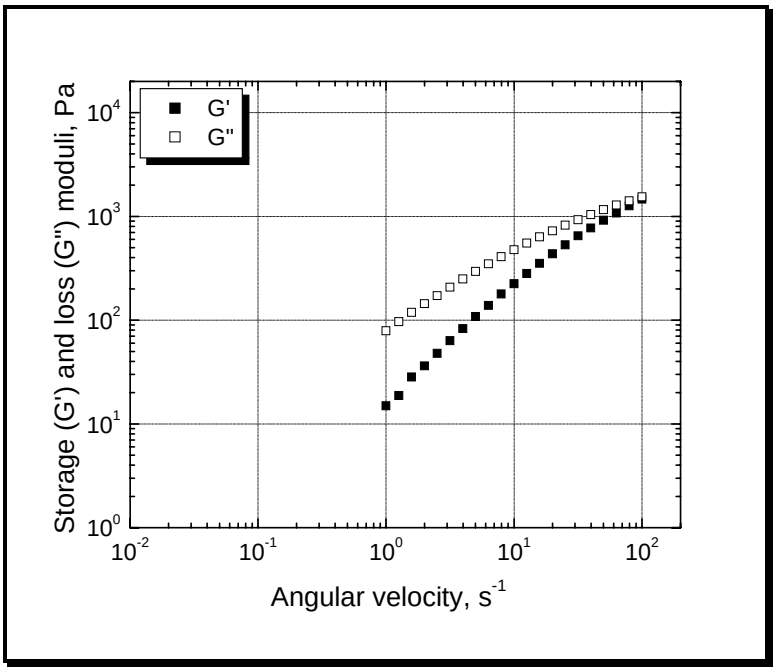


Figure 4.8: Dynamic moduli for 7 wt% cellulose/IL solution 90°C

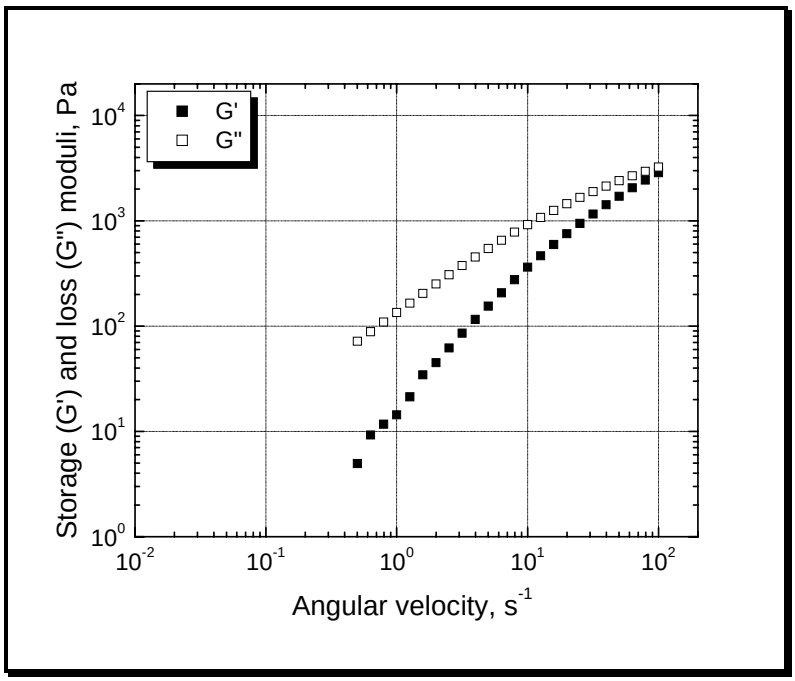


Figure 4.9: Dynamic moduli for 10 wt% cellulose/IL solution 90°C

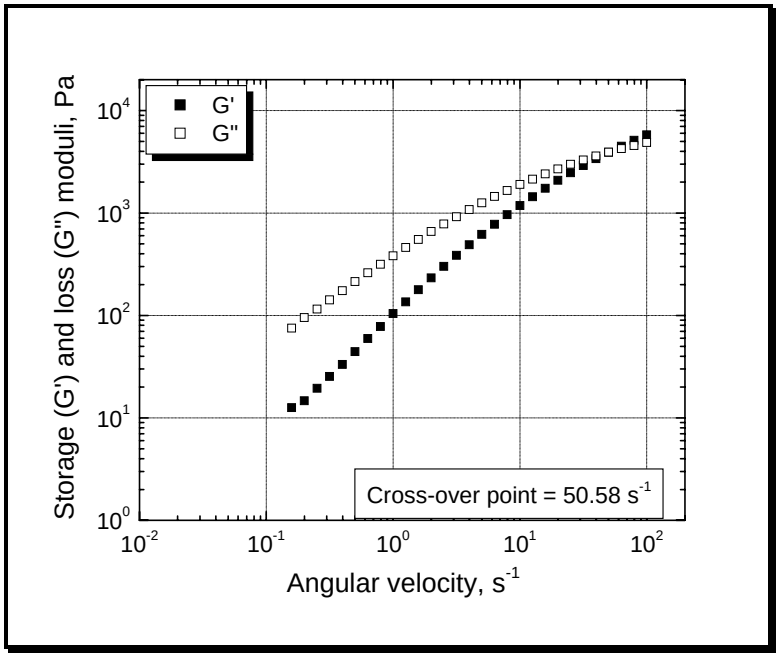


Figure 4.10: Dynamic moduli for 12 wt% cellulose/IL solution 90°C

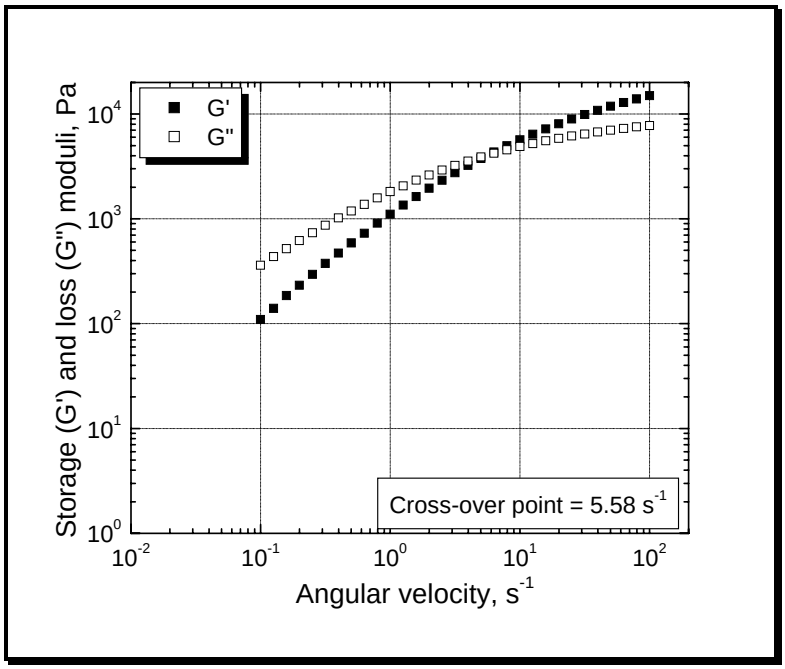


Figure 4.11: Dynamic moduli for 15 wt% cellulose/IL solution 80°C

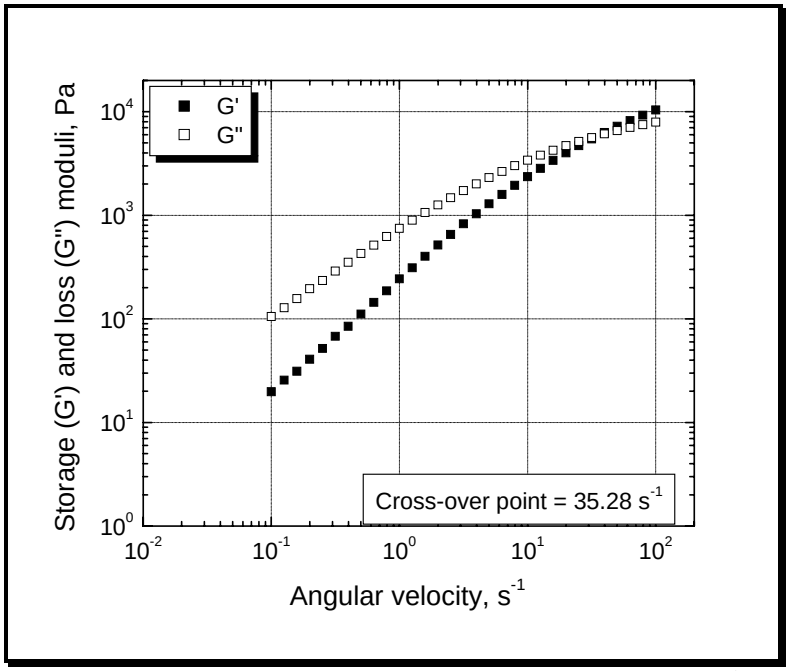


Figure 4.12: Dynamic moduli for 15 wt% cellulose/IL solution 90°C

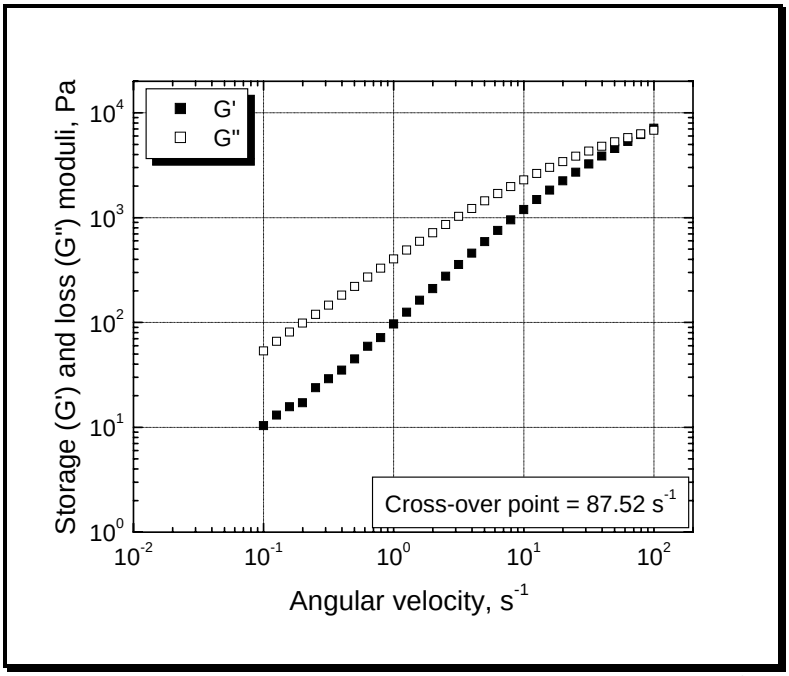


Figure 4.13: Dynamic moduli for 15 wt% cellulose/IL solution 100°C

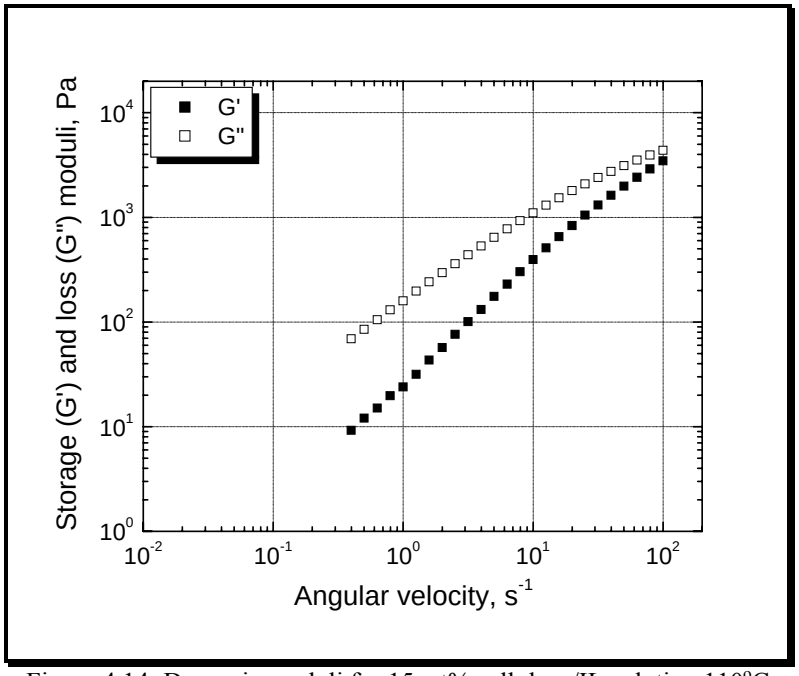


Figure 4.14: Dynamic moduli for 15 wt% cellulose/IL solution 110°C

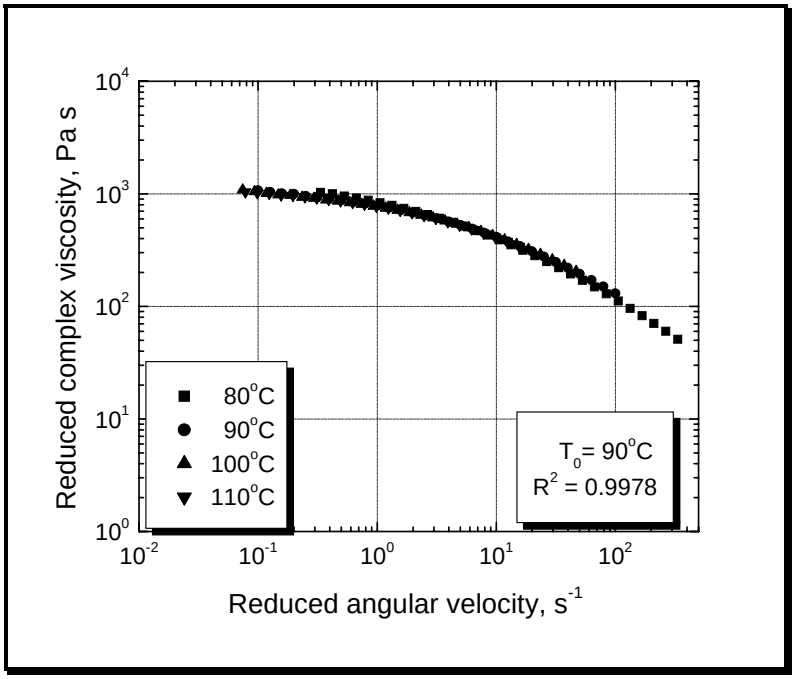


Figure 4.15: Complex viscosity master curve of 15 wt% cellulose/IL solution

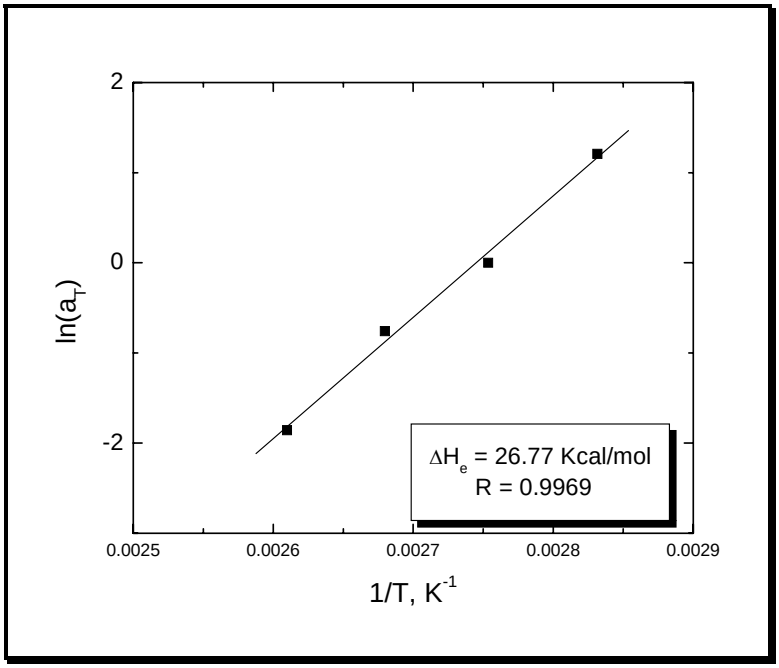


Figure 4.16: Arrhenius plot for the shift factors of 15 wt% cellulose/IL solution master curve

Table 2: Activation energies for flow of IL solution of different concentrations

Concentration of IL solution, %	Activation energy for shear flow, Kcal/mol	Coefficient of determination for Arrhenius plot
3	15.56	1*
7 (80° & 90^oC)	25.81	1*
7 (80°, 90°, & 100^oC)	43.22	0.980
10	21.99	0.997
12	29.09	0.998
15	26.77	0.997

*Note: Only two points were used.

Table 3: Activation Energy for Flow of Various Polymers [39]

Polymer	ΔE_a, (Kcal/mol)
Polyethylene (high density)	6.3-7.0
Polyethylene (low density)	12
Polystyrene	25
Polycarbonate	26-30
Polyvinyl butyral	26
Styrene acrylonitrile copolymer (SAN)	25-30

4.2 Objective Two

To examine the effects of the degree of polymerization of cellulose on [C_4mim]Cl/cellulose solutions

As the DP increased, the solution viscosity also increased (Figures 4.17-4.19). The torque was below the lower limit of the equipment for the DP 670 solution at 100°C. The viscoelastic properties of the IL/cellulose solutions varied with the DP. The lower the DP the more the solution behaved like a viscous liquid instead of a viscoelastic liquid. Figure 4.7 and Figure 4.20 show the dynamic moduli for the DP 670 and DP 1720 solution at 90°C, neither of which had a cross-over point. These solutions behaved like viscous liquids. The solution approached a cross-over point just beyond 100 s^{-1} for the DP 1720 solution