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Rheology of Lignin and Lignin/PET Blends

Jesse Daniel Bush
University of Tennessee - Knoxville

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To the Graduate Council:

I am submitting herewith a thesis written by Jesse Daniel Bush entitled "Rheology of Lignin and Lignin/PET Blends." I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemical Engineering.

Simioan Petrovan, Major Professor

We have read this thesis and recommend its acceptance:

John R. Collier, Billie J. Collier

Accepted for the Council:
Dixie L. Thompson

Vice Provost and Dean of the Graduate School

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Anne Mayhew
Vice Chancellor and
Dean of Graduate Studies

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RHEOLOGY OF LIGNIN AND LIGNIN/PET BLENDS

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

Jesse Daniel Bush
May 2006

Dedication

This thesis is dedicated to my late father, Gregory Bush, for teaching me about never giving up, my mother, Laura Bush, for her unending love and support, my brother, William Bush, for knowing and understanding me as no one else can, my grandparents, Radford and Irene Carroll, for always being a pillar of strength in my life, and my fiancé, Danna Reed, for her belief and devotion.

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Finally, I would like to thank my family and friends who never failed to be there when needed.

Abstract

Lignin is the second most abundant biomass resource on the planet. It results in industrial quantities as a byproduct of pulping industry and is mostly used as fuel in the pulping chemicals recovery process. Due to the high content of carbon and hydrogen, it can be also used for making carbon fibers. In this thesis some rheological characteristics of the lignin/polyester blends are presented. Polyesters are added to enhance the process ability of the lignin for manufacturing carbon fiber precursors by melt spinning. The effect of polyester addition on viscosity and dynamic moduli of different lignins (organosolv, washed kraft, and kraft mixed wood) is studied. All blends and pure lignins show a shear thinning behavior, except mixed wood lignins at low angular velocities, where a short range of shear thickening is recorded. Organosolv and washed kraft lignins have viscosity comparable with that of some melt blowing grade PPs, suggesting that these lignins and their blends may be used to manufacture nonwovens by the melt blowing process. Mixed wood lignin viscosity is much higher and the shear thickening at low angular velocities could be explained by crosslinking or condensation of different types of lignins, from softwood and hardwood species used in pulping. All lignins and their blends with PET behave as viscous or viscoelastic fluids, depending on temperature and composition, as shown by the dynamic moduli curves versus angular velocity. Mixed wood lignin features a broader range of viscoelastic behavior at low angular velocities.

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NOMENCLATURE AND ABBREVIATIONS

Nomenclature

A	area of the plate covered by material
V	velocity
F	force
h	distance between two parallel plates
τ	shear stress
$\dot{\gamma}$	strain rate
η	viscosity
γ	shear strain
γ_o	strain amplitude
τ_{o}	stress amplitude
ω	strain frequency
δ	phase angle
t	time
τ'	in-phase or elastic stress
τ'	out-of-phase or viscous stress
G'	storage modulus
G''	loss modulus
G^*	complex modulus
η^*	complex viscosity

η'	dynamic or in-phase viscosity
η''	dynamic loss or out-of-phase viscosity
f	frequency of oscillations
η_s	shear viscosity
a_T	temperature shift factor
η_∞	infinity-shear-rate viscosity
η_o	zero-shear-rate viscosity
T	temperature
T_o	reference temperature
η_r^*	reduced complex viscosity
ω_r	reduced angular velocity
λ	time constant or relaxation time
n	power-law exponent
ΔH	activation energy

Abbreviations

PAN	polyacrylonitrile
PET	polyethylene terephthalate
ARES	Advanced Rheometric Expansion System
ASAM	alkaline sulfite-anthraquinone-methanol

TDI	toluene diisocyanate
PP	polypropylene
ORNL	Oak Ridge National Laboratory
UT	University of Tennessee
OS	organosolv lignin
MWIAT	mixed wood indulin AT lignin
1369	washed 1369 lignin

CHAPTER 1. INTRODUCTION

1.1 Carbon fibers: uses, production, and unmet opportunities

Carbon fibers are characterized as being a light weight material with low density, high temperature resistance, high modulus, and high strength.[1, 2] These characteristics have helped carbon fibers dominate as a composite material in the fields of aerospace, sporting goods, and automotives. As price has continued to drop, use of carbon fibers to reinforce concrete has been adopted by the construction industry.[1,2] Carbon fibers consist of hexagonal carbon layers that are stacked forming small coherent units called crystallites which are only a few nanometers in the stacking direction.[2] Carbon fibers are produced from precursors. A precursor should give a high carbon yield, process economically, and easily convert to carbon fiber.[15] Carbon fibers were first produced commercially in 1959 by Union Carbide Corp., USA.[2] These first commercial fibers were rayon-based; since their development extensive research has been done to find more suitable raw materials for carbon fibers in the UK and Japan. Polyacrylonitrile (PAN) was successfully converted into carbon fibers in 1961 by Shindo.[2] PAN is a polymer with well known properties of low gas permeability, chemical resistance, and hardness and rigidity.[13] The mechanical properties of the PAN-based carbon fibers were much better than the previous rayon-based making PAN the most popular of the precursors.[2,15] The total projected consumption of PAN-based carbon fibers in 2007 is 23,000 tonnes.[15]

Commercial production has also been achieved from pitch precursors.[3] Pitch is a liquid-crystalline material which will readily orient during fiber formation, thus creating fibers with high moduli and thermal conductivity.[4] Pitch precursors have a higher yield than PAN, but are more graphitic in nature, therefore producing carbon fibers with poorer compression and transverse properties.[15] The same process steps (precursor fiber formation, stabilization, and carbonization) are used in producing PAN-based and pitch-based carbon fibers. The different precursors (polymeric versus liquid-crystalline) used for the two processes cause the final properties of the carbon fibers to be significantly different.[4] Of the production costs of PAN based carbon fibers, 51% is attributed to PAN precursor fiber manufacturing, followed by 22% to stabilization, and 15% carbonization.[15]

In addition to individual carbon fibers, there is also interest in the production of carbon fiber mats. The precursor carbon fiber mats could be produced in the same manner as polymer mats in the nonwovens industry, namely by a melt blowing process. A schematic in Figure 1 shows a typical melt blowing system. In this system a polymer melt is extruded through a die with multiple small holes and hot air streams flowing at high velocity elongate and cool the polymer jets into fine fibers that are blown onto a collector conveyor where they bond into a nonwoven web.

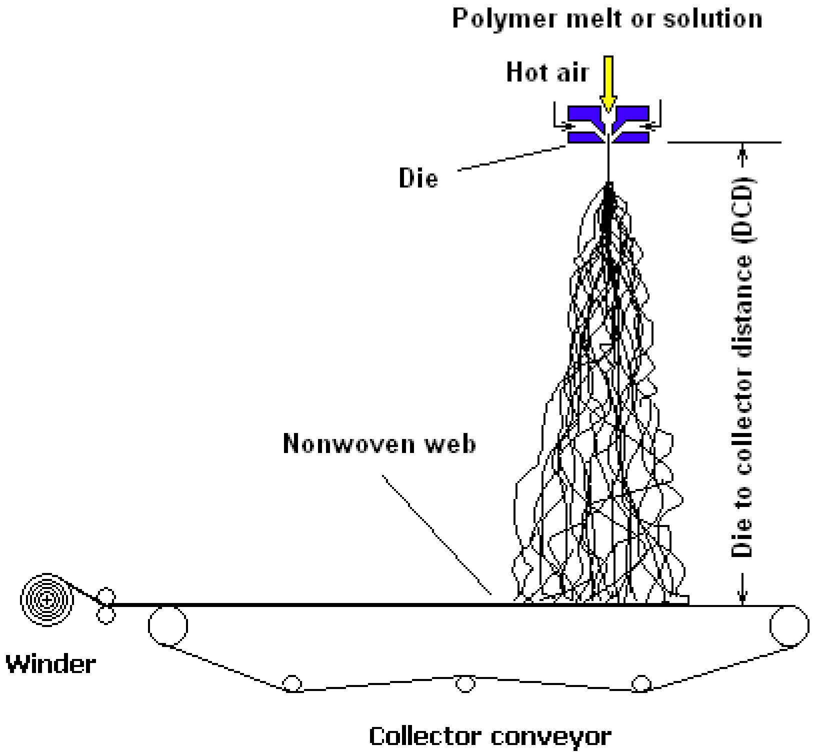

Figure 1. Schematic of melt blowing process

1.2 Motivation and relevance for present work

Because of the versatility and strength of carbon fibers there is significant room for growth if a suitable, less expensive, precursor is discovered. Production of carbon fibers from high-volume, low cost, renewable and recycled feedstock would reduce precursor and processing costs.[18] Previously it has been shown that lignin-blend fiber can be melt-extruded as a small tow. Graphitized lignin-blend fibers can be used in resin-fiber composites with normal fracture patterns, and to give good fiber/resin adhesion the smooth lignin-blend fibers can be plasma treated and silanated.[18]

Understanding and controlling the structure during the fiber formation step is vitally important to the optimization of the carbon fiber manufacturing process. Rheological characteristics are fundamental for the manufacturing of the precursor fibers from polymeric melts or solutions. Measurement of rheological properties of polymeric materials can greatly help to understand their structure. Also, rheological properties will be helpful in formulating polymer systems to produce desired physical properties of final products. Finally, rheological properties are used to obtain processing conditions and design the processing equipment.

In this research, rheological properties of three different polyethylene terephthalate (PET)/lignin blends were measured using an Advanced Rheometric Expansion System (ARES). Complex viscosity and dynamic moduli were measured for lignin blends at different temperatures.

CHAPTER 2. LITERATURE REVIEW

2.1. Lignin

Lignin, an aromatic polymer in wood, is the second most abundant organic material in nature.[14, 5] The composition of dry wood is primarily cellulose, lignin, hemicelluloses, and minor amounts (less than 10%) of other organic and inorganic materials.[5] Lignin makes up an average of 29% of the wood substance in softwoods and 21% in hardwoods.[14] Cellulose and hemicelluloses make up an average of 43% and 28% respectively in softwoods and 45% and 34% in hardwoods.[14] Lignin is a three-dimensional cross linked polymer and because of this structural feature it can be separated from the wood only as degradative products. The optimum strength of the wood structure is conferred by the continuous and inward concentration decreasing distribution of the lignin across the fiber wall. Fibers from the wood structure can be separated by mechanical and/or chemical treatments. Pure mechanical separation is the object of ground wood production for making newspaper and other products for which permanence properties are not very important. At the other extreme is the chemical pulping, where due to the very harsh chemical treatment and high temperatures, most of the lignin is degraded and solubilized in the cooking liquor. Lignin is subject to condensation reactions in alkaline or acid medium[14] and also demonstrated during the heating of wood.[31] Physical and chemical properties of commercial lignins depend on the pulping technique used to perform the delignification process and may be dependent also on the fibrous raw material.