and the DP 3900 had a cross-over point (Figure 4.21). In Table 4 the cross-over points of the 3 wt% solutions with different DPs can be seen. The cross-over point shifted to lower angular frequencies as the DP increased. Figure 4.22 shows loss modulus at 100 s^{-1} with respect to the temperature for the solution with different DPs. No interaction between the temperature and DP occurs because the slopes of the loss moduli are approximately parallel.

One way of quantifying the effect of temperature on the shear viscosity is shifting the viscosity curves at different temperatures on a reference temperature viscosity curve which generates a master curve and shift factors. These shift factors were used to calculate the activation energy for flow. The master curve for the DP 3900 solution is presented in Figure 4.23 and the Arrhenius plot for this solution in Figure 4.24. A similar master curve and an Arrhenius plot were generated for the DP 1720 solution and the results are presented in Table 5.

4.3 Objective Three

To examine the effects of preparation method on the [C_4mim]Cl/cellulose solutions (stirring manually vs. high shearing mixing)

The viscosity curves for 3 wt% DP 3900 cellulose solutions that were prepared by manual and mechanical mixing are shown in Figure 4.25. The manually mixed solution had a higher viscosity. For the 10 wt% DP 670 solution the mechanically mixed solution had a higher viscosity (Figure 4.26). From these results, the effect of preparation method on viscosity was dependent on the DP of the cellulose dissolving pulp. Perhaps the cellulose chains were broken during the harsher mechanical mixing of the 3% DP 3900 solution, causing a lower viscosity. Increasing the testing temperature brought about a decrease in viscosity for both the manually and mechanically mixed solutions.

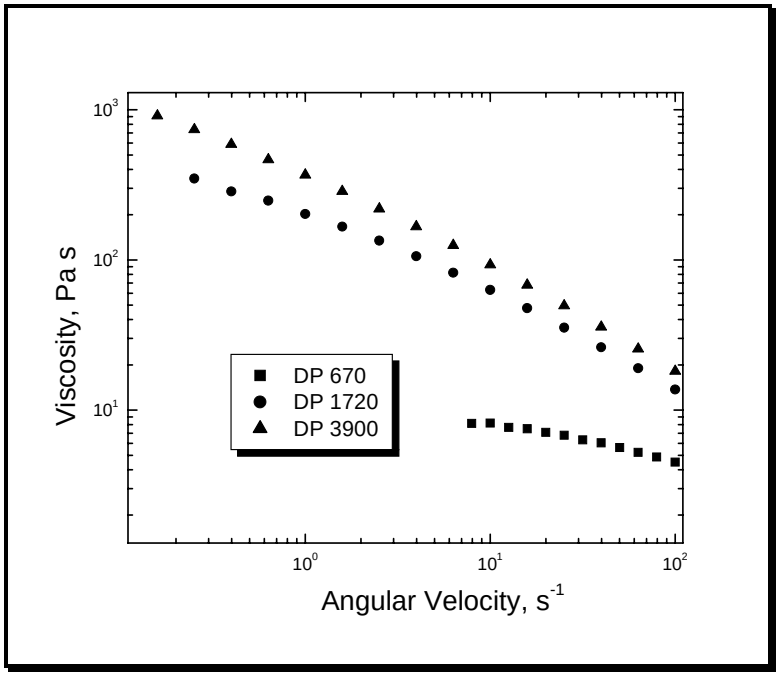


Figure 4.17: 3 wt% cellulose/IL solutions manually prepared using different DPs at 80°C

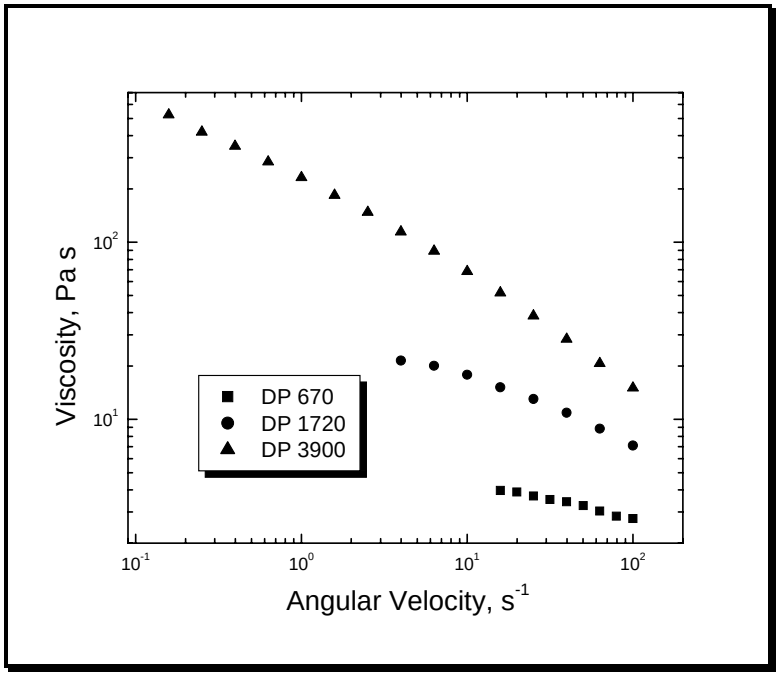


Figure 4.18: Viscosity of 3 wt% cellulose/IL solution manually prepared with different DPs at 90°C

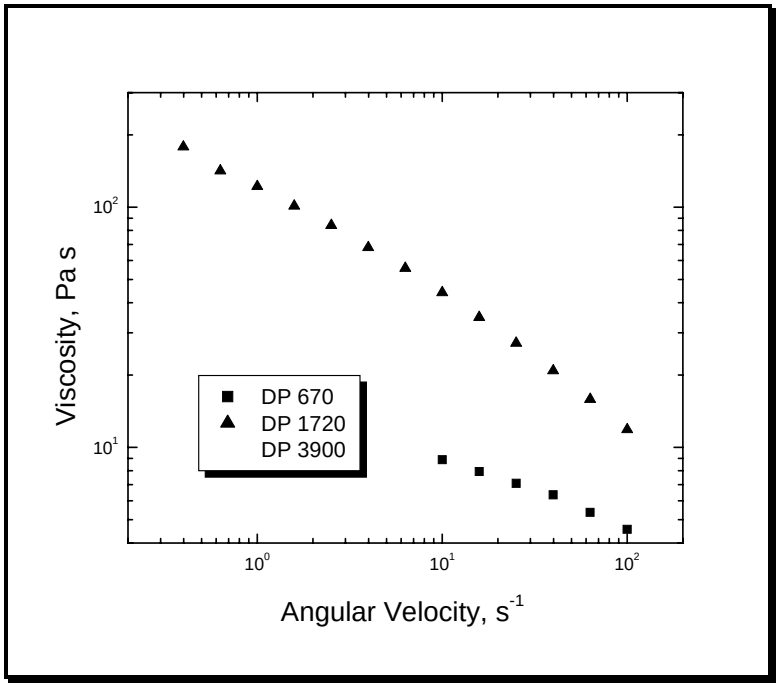


Figure 4.19: Viscosity of 3 wt% cellulose/IL solution manually prepared using different DPs at 100°C

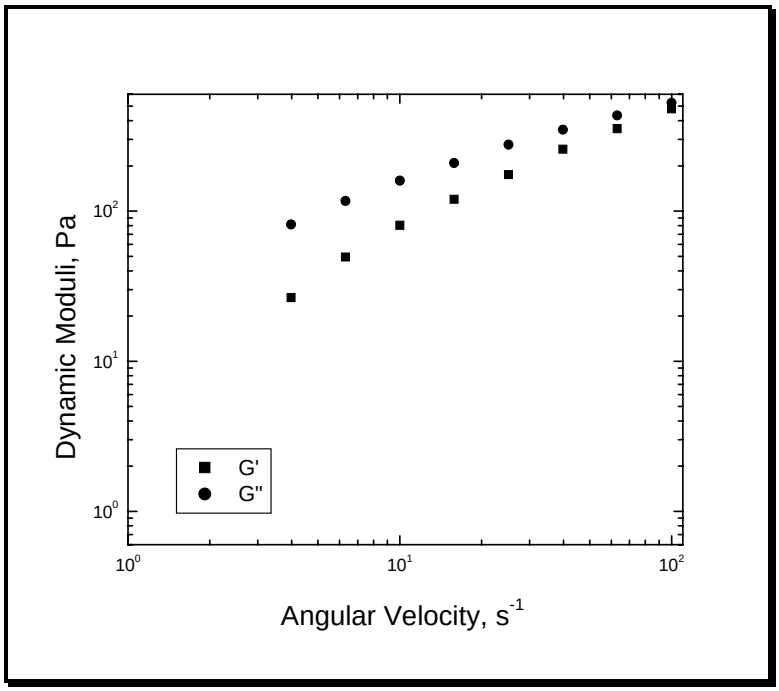


Figure 4.20: Loss and storage moduli of 3 wt% DP 1720 cellulose/IL solution at 90°C