2.1.1 Kraft pulping

Among the pulping techniques, kraft pulping is the most common process. The kraft, or sulfate, process is usually credited to C.F. Dahl[6], who modified the soda process, the first chemical pulping method using sodium hydroxide (NaOH) as a delignification reagent. Dahl experimented with adding salt cake, sodium sulfate, to the recovery furnace in an effort to find a substitute for the expensive soda ash, sodium carbonate.[6] Sodium sulfate is reduced to sodium sulfide (Na_2S) in the furnace. Thus, sulfide was introduced into the liquor system resulting in accelerated delignification creating a much stronger pulp. Delignification is simply the breaking down of the chemical structure of lignin.[6] This also gave the process a name as kraft is the word for strength in both Swedish and German. Because of the necessity for economical recovery of pulping chemicals, dominance by the kraft process came only after the Tomlinson recovery furnace was developed. This furnace combined heat and chemical recovery in the same unit with final evaporation and burning of spent liquor, or black liquor, which contains degraded products from the natural lignin. The extent of degradation depends on the severity of the pulping process. Finally chlorine dioxide bleaching was introduced to increase the brightness level of the pulp.[6]

Kraft pulping has the distinct advantage of being able to pulp essentially all wood species. It produces very strong quality pulp at a cost that no alternate method to date has been able to match. The kraft method has been around so long it has reached a very high stage of development, becoming increasingly more efficient. Kraft pulping disadvantages include producing low yields of pulp that is hard to bleach, it needs a large wood resource area, it is difficult to suppress the odoriferous compounds it produces, and it has high environmental impacts and troublesome bi-products.[28]

2.1.2 Organosolv pulping

The organosolv pulping process has been getting increased attention due to the lower capital cost, significantly lower environmental impact, and smaller scale, allowing smaller wood resource areas.[10] The use of organic chemicals to separate wood into its components was originally used to study lignin and carbohydrate chemistry. The organosolv process has proven to produce pulp with a quality near that of the kraft process. In recent years new methods of organosolv pulping have been developed in the search for a replacement for the kraft pulping process. Of these methods only those processes using lower aliphatic alcohols or lower organic peroxyacids have shown economic feasibility.[16]

2.1.2.1 Alcohols

Many different methods have been developed for alcohol pulping. The primary alcohols used in this pulping process are methanol and ethanol. Other alcohols such as propanol, isopropanol, butanol, and glycols have been proposed, but other than ethylene glycol, which is less attractive because it has a relatively high boiling point (471K), the other alcohols are more expensive than methanol and ethanol. Therefore very little attention has been paid to them.[16]

Methanol has been widely used as an additional chemical in kraft pulping. It will form inflammable vapors at relatively low temperature and therefore any process using it needs to be carefully designed and operated. Methanol has been utilized because it will increase the delignification rate of the lignocellulosic material by improving penetration of the pulping liquor. It also has a low boiling point making recovery by distillation relatively easy. The different methods of pulping utilizing methanol are catalyzed methanol pulping, sulfite pulping, alkaline sulfite-anthraquinone-methanol process (ASAM), soda pulping, and Organocell (MD) pulping.[16]

Of these methods ASAM seems to be the most promising of these methanol pulping methods. Compared to the kraft process ASAM has higher yield in softwood pulping, better pulp strength, chlorine free bleaching, no odor, low fresh water consumption, higher temperature and pressure, longer cooking time, and increased chemical demand for cooking. Existing kraft mill equipment may be used, although the presence of methanol requires additional equipment and makes the recovery cycle more complicated and expensive.[16]

Ethanol has been used to separate wood components and is one of the more promising organic pulping chemicals. Lignin has been eliminated from exploded wood by washing with ethanol. Ethanol pulping is more suitable for hardwoods than for softwoods. It penetrates the structure of the wood easily, giving uniform delignification.

Ethanol pulping requires high pressures and temperatures. This results in potential hazards of fire, explosion, and release of toxic chemicals. The different methods of pulping utilizing ethanol are catalyzed and autocatalyzed pulping, Alcell process, alkaline ethanol pulping, and ethanol in sulfite pulping.[16]

Of these methods the Alcell process is the most advanced, producing hardwood pulps of a satisfactory quality. The claimed advantages of the Alcell process are that it can operate at a smaller scale that the kraft process, the quality of pulp is competitive, the production costs are lower and can be utilized on a smaller scale, the process isolates lignin in a relatively pure form, hemicelluloses saccharides are recovered, and it is environmentally friendlier. In some cases aliphatic acids, aromatic acids and phenols have been found in the black liquor for aqueous ethanol pulping. This may suggest that the purity of the solvent may not be as claimed. Depending on the amount of ethanol used, investment in a recovery may be necessary.[16]

2.1.2.2. Organic acids

The only organic acids that have been intensively studied as pulping reagents are formic and acetic acid. When using acids, safety is always a concern. Atmospheric pulping can be utilized to make the operation of a plant safer. Operation cost are reduced by the fact that catalysts are not necessary when using organic acids, but complicated solvent recovery increases cost. There is also a need for corrosion resistant materials that would increase investment cost.[16]

The use of formic or acetic acid and corresponding peroxy acids is one of the most promising organosolv processes. It causes a hydrolytic breakdown of wood polymers into smaller and more soluble molecules. Peroxy acid is a highly selective chemical and does not react with cellulose and other wood polysaccharides. This method is called Milox pulping. The Milox process uses no sulfur and chlorine chemicals. Solvent recovery is relatively complicated in Milox pulping due to the formation of a binary azeotrope of formic acid and water and ternary azeotrope with water and acetic acid. This process is still developing and future work look towards improving the quality uniformity of the pulp, minimizing the loss of forming acid, minimizing the amount of water used in the process, and assessing the value of the by-products. It makes lignin more soluble by oxidation and more hydrophilic.[16]

2.2. Rheology

Rheology is the science of the deformation and flow of materials under imposed stress.[12,17] Rheological properties vary according to molecular structure, therefore differences in molecular structure can be determined by rheological measurements. Some of the structural differences that can be identified include: molecular weight, molecular weight distribution, long chain branching, cross linking and the dispersion of fillers. Molecular structure determines much of the behavior observed when processing a material.[25] So it follows that the rheology of a polymer material defines how the polymer can be formed, processed, and shaped.[12,17] Capillary and rotational rheometers are used to measure viscosity and other rheological characteristics.

2.2.1 Rheology measurements

Rotational rheometers can be operated in different modes and are equipped with different sets of tools or geometries, such as; parallel plates, cone and plate, bob and cup, concentric cylinder. With a parallel rotational rheometer, Figure 2, torque is applied by a motor and the shear stress is determined for this applied torque. Rotational speed and the gap, where the fluid is tested, are used to determine the shear rate.[26]. Viscosity represents the resistance to flow and is considered the most important flow property of any material. Viscosity, as defined in equation 1, is the ratio of the imposed shear stress to the shear rate. In parallel plate Shear stress, τ, is a force, F, applied tangentially, divided by area, A. Shear rate (gamma dot) is velocity, V, divided by the gap between the plates, h.

$$\eta = \frac{F/A}{V/h} = \frac{\tau}{\dot{\gamma}} \qquad (1)$$

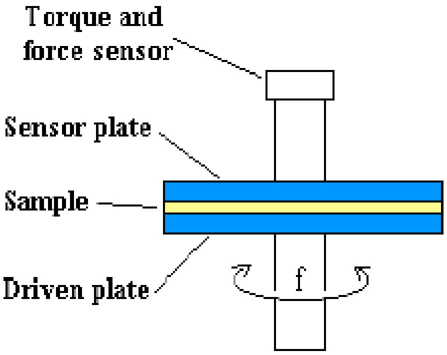

Figure 2. Schematic of a rotational rheometer

Dynamic properties can be determined by imposing sinusoidal stress or strain on a rotational rheometer, Figure 2. Polymer molecular characteristics, temperature, frequency, stress, and strain all influence dynamic properties.[25] In this measurement the known sinusoidal external conditions imposed are frequency and amplitude and the response of the fluid to these conditions is measured. When subjected to a sinusoidal stress, a perfectly elastic material develops stresses that are in-phase with the strain imposed. A Newtonian viscous fluid subjected to the same stress will not be in-phase, but instead a 90^{o} phase difference between stress and strain is observed. For polymer fluids that are viscoelastic (partly viscous and partly elastic) a phase difference (or phase angle) between 0^{o} to 90^{o} should occur.[26] An example of a sinusoidal oscillation technique is shown in Figure 3. The following rheological characteristics can be measured with a dynamic rotational rheometer.

Shear strain and shear stress

$$\gamma = \gamma_0 \sin \omega t \qquad (2)$$

$$\tau = \tau_0 \sin(\omega t + \delta) \qquad (3)$$

where

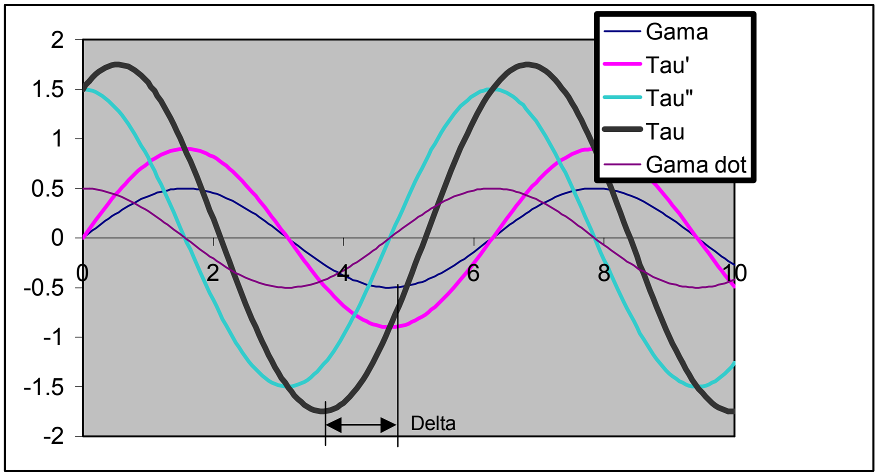

Figure 3. Sinusoidal oscillations technique. Stress is shifted by a phase angle delta; τ' is in-phase or elastic component of the stress; τ" is out-of-phase (90°) or viscous component of the stress; τ" is in-phase with with the rate of strain wave $\dot{\gamma}$.