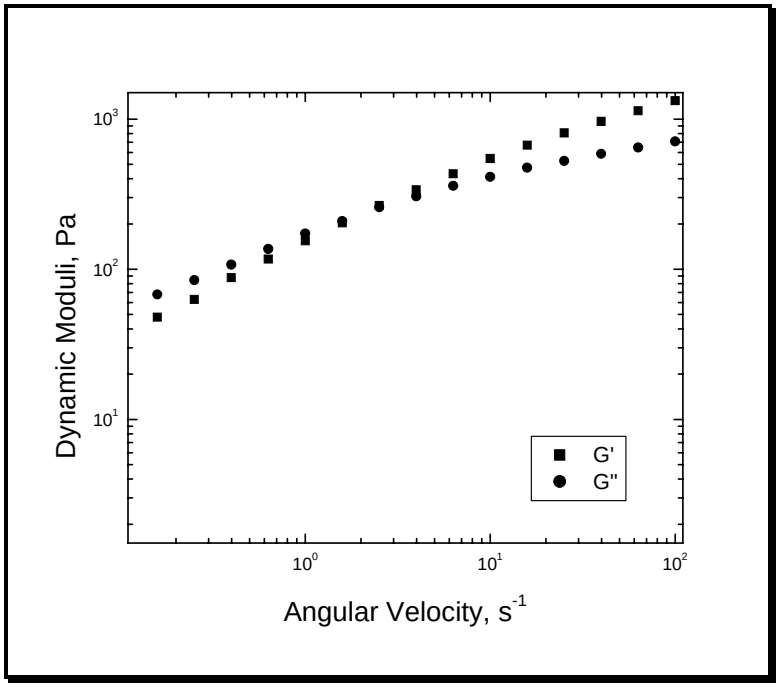


Figure 4.21: Loss and storage moduli of 3 wt% DP 3900 cellulose/IL solution manually prepared at 90°C

Table 4: Cross-over points of solutions with various DPs

Degree of Polymerization	Cross-over point		Temperature, °C
	ω	G'(=G")	
670	NA	NA	80
670	NA	NA	90
670	NA	NA	100
1720	2.897	256.3	80
1720	NA	NA	90
1720	NA	NA	100
3900	0.6058	204.4	80
3900	2.014	234.2	90
3900	11.08	329.5	100

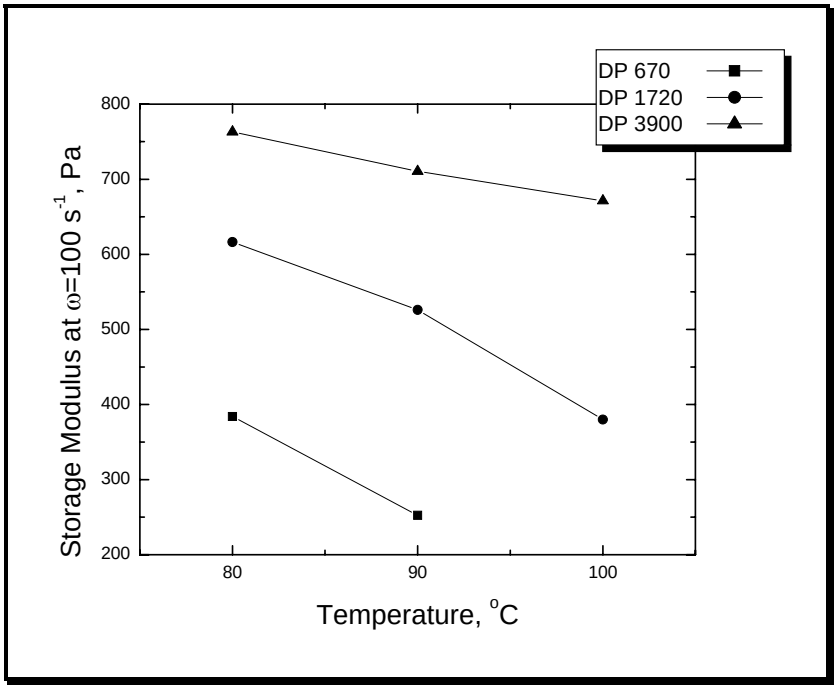


Figure 4.22: Interaction between temperature and degree of polymerization for a 3 wt% cellulose solution

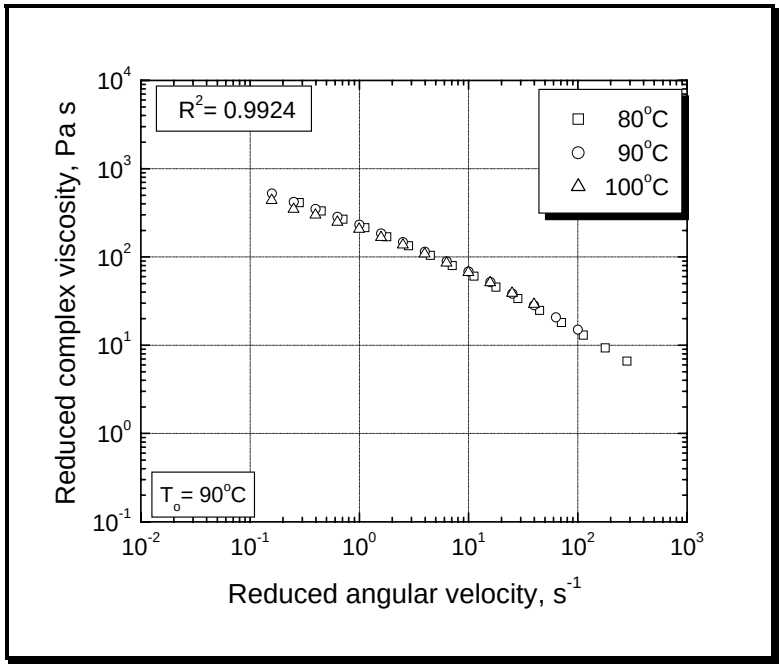


Figure 4.23: Master curve for 3 wt% DP 3900 cellulose/IL solution manually prepared

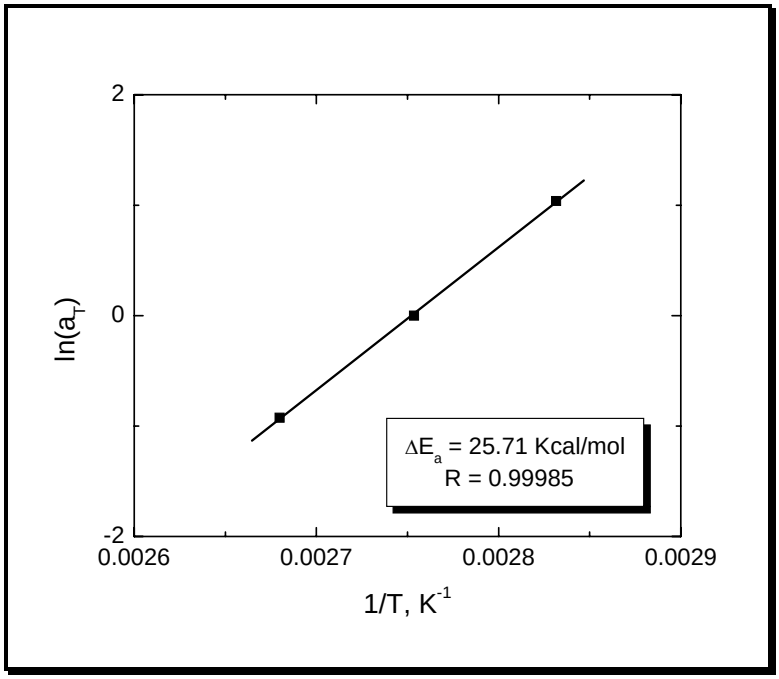


Figure 4.24: Arrhenius plot for 3 wt% DP 3900 cellulose/IL solution manually prepared

Table 5: Activation energy of flow for IL/cellulose solutions manually prepared with various DPs

Degree of Polymerization	ΔE_a, (Kcal/mol)	R^2
670	NA	NA
1720	44.56	0.9576
3900	25.71	0.9997

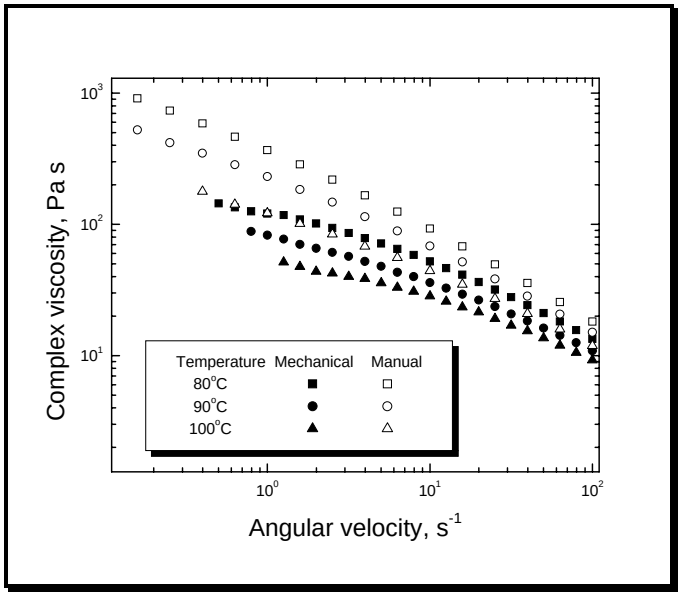


Figure 4.25: Complex viscosity of 3 wt% DP 3900 cellulose/IL solution manually and mechanically prepared

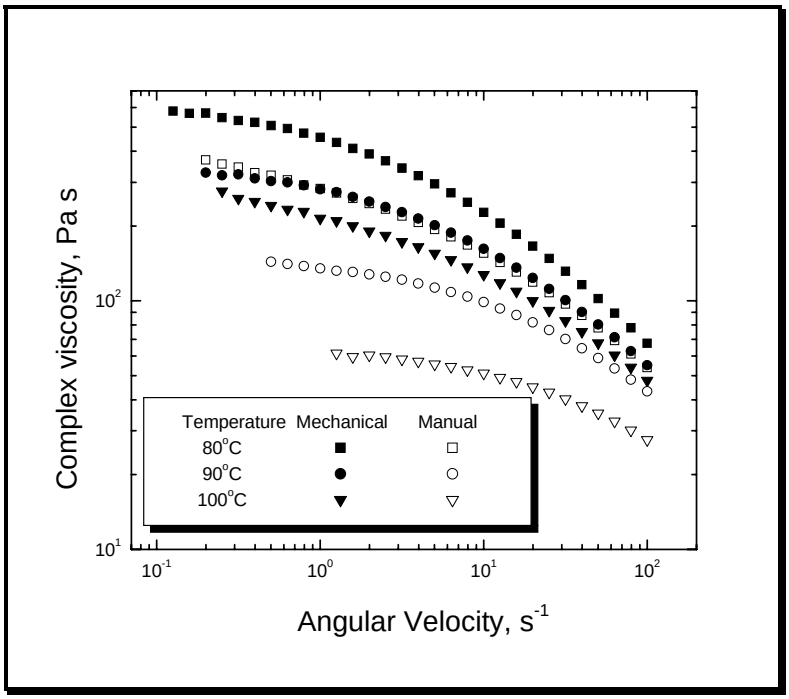


Figure 4.26: Complex viscosity of 10 wt% DP670 cellulose/IL solution manually and mechanically prepared

The viscoelastic properties of the IL solutions at 90°C are displayed in Figures 4.27-4.28. Both preparation method and DP are important parameters for a solution's viscoelasticity. Three percent solutions prepared with DP 3900 cellulose exhibited a cross-over point regardless of the preparation method. The 10 wt% solution prepared with DP 670 cellulose was dependent on preparation method. The mechanically prepared solution had a cross-over point, but the manually prepared solution did not have a cross-over point at 90° and 100°C. It behaved as a viscous liquid at these temperatures because the loss modulus was higher than the storage modulus. The solutions with the cross-over point at high deformation rates behaved as viscoelastic liquids.