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 sec

The stress wave can be decomposed into two waves

$$\tau = \tau' + \tau'' = \tau_0' \sin \omega t + \tau_0'' \cos \omega t \qquad (4)$$

τ' and τ" are defined in Figure 3.

The decomposition suggests two dynamic moduli, G', elastic (storage) modulus and G", viscous (loss) modulus. When plotted graphically versus ω, if G' is greater than G" the fluid is considered elastic and when G" is greater than G' it is considered viscous. The point in which they are equal is called the crossover point, the reciprocal of which is the relaxation time, λ. G' and G", can be considered to be the real part and the imaginary part of the complex modulus, G*, given by these two perpendicular vectorial components.[27, 24]

$$G' = \frac{\tau_0'}{\gamma_0} \qquad (5)$$

$$G'' = \frac{\tau_0''}{\gamma_0} \qquad (6)$$

$$G^* = G' + iG'' \qquad (7)$$

A viscoelastc body is considered linear if G’ and G” and δ are independent of the amplitudes of the specific strain in harmonic oscillations.[24, 27] Following linear algebra

$$|z| = |x + iy| \equiv \sqrt{x^2 + y^2} \qquad (8)$$

$$|G^*| \equiv \sqrt{G'^2 + G''^2} \qquad (9)$$

Similarly the complex viscosity, η*, is also given by two perpendicular vectorial components. Complex viscosity is considered a linear viscoelastic property and can be used to evaluate the flow properties of a polymer.[25, 24]

$$\eta^* = \sqrt{(\eta')^2 + (\eta'')^2} = \sqrt{\left(\frac{G''}{\omega}\right)^2 + \left(\frac{G'}{\omega}\right)^2} = \frac{|G^*|}{\omega} \qquad (10)$$

where

η’ = dynamic viscosity

η " = dynamic loss viscosity or out-of-phase viscosity

Straining conditions known as dynamic loading let the deformations change in time by the harmonic law.[24] Strain rate in turn becomes,

$$\dot{\gamma} = \frac{d\gamma}{dt} = \dot{\gamma}_0 \cos \omega t \tag{11}$$

$$\omega = 2\pi f \tag{12}$$

where f is the frequency of oscillations.

With capillary rheometers, as in Figure 4, pressure is applied by a piston, or ram, and the shear stress in the capillary is determined from this pressure. Flow rate is used to determine the apparent shear rate. The shear viscosity can then be calculated.

$$\eta_s = \frac{\tau}{\dot{\gamma}} \tag{13}$$

Capillary rheometers are used to measure rheological characteristics at high shear rates, because of high pressures and flow rates applied in the devices. Rheological characteristics at lower deformation rates allows for extension of the range of the shear rate in the capillary rheometer, according to the Cox-Merz rule, which is valid for most polymeric systems.[29]

$$\eta^*(\omega) = \eta_s(\dot{\gamma}) \quad at \quad \omega = \dot{\gamma} \tag{14}$$

Most of the polymeric systems show shear thinning (viscosity decreases as shear rate increases) or shear thickening (increase of viscosity with the increase in shear rate) behavior.

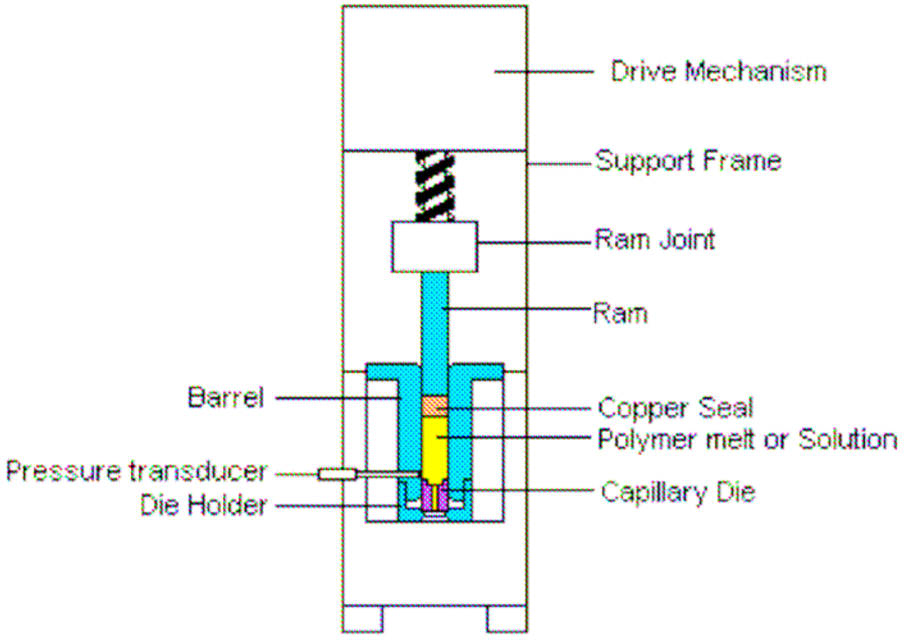

Figure 4. Schematic of a capillary Rheometer

2.3. Lignin and lignin blends

2.3.1. Recent uses and studies of lignin

Most of the commercial lignin is burned for energy and pulping chemical recovery and only about 1% is used as a chemical product in different areas.[10,11] Lignin can be used as natural filler in various polymer matrices to influence mechanical, physicochemical, and surface properties. It has been found that the tensile strength of different polymer products continually decreases with increasing lignin content.[11]

In a recent study by Cetin and Ozmen[23], lignin was used as a basis for adhesives for particleboard panels. This work attempted to develop a phenolic resin to partially replace phenol with a modified organosolv lignin in phenol-formaldehyde. Comparatively the organosolv based resins showed good strength and stiffness, and the tensile strength properties were equal or better. The study demonstrated that organosolv lignin was a feasible replacement for up to 30% of the phenol.[23]

Baumberger et al.[22] studied the use of kraft lignin mixed with wheat starch in extrusion of films. Films containing up to 30% lignin were obtained and evaluated by stress-strain tests at different humidity levels. Dissolution tests and water sorption isotherms showed that overall water affinity of the films was reduced by lignin addition and casting experiments showed a slight plastification of starch that may be due to the lower molecular weight fraction of kraft lignin.[22]

Lignin was used in a study done by Rotstein et al.[21] on the prevention of cholesterol gallstones in hamsters. Cholesterol gallstones were found in 21 of 24 of the control animals. Cholesterol gallstones were found in only 11 of 25 of the animals fed with lignin. Lignin appeared to prevent cholesterol gallstones by improving cholesterol saturation of bile.[21]

Rozman et al.[20] conducted preliminary studies on the use of Alcell lignin as a coupling agent in biofiber composites. The lignin was chemically modified with toluene diisocyanate (TDI). Using Fourier transform infrared analysis, a reaction between lignin and TDI was observed. The modified lignin imparted a greater compatibility in the biofiber composites. Better mechanical properties were shown by the composites with the modified lignin than in those with unmodified lignin.[20]

2.3.2. Recent studies of lignin as a basis of carbon fibers

In a study by Kubo and Kadla carbon fibers were produced from both a blend of kraft lignin and PET and of kraft lignin and polypropylene (PP). The lignin and the two polymers were thermally blended and spun into fibers. The fibers produced had a minimum diameter of >30µm. To prevent fusion of individual fibers a thermal stabilization step was used before carbonization. It was noted that thermo stabilization heating rates were higher for PET/lignin blends than for pure lignin fibers. Carbon fiber yield was noted to decrease with increasing incorporation of the synthetic plastic, but at 25% plastic, yield was still higher than that reported for petroleum pitch. It was also noted that the blend composition affected the surface morphology of the carbon fibers.[19]

Scientists at Oak Ridge National Laboratory (ORNL) have studied the development of low-cost carbon fibers from renewable resources in order to decrease the cost and increase the availability of carbon fiber. Work done with lignin based fibers, in collaboration with the University of Tennessee (UT) Chemical Engineering department, has shown proof of concept with the melt extrusion and spinning of 28 filament tow. There was an apparent increase in mechanical properties and fiber diameters were measured at ~15µm. This provided an understanding of improvements needed for larger scale manufacturing. Preliminary data suggested that yields of up to 50% are feasible. Composite mechanical properties were obtained from small epoxy resin composites made using carbon fibers from the UT 28 filament tow. Developments were also made in initial process control technologies and purification methods that remove or mitigate volatiles within lignin. In continuing work, ORNL will attempt to use lignin blend feedstock to develop methods for producing industrial quality carbon fibers. In work with project partners like UT, ORNL will attempt to address raw fiber production issues and evaluate carbon fiber production from lignin based multifilament tow.[18] The purpose of this research is to help address some of the raw fiber production issues by a rheological study of lignin and lignin/PET blends.

CHAPTER 3. MATERIALS AND INSTRUMENTS

3.1. Materials

Experiments were conducted with three different lignins, an organosolv lignin (OS) from the Aldrich group, a mixed wood indulin AT kraft lignin (MWIAT), and a washed 1369 kraft lignin (1369) both from ORNL. The lignins were selected from a larger group because of the variety of lignin that they represent and their ability to be easily shaped into circular discs through compression molding at ~200 C. The organosolv lignin represents the only non-kraft lignin in the study. The mixed wood refers to the lignin removed from both hard and soft woods used in the pulping process. Lignins are contaminated with salt, among other things, from the pulping process. When a lignin is washed with acidified distilled water the salt can be brought down to the desired level. The lignin was blended with PET from Eastman Chemical.