As the temperature increased the cross-over point shifted to higher angular velocities, decreasing the viscoelastic domain (Figures 4.29-4.31). The reciprocal of the cross-over point angular velocity has units of time and is an indication of the relaxation time of the macromolecular chains from the solution, which is an important parameter of the fiber forming process. The cross-over points for the different solutions at various temperatures can be seen in Table 6.

There was apparently no interaction between preparation method and temperature for the 3 wt% DP 3900 solution (Figure 4.32). For the 10 wt% DP 670 (Figure 4.33) however there may be an interaction, i.e, the effect of temperature on loss modulus may be dependent on preparation method. It should be noted that the manually prepared 10 wt% DP 670 was the first solution prepared and tested within this study; therefore, it is highly likely that it had greater experimental error.

The Arrhenius Plot for the complex viscosity of 3 wt% DP 3900 solution manually prepared is given in Figure 4.34. The coefficient of determination (R^2=0.9997) shows that the shifting procedure was very accurate. Equation 15 shows the temperature dependence of a_T to be an Arrhenius dependence. Similar master curves were generated for other solutions and activation energies, calculated from the Arrhenius plots, are presented in Table 7. The activation energies for mechanically mixed solutions are lower due to either a lower average distribution of DP after mixing or a change in the character of the solution.

4.4 Objective Four

To determine the effects of lignin and xylose additives on rheological behavior

Viscosity curves for the IL/cellulose/lignin, IL/cellulose/xylose, and IL/cellulose/lignin/xylose solutions at various temperatures are shown in Figures 4.35-4.41. In this set of solutions as well as other solutions that have already been discussed, the viscosity curves showed shear thinning behavior at all temperatures and

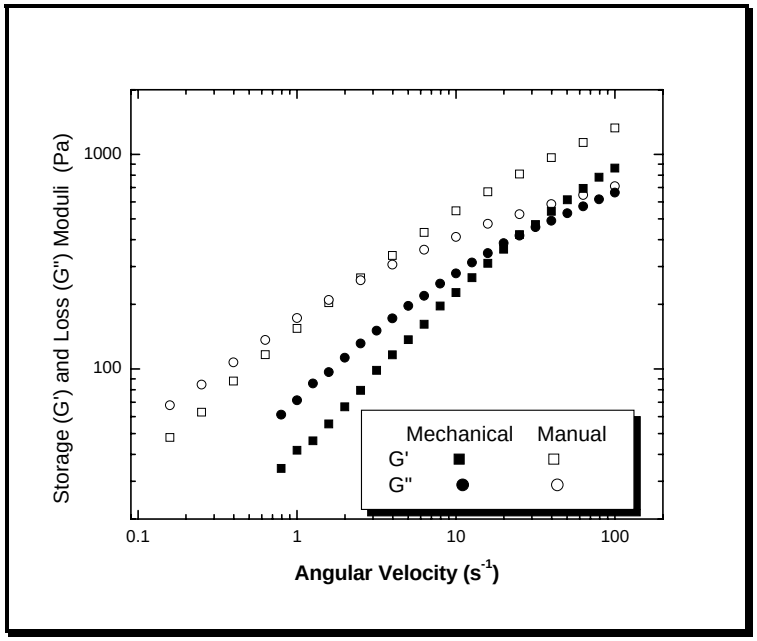


Figure 4.27 Dynamic moduli for 3 wt% DP 3900 cellulose/IL solution at 90°C mechanically and manually prepared.

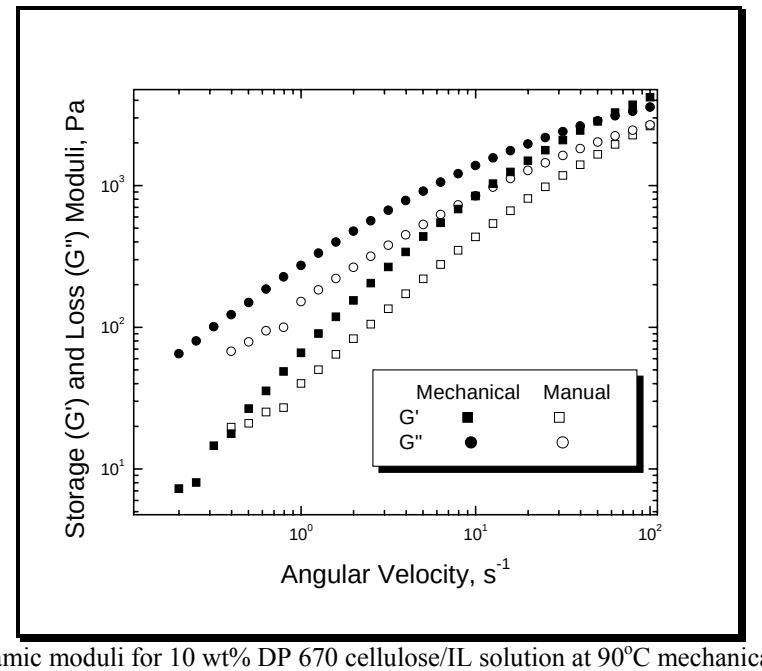


Figure 4.28: Dynamic moduli for 10 wt% DP 670 cellulose/IL solution at 90°C mechanically and manually prepared.

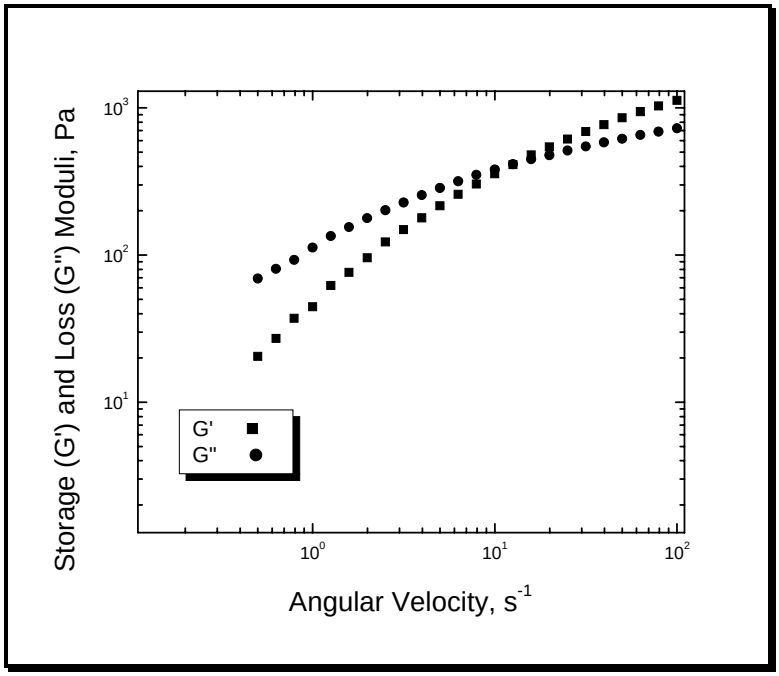


Figure 4.29: Dynamic moduli for 3 wt% DP 3900 cellulose/IL solution at 80°C mechanically prepared.

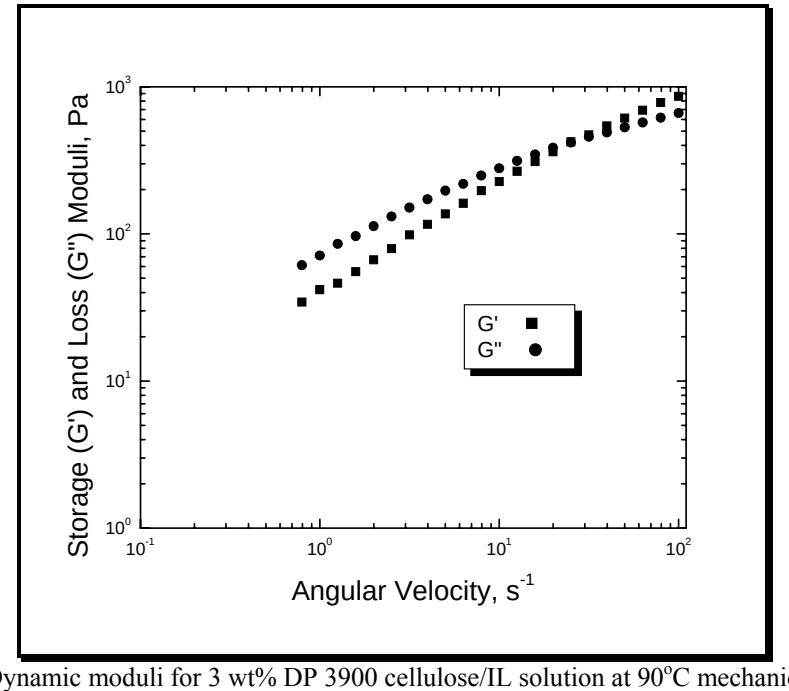


Figure 4.30: Dynamic moduli for 3 wt% DP 3900 cellulose/IL solution at 90°C mechanically prepared

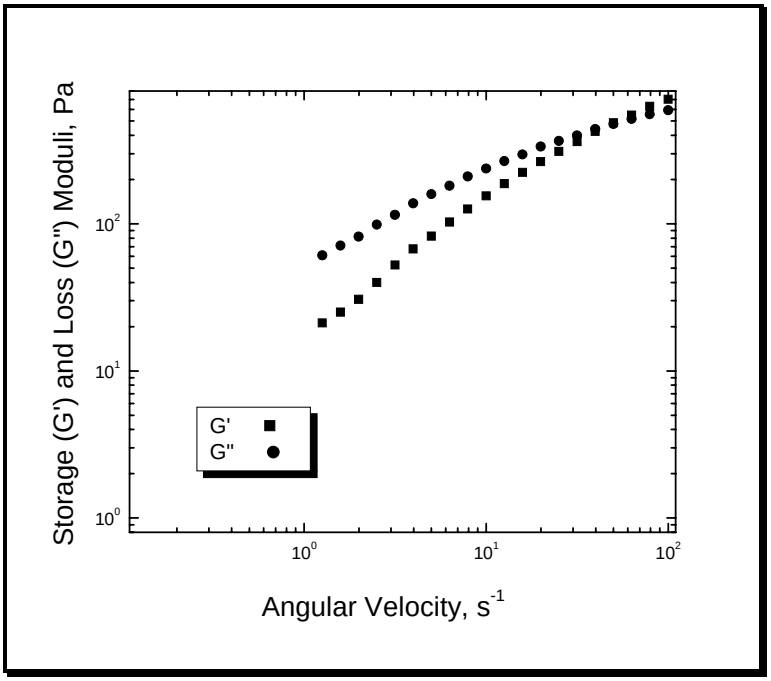


Figure 4.31: Dynamic moduli for 3 wt% DP 3900 cellulose/IL solution at 100°C mechanically prepared

Table 6: Cross-over points for different preparation methods and DPs various solutions

Concentration of Cellulose	Preparation Method	Degree of Polymerization	Cross-over point		Temperature °C
			ω	G'(=G")	
10	Mechanical	670	27.49	2751	80
10	Mechanical	670	52.00	2900	90
10	Mechanical	670	84.84	3128	100
3	Manual	3900	0.6058	204.4	80
3	Manual	3900	2.014	234.2	90
3	Manual	3900	11.08	329.5	100
3	Mechanical	3900	12.67	413.5	80
3	Mechanical	3900	25.24	423.7	90
3	Mechanical	3900	46.33	466.2	100
10	Manual	670	66.38	2786	80
10	Manual	670	NA	NA	90
10	Manual	670	NA	NA	100

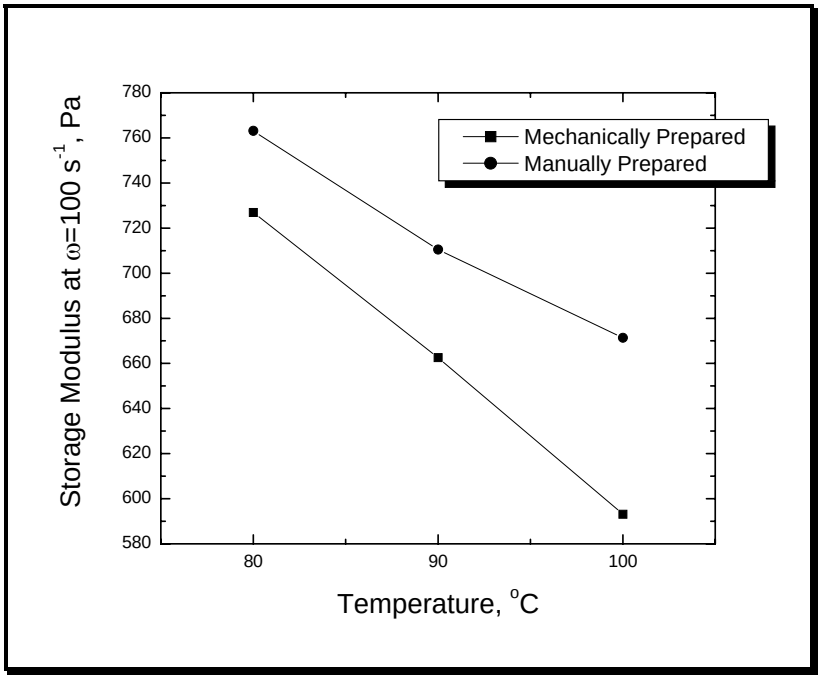


Figure 4.32: Interaction of temperature and mixing method of 3 wt% DP 3900 cellulose solution

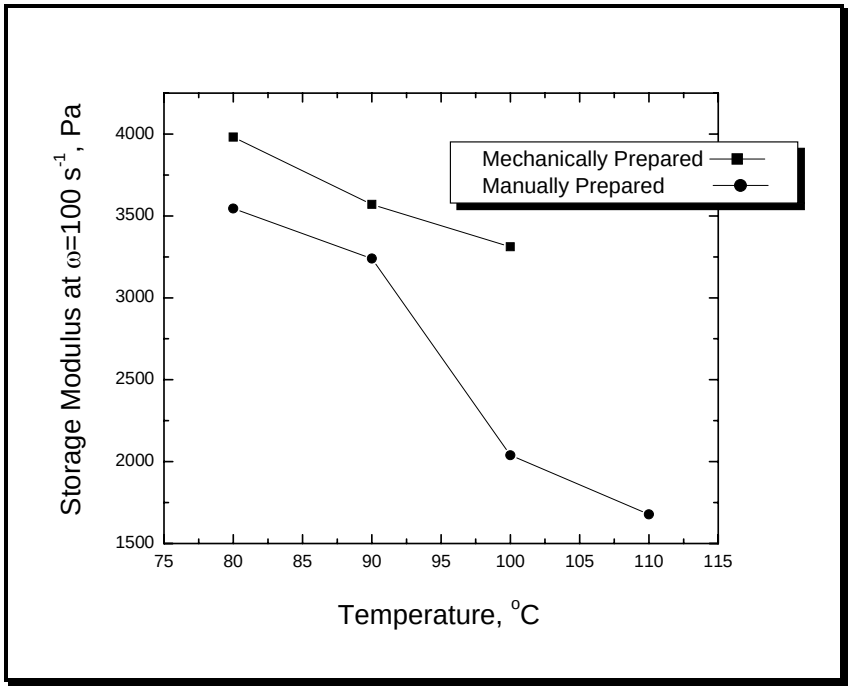


Figure 4.33: Interaction of temperature and mixing method of 10 wt% DP 670 solution between a temperature range of 80°-110°C

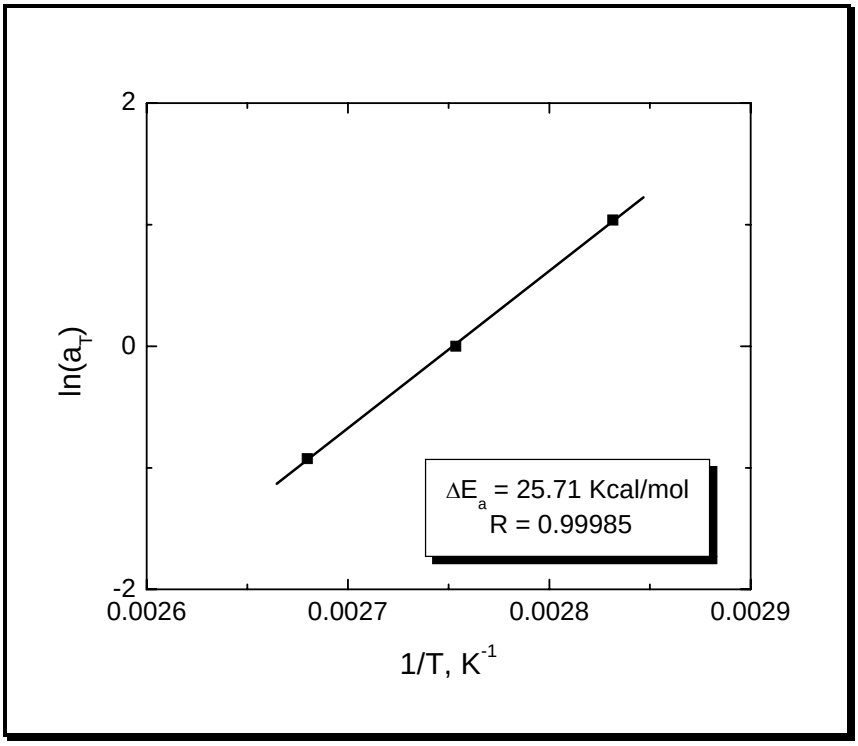


Figure 4.34: Arrhenius Plot for 3 wt% DP 3900 cellulose/IL solution manually prepared

Table 7: Activation energies for flow of IL solutions with different mixing methods

Concentration of IL solution, %	Degree of Polymerization	Method of Preparation	Activation energy for shear flow, Kcal/mol	Coefficient of determination for Arrhenius plot
3	3900	Manual	25.71	0.9997
3	3900	Mechanical	12.17	0.9999
10	670	Manual	21.99	0.9943
10	670	Mechanical	10.53	0.9410

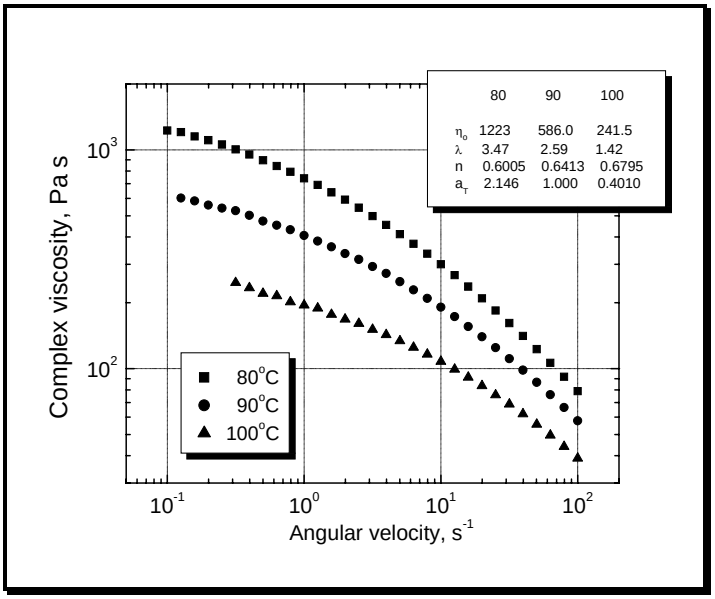


Figure 4.35: Complex viscosity of 9 wt% cellulose/1 wt% lignin/IL solution

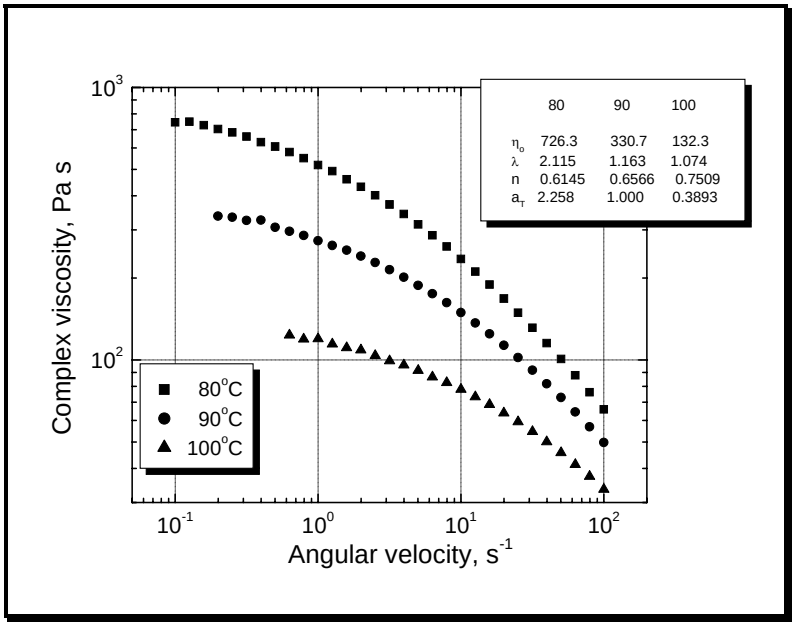


Figure 4.36: Complex viscosity of 8 wt% cellulose/2 wt% lignin/IL solution

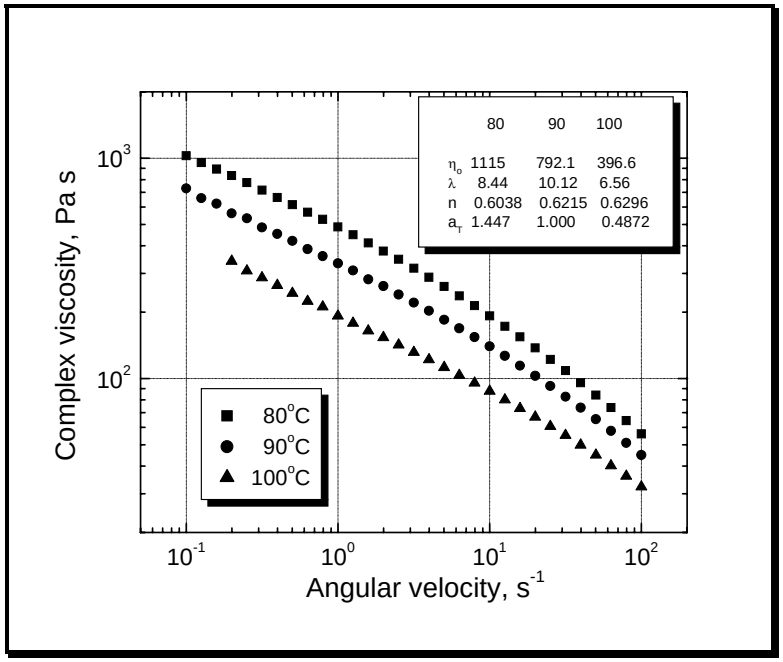


Figure 4.37: Complex viscosity of 8 wt% cellulose/1 wt% lignin/1 wt% xylose/IL solution