3.2 Equipment and experimental technique

Measurements of the dynamic rheological characteristics were done using the Advanced Rheometric Expansion System (ARES), TA instruments. Dynamic properties are determined by performing dynamic frequency sweep tests at different temperatures. Parallel plate geometry of 25mm plates was used for all experiments. Temperature was controlled by a forced air convection oven. Test conditions were obtained through preliminary tests, such that the minimum and maximum fell within the torque range of the ARES. The lower plate of the ARES is attached to a computer controlled motor, while the upper plated is attached to computer interfaced torque and force transducers. Based on the torque measured by the computer the ARES will switch between a lower and higher range transducer automatically.

The three lignins were blended with PET at percentages of 100, 95, 85, and 75% lignin. The PET was dried for 24 hours in a vacuum oven and ground into powder before blending with the lignin. The blends were pressed into circular discs by compression molding at ~200 C.

The sample was inserted between the two circular plates heated to the testing temperature. The ARES was used for a dynamic strain sweep of OS lignin at 85/15 lignin/PET blend at 165 C. A strain sweep holds frequency and temperature constant while making step increases in strain. This helps to determine the limits of linear viscoelasticity and torque levels, and characterizes samples that exhibit extreme nonlinear behaviors. Dynamic frequency sweep data were gathered using the ARES for all lignin and lignin blends. A frequency sweep takes measurements at different frequencies while holding strain and temperature constant. This sweep should ideally be within the linear viscoelastic region given by the strain sweep. Temperatures for the dynamic frequency sweeps were selected based on observations of first signs of melting.

CHAPTER 4. RESULTS AND DISCUSSION

4.1 Organosolv complex viscosity

The viscosity of OS and OS blended with 5, 15, and 25% PET was measured at 155, 165, and 175 C. A dynamic strain sweep from 0.01 to 100 rad/sec was run on the 85/15 OS lignin/PET at 165 C to test the linear viscoelastic region of lignin/PET blends. The results in Figure 5 show an approximately linear region within the range of strains. A strain of 1% was chosen for all other tests. Figures 6 to 9, show complex viscosity vs. angular velocity of OS and OS blends at 155, 165, and 175 C respectively. Multiple runs were preformed on 85/15 OS/PET at 165 C to check experimental errors. The error bars are shown in Figure 7. All samples show a shear thinning trend at all temperatures and concentrations. They also show a decrease in complex viscosity with increasing temperature. For all temperatures and blends, fibers were formed when the plates of the ARES were pulled apart. The fibers were fine and brittle, on both top and bottom plates, about an inch long, and numbered around 10-15.

Figures 10 to 12 show the complex viscosity against angular velocity of lignin and lignin blends at the different compositions. The higher the percentage of PET in the sample, the higher is the viscosity. There is very little difference in complex viscosity between 0 and 5% PET. Complex viscosity increases at all three temperatures upon increasing the PET percentage to 15 and 25%.

As shown in Figure 13, The highest viscosities are found in the 25 and 15% blends at 155 C, followed by 25% at 165 C and 5% at 155 C. The three lowest viscosities are 0% at 175 C, 5% at 175 C, and 15% at 175 C. This suggests for the OS blends temperature has more influence on viscosity than percentage of PET from 0 to 5%. As the angular velocity gets higher there is a trend towards infinity-shear-rate viscosity in OS blends. The viscosity of OS blends is comparable to that of melt blowing grade PPs (zero-shear-rate viscosity at 200 C of 708 and 320 Pa s for melt blowing grade PP of 22 and 35 g/(10 min), respectively). This suggests that lignin could be used for the manufacture of nonwoven mats by melt blowing process.