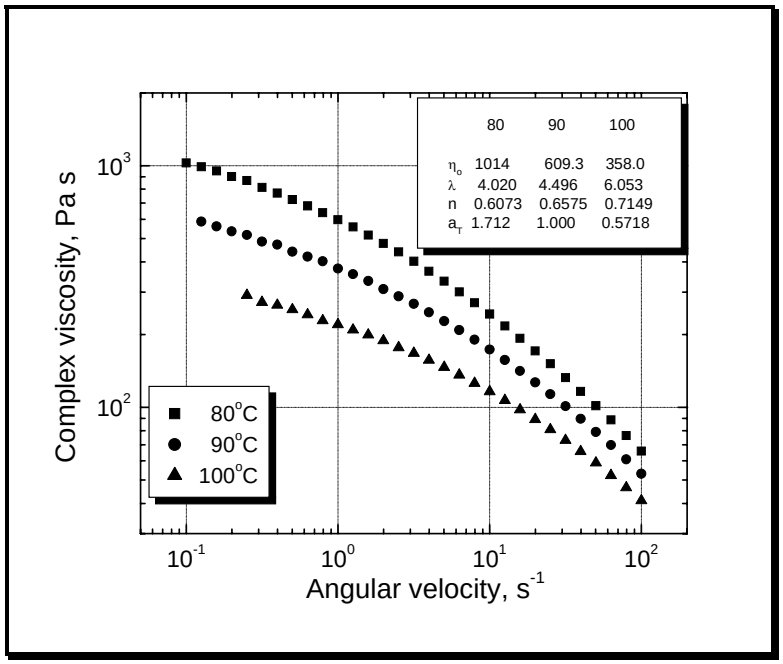


Figure 4.38: Complex viscosity of 1 wt% xylose/9 wt% cellulose/IL solution

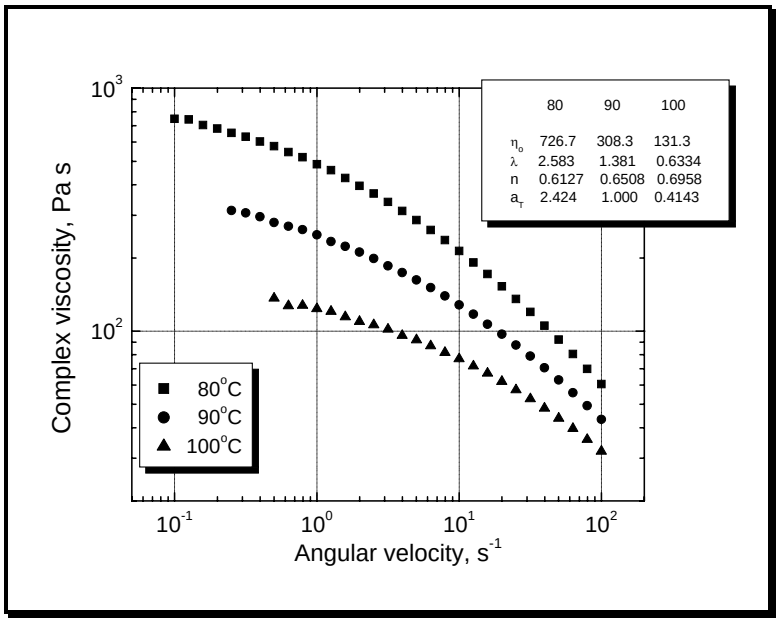


Figure 4.39: Complex viscosity of 8 wt% cellulose/2 wt% xylose/IL solution

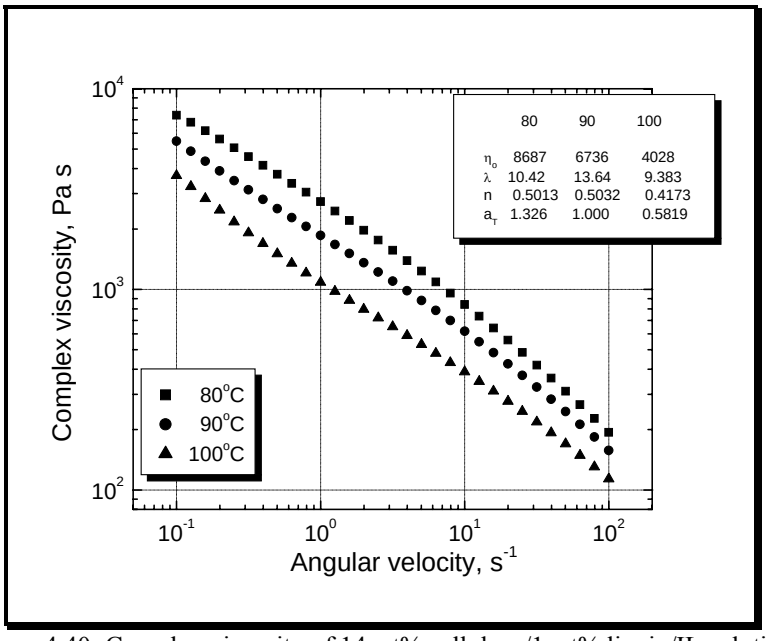


Figure 4.40: Complex viscosity of 14 wt% cellulose/1 wt% lignin/IL solution

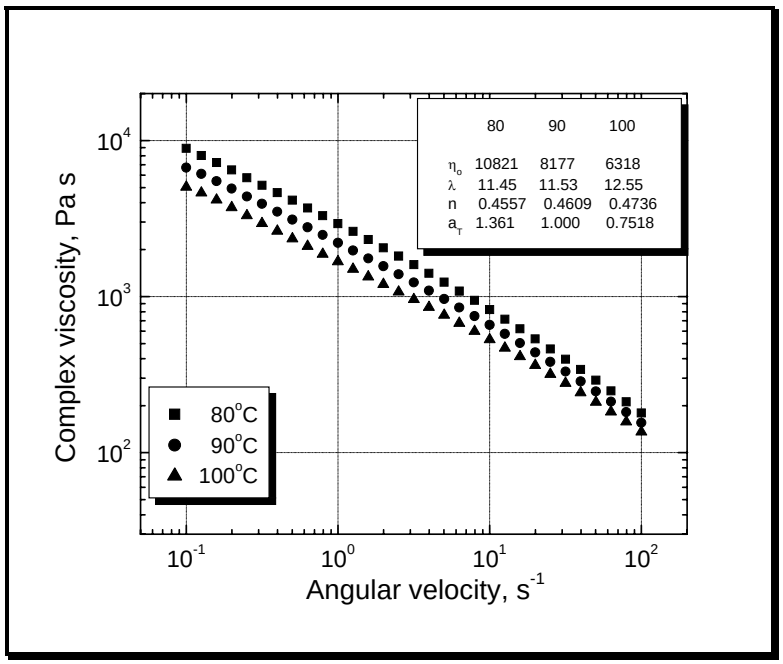


Figure 4.41: Complex viscosity of 14 wt% cellulose/1 wt% xylose/IL solution

concentrations. Viscosity increased with concentration and decreased with increased temperature.

Compared to solutions without additives, the viscosities of solutions with lignin and xylose were significantly higher as seen in Figures 4.42-4.44. For solutions with lignin this could be due to the fact that lignin has a higher viscosity, even at higher temperatures (Figure 4.45). The solutions with 1 wt% additive had the highest viscosities.

The more lignin or xylose present in the solution the lower the viscosity. This decrease could be due to the lower molecular weight of lignin and xylose which has been proven to directly affect the viscosity. No interaction was apparent between temperature and additive concentration (Figure 4.46). Similar results were seen for the 15 wt% additive samples.

The viscoelastic properties of the IL solutions at 90°C can be seen in Figures 4.47-4.53. The amount of cellulose was an important parameter for the solution's viscoelasticity, but the type of additive had little effect (Table 8). As the temperature of the sample increased the cross-over point shifted to a higher angular frequency (Table 9). All of the solutions with 10 wt% additives had cross-over points at 80, 90, and 100°C, except the solutions with 8 wt% cellulose at 100°C. The 10 wt% cellulose solution had a cross-over point only at 80°C. The solutions with 15 wt% additives had cross-over points except the

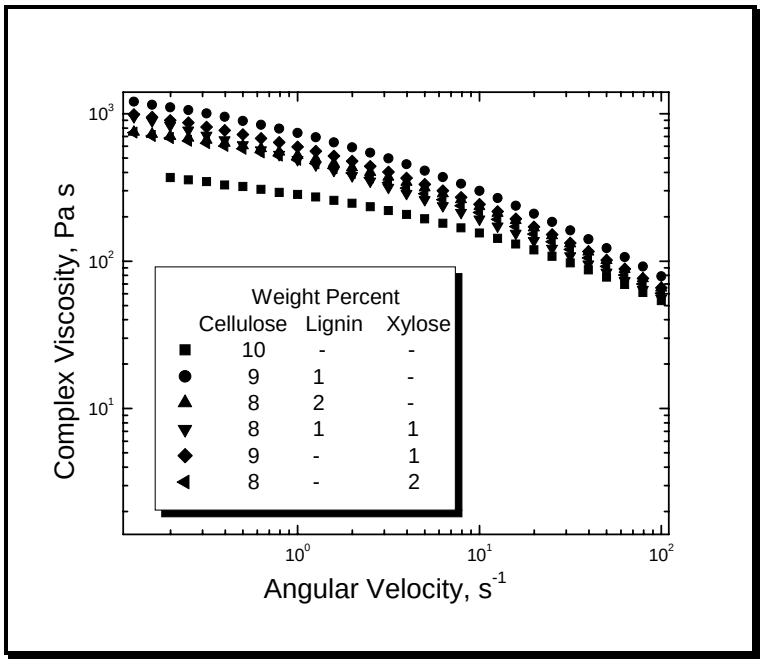


Figure 4.42: Complex viscosity of IL/cellulose solutions with lignin and/or xylose present at 80°C

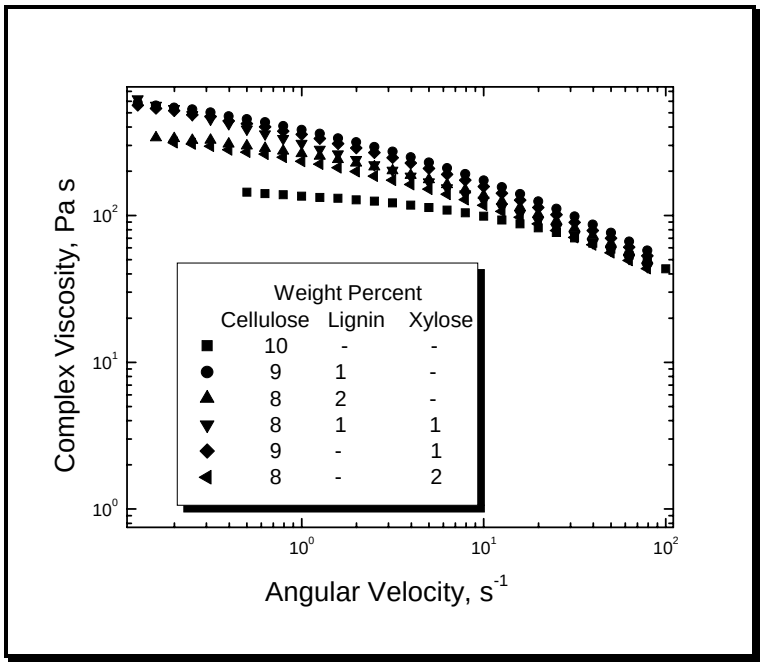


Figure 4.43: Complex viscosity of IL/cellulose solutions with lignin and/or xylose present at 90°C

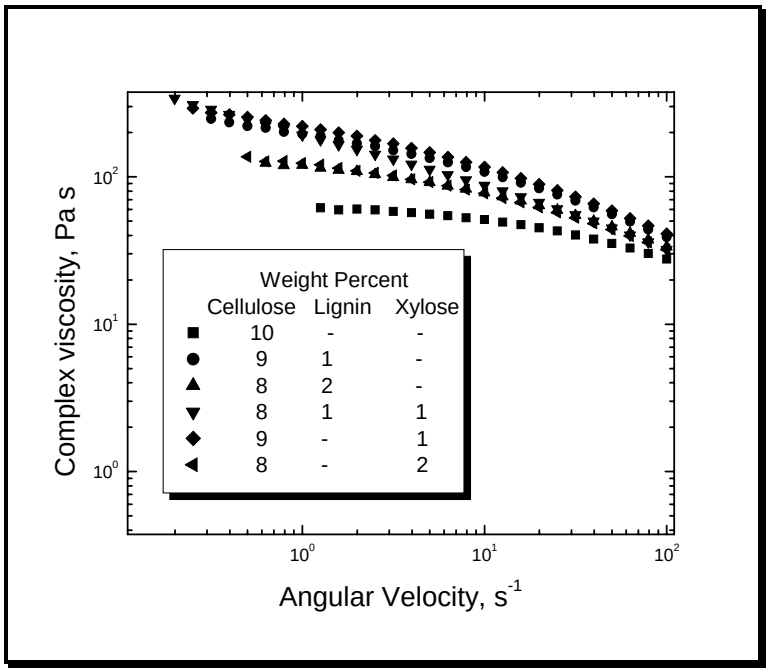


Figure 4.44: Complex viscosity of IL/cellulose solutions with lignin and/or xylose present at 100°C

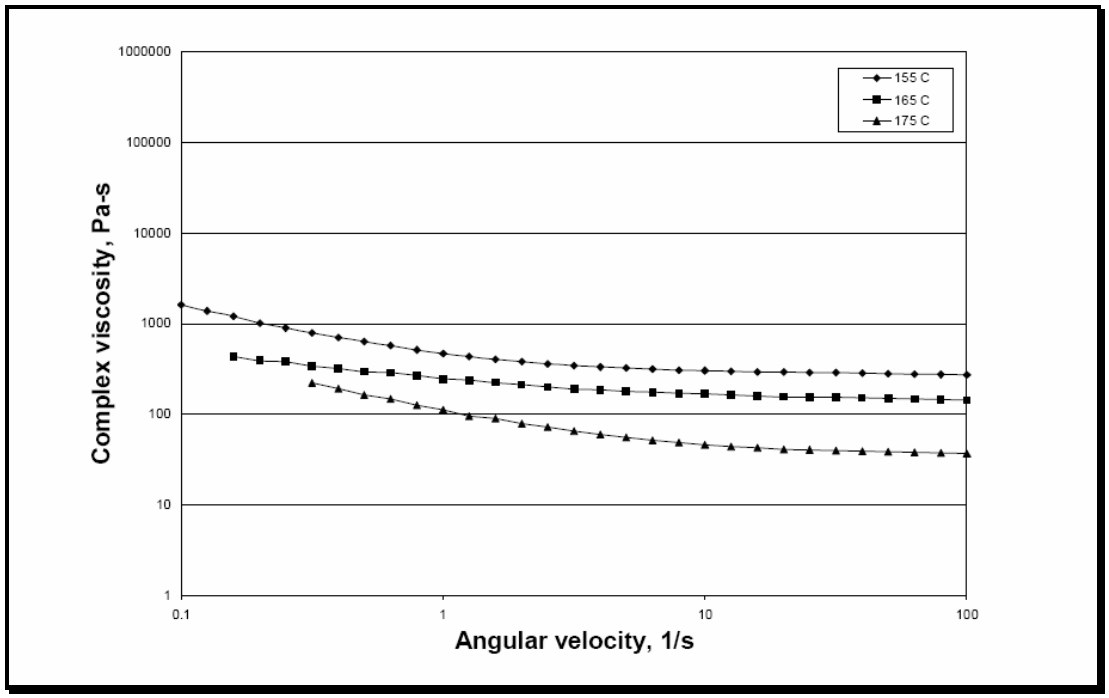


Figure 4.45: Complex viscosity of organisolv lignin [45]

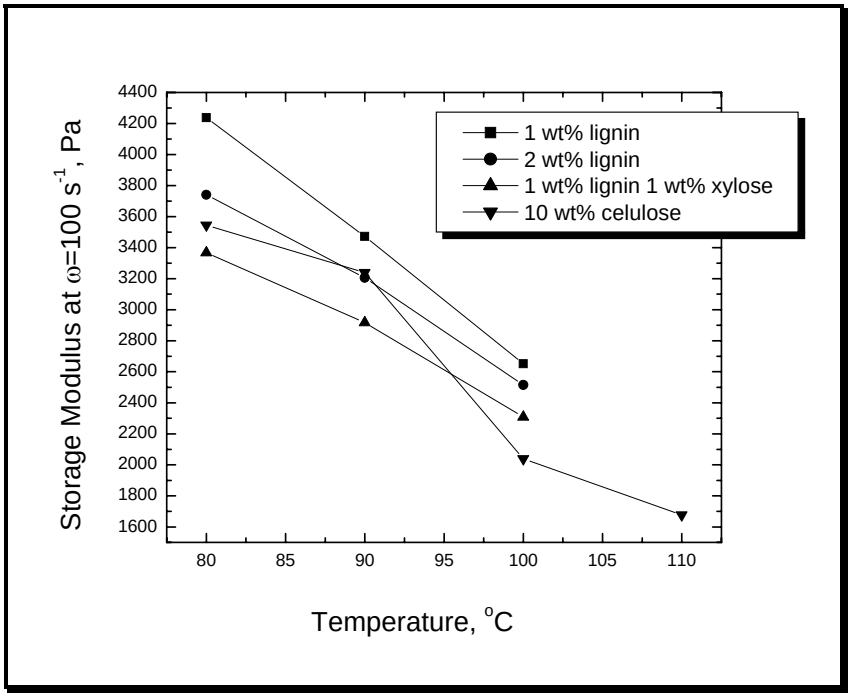


Figure 4.46 Interaction between temperature and additives for a 10 wt% additive solution

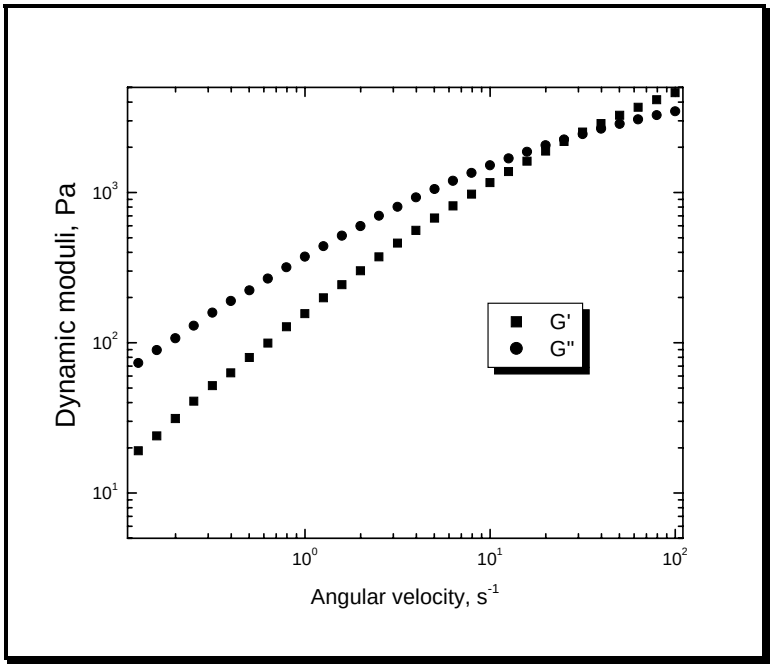


Figure 4.47: Dynamic moduli of 9 wt% cellulose/1 wt% lignin/IL solution at 90°C

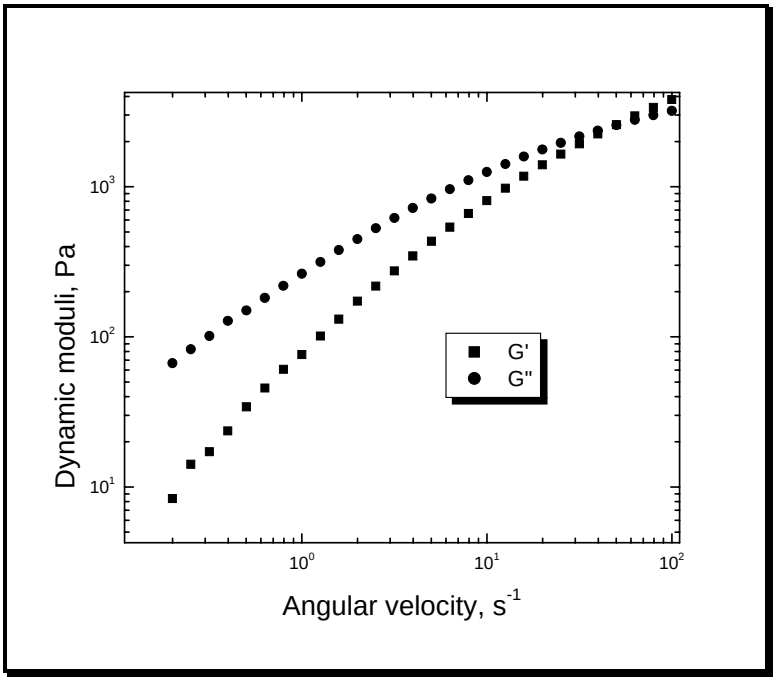


Figure 4.48: Dynamic moduli of 8 wt% cellulose/2 wt% lignin/IL solution at 90°C

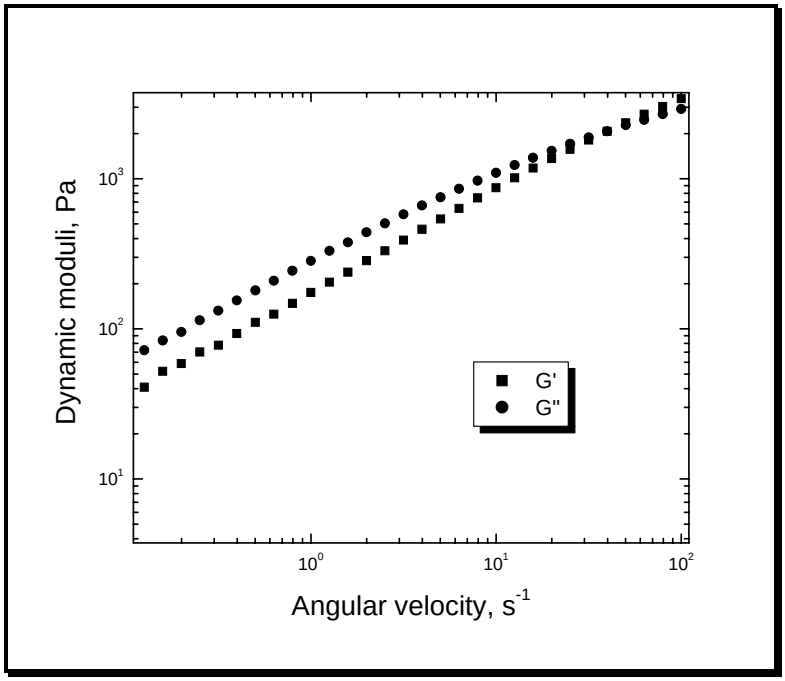


Figure 4.49: Dynamic moduli of 8 wt% cellulose/1 wt% lignin/1 wt% xylose/IL solution at 90°C

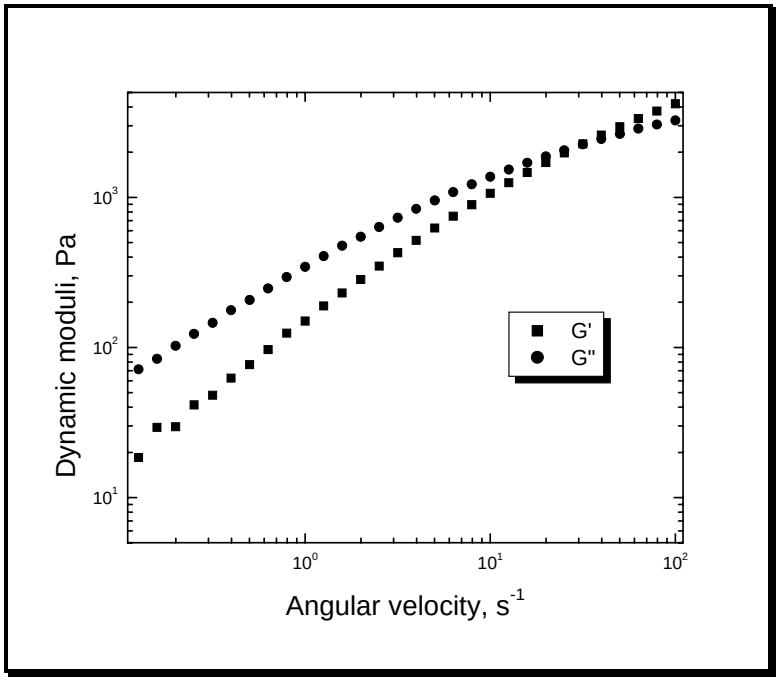


Figure 4.50: Dynamic moduli of 9 wt% cellulose/1 wt% xylose/IL solution at 90°C

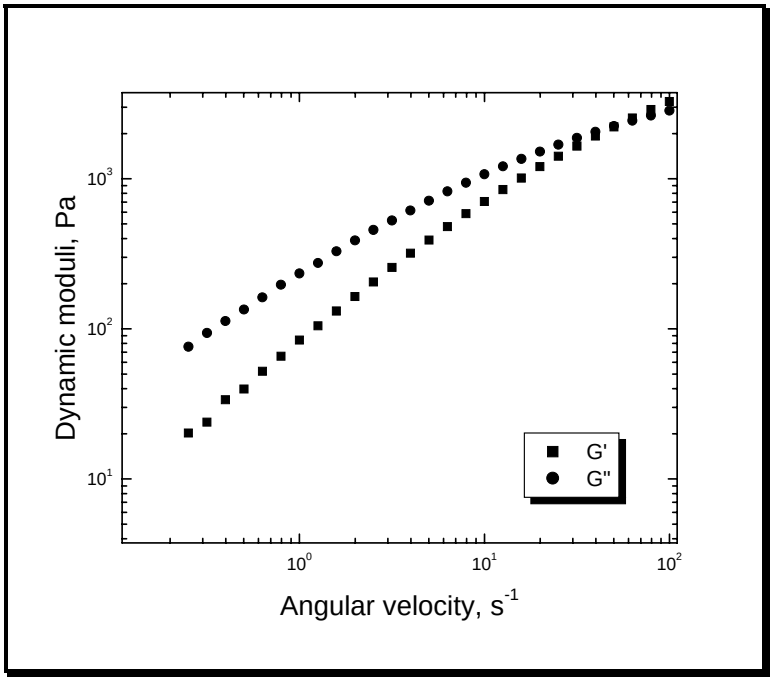


Figure 4.51: Dynamic moduli of 8 wt% cellulose/2 wt% xylose/IL solution at 90°C

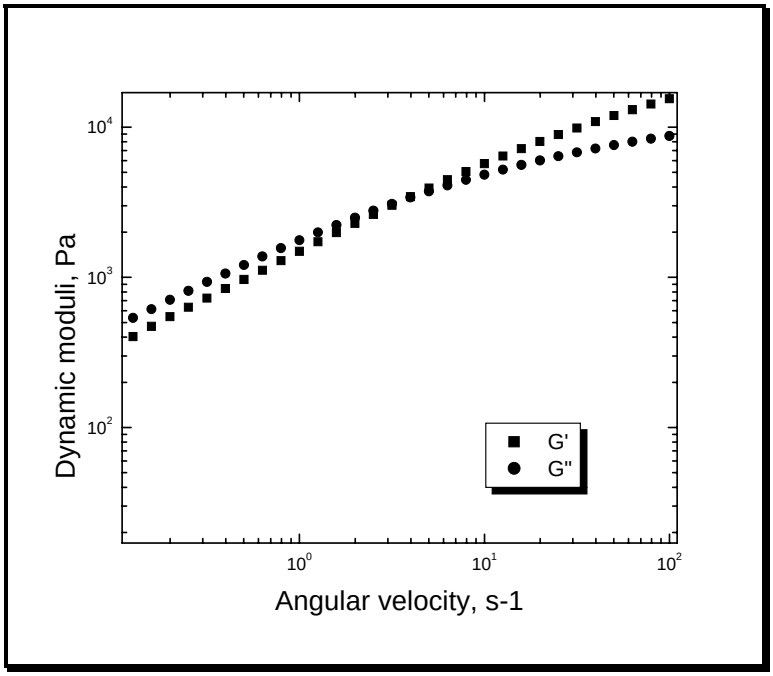


Figure 4.52: Dynamic moduli of 14 wt% cellulose/1 wt% lignin/IL solution at 90°C

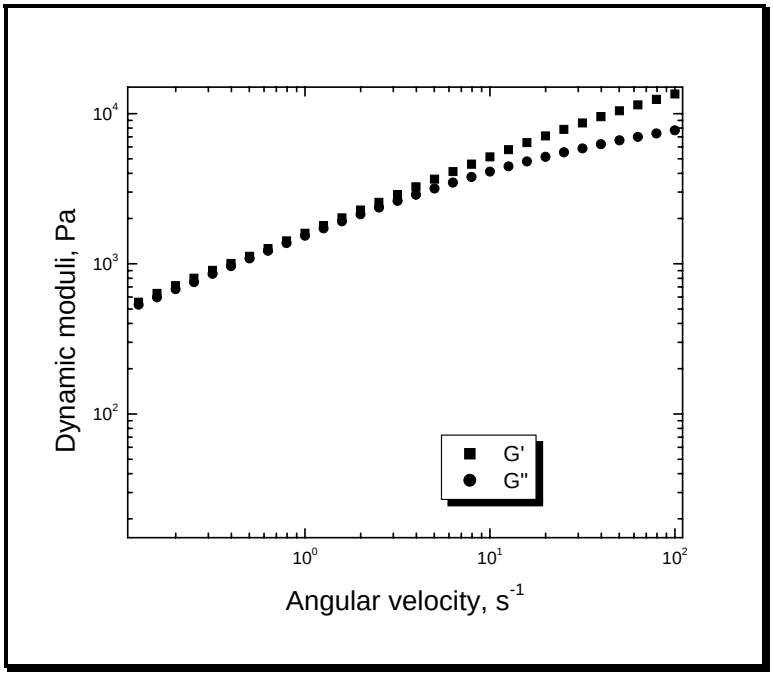


Figure 4.53: Dynamic moduli of 14 wt% cellulose/1 wt% xylose/IL solution at 90°C

Table 8: Change in cross-over points with respect to the concentration of additives

Concentration				Cross-over point		Temperature °C
Total Additives	Cellulose	Xylose	Lignin	ω	G'(=G")	
10	8	1	1	19.34	1915	80
10	8	2	0	19.58	2138	80
10	8	0	2	19.21	2328	80
10	8	1	1	39.90	2077	90
10	8	2	0	53.14	2294	90
10	8	0	2	48.60	2544	90
10	8	1	1	NA	NA	100
10	8	2	0	NA	NA	100
10	8	0	2	NA	NA	100
10	9	0	1	10.50	2056	80
10	9	1	0	14.47	2070	80
10	9	0	1	28.24	2350	90
10	9	1	0	30.36	2216	90
10	9	0	1	74.15	2392	100
10	9	1	0	70.63	2462	100
15	14	0	1	1.299	3011	80
15	14	1	0	0.3907	1294	80
15	14	0	1	3.693	3300	90
15	14	1	0	NA	NA	90
15	14	0	1	9.645	3310	100
15	14	1	0	0.1073	374.0	100
10	10	0	0	66.38	2786	80
10	10	0	0	NA	NA	90
10	10	0	0	NA	NA	100

Table 9: Change in cross-over points with respect to temperature

Concentration				Cross-over point		Temperature °C
Total Additives	Cellulose	Xylose	Lignin	ω	G'(=G")	
10	8	0	2	19.21	2328.4	80
10	8	0	2	48.60	2544	90
10	8	0	2	NA	NA	100
10	8	2	0	19.58	2137.6	80
10	8	2	0	53.14	2294.4	90
10	8	2	0	NA	NA	100
10	8	1	1	19.34	1914.9	80
10	8	1	1	39.90	2077.2	90
10	8	1	1	NA	NA	100
10	9	0	1	10.50	2056	80
10	9	0	1	28.24	2350	90
10	9	0	1	74.15	2392	100
10	9	1	0	14.47	2070	80
10	9	1	0	30.36	2216	90
10	9	1	0	70.63	2462	100
10	10	0	0	66.38	2786	80
10	10	0	0	NA	NA	90
10	10	0	0	NA	NA	100
15	14	0	1	1.299	3011	80
15	14	0	1	3.693	3300	90
15	14	0	1	9.645	3310	100
15	14	1	0	0.3907	1294.	80
15	14	1	0	NA	NA	90
15	14	1	0	0.1073	374.0	100

solution with 14 wt% cellulose and 1 wt% xylose. The loss and storage moduli for the 14 wt% cellulose and 1 wt% xylose solution were almost equal from an angular velocity range of 0.1 to 2.5 s^{-1}, suggesting that the distribution of DP may be broader than other samples tested.

The Carreau parameters are given for the solutions with additives in Figure 4.35-4.41. The Carreau parameters for the solutions without additives are given in Figure 4.3 and Figure 4.5. The master curve for the complex viscosity of 9 wt% cellulose/1 wt% xylose solution/IL solution is given in Figure 4.54. The coefficient of determination (R^2= 0.99964) shows that the shifting procedure is very accurate. The temperature dependence of a_T is often found to be an Arrhenius dependence as seen in Figure 4.55. Similar master curves were generated for other solutions and activation energies. Activation energies calculated from the Arrhenius plots, are presented in Table 10.

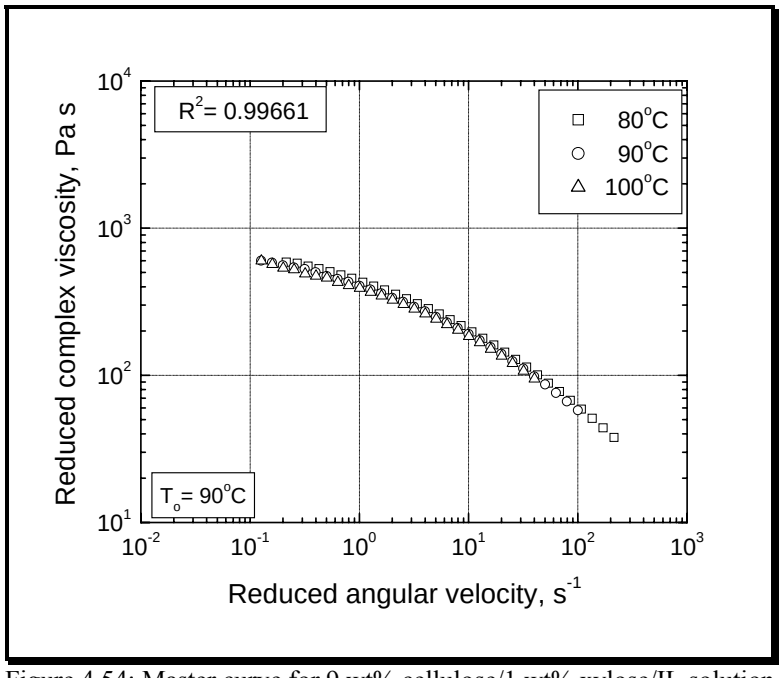


Figure 4.54: Master curve for 9 wt% cellulose/1 wt% xylose/IL solution

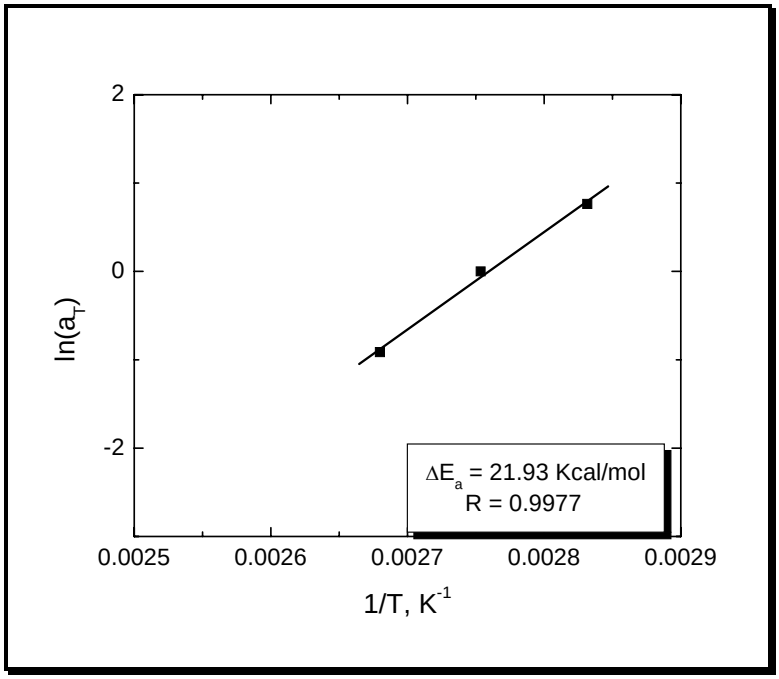


Figure 4.55: Arrhenius plot for 9 wt% cellulose/1 wt% xylose/IL solution

Table 10: Activation energy for shear flow for IL/cellulose solutions with additives

Concentration				ΔE_a (Kcal/mol)	R^2
Total Additives	Cellulose	Xylose	Lignin		
10	8	0	2	23.00	0.9966
10	8	1	1	14.21	0.9608
10	8	2	0	23.12	0.9998
10	9	0	1	21.93	0.9954
10	9	1	0	14.35	0.9993
10	10	0	0	21.99	0.9943
15	14	0	1	10.75	0.9622
15	14	1	0	7.769	0.99996
15	15	0	0	26.77	0.9969

5. Conclusions and Recommendations

5.1 Conclusions

Cellulosic solutions of different concentrations in the IL solvent ([C_4mim]Cl) were prepared by dissolution of dissolving pulp of DP 670. Rheological characteristics, complex viscosity and dynamic moduli, were determined at different temperatures. These solutions behaved as viscous or viscoelastic liquids, depending on the concentration and temperature. At high concentrations, low temperatures, and high angular velocities, the IL solutions of cellulose featured a viscoelastic character which has the potential for fiber spinning. Dilute and concentrated solutions behaved as viscous liquids at low angular velocities, indicating lower potential for fiber spinning using established techniques.

IL/cellulosic solutions of DP 670, 1720, and 3900 were prepared and tested for their rheological characteristics. The complex viscosity and dynamic moduli were determined at different temperatures. The 3 wt% DP 670 solution behaved as a viscous liquid at all temperatures tested. The DP 1720 solution displayed a viscoelastic character at low temperature and behaved as a viscous liquid at high temperatures. The DP 3900 solution showed viscoelastic characteristics at the temperatures tested.

Manually prepared IL/cellulose solutions were compared to those mixed mechanically. The solutions were then tested for their rheological properties. The 10 wt% DP 670 solution prepared mechanically had a higher viscosity than the 10 wt% DP 670 solution manually prepared. For the 3 wt% DP 3900 solution, the manually prepared solution had a higher viscosity than the mechanically prepared solution. Both mechanically prepared solutions displayed viscoelastic properties. The manually prepared 3 wt% DP 3900 also displayed viscoelastic properties though the cross-over point was at a lower angular velocity than both of the mechanically prepared solutions. The manually prepared 10 wt% DP 670 solution displayed properties of a viscous liquid. The 3 wt% DP3900 showed no interaction between the mixing method and the temperature. Some interaction between mixing method and temperature for 10 wt% DP 670 was indicated, but definitively determined.

Lignin and xylose were added in various concentrations to IL/cellulose solutions to simulate the properties of wood. These additives increased the complex viscosity of the solutions compared to solutions with no lignin or xylose, but higher concentrations of additives lowered the viscosity. The solutions with additives also displayed viscoelastic properties. No interaction occurred between additives and temperature.

Master curves for the complex viscosity were generated and activation energies were calculated from the Arrhenius plots of the shift factors. The activation energy for flow of cellulose solutions in ILs is higher that that of some polymeric melts, such as low density

or high density polyethylenes. IL/cellulose solutions had rheological characteristics similar to some melt blowing grade polypropylene melts or lyocell solutions of comparable concentration, suggesting feasible processing procedures, such as spinning or melt blowing, for the manufacture of fiber or nonwoven products.

5.2 Recommendations

1. Test more solutions that are mechanically prepared
2. Determine how the rheological properties of the solutions change over time
3. Test solutions of higher DPs and lignin and/or xylose
4. Test solutions with the additives at higher concentrations than the cellulose

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Vita

Joy Louise Watson was born in South Carolina. In addition to attending high school there, she also attended summer programs sponsored by the National Science Foundation as well as the state Governor's School for Science and Math. Her undergraduate major is in chemical engineering from the University of Tennessee where she was Co-op Ambassador and Graduate Assistant. She has studied overseas and is proficient in another language. Her work experience includes positions with three major paper corporations. In December 2006 she will earn a Master of Science degree in Chemical Engineering from the University of Tennessee. Hobbies include shopping, traveling at a moments notice, pestering angelic little sister, and being a dork*.

*Disclaimer: The vita was written by Joy Louise Watson's mother and sister. It is the "angelic little sister" who is a dork and a doufus. (I love them dearly and could not have succeeded without their love and support.)