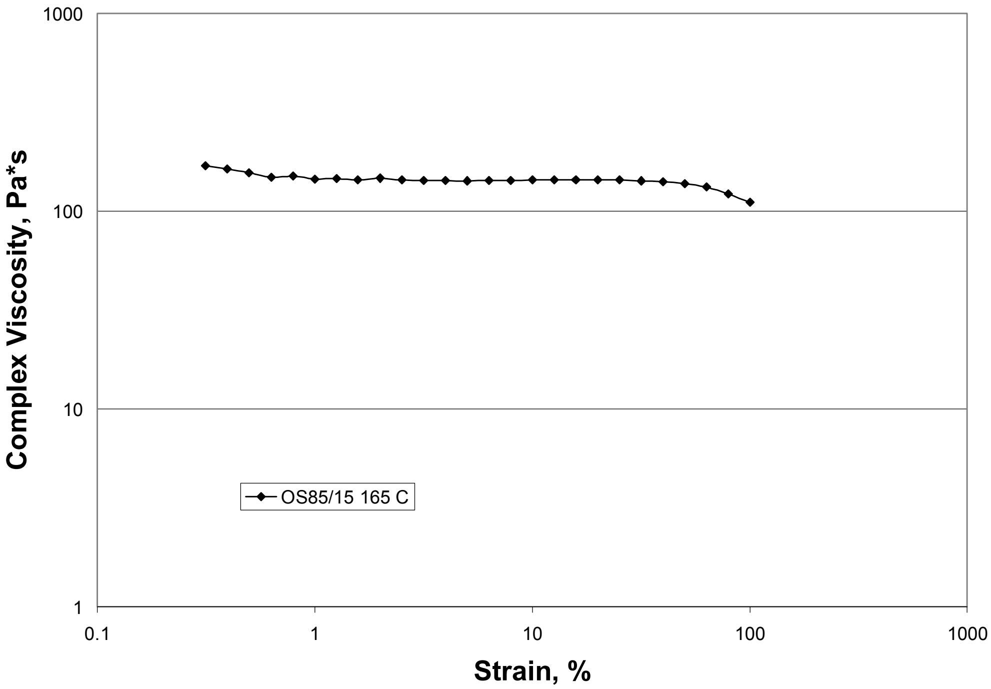

Figure 5. Viscosity against strain for 85/15 OS/PET at 165 C

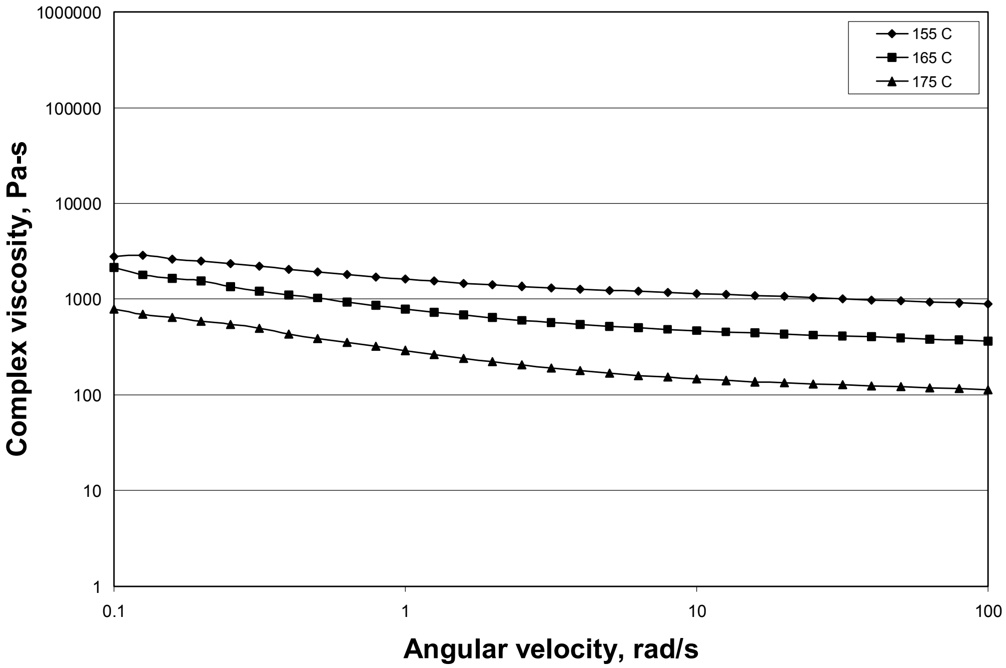

Figure 6. Complex viscosity against angular velocity for 75/25, OS/PET mixture

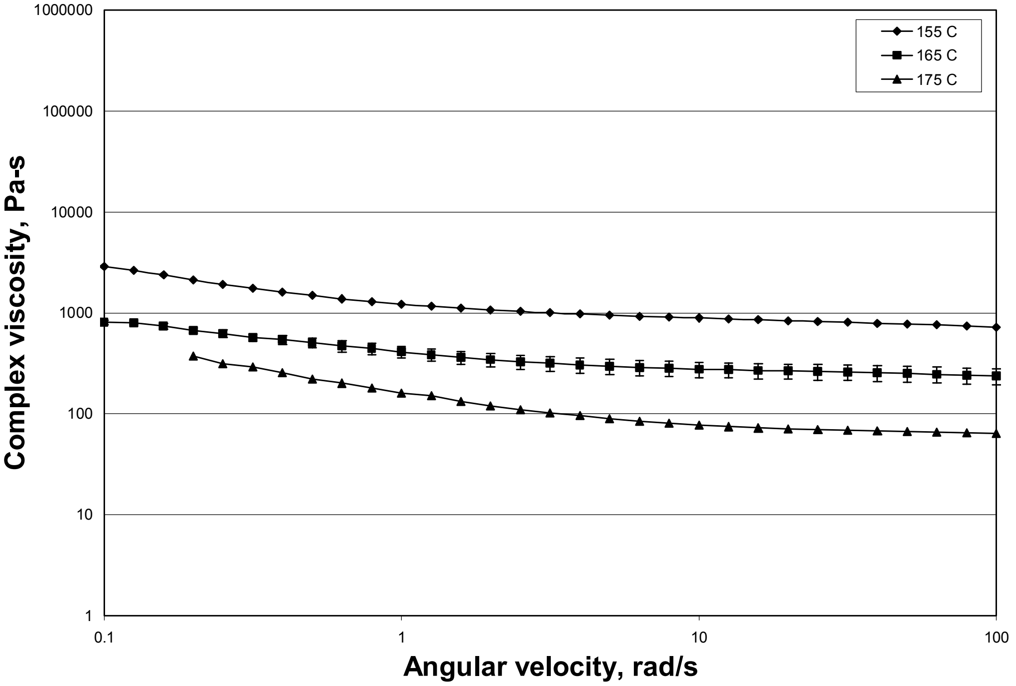

Figure 7. Complex viscosity against angular velocity for 85/15, OS/PET mixture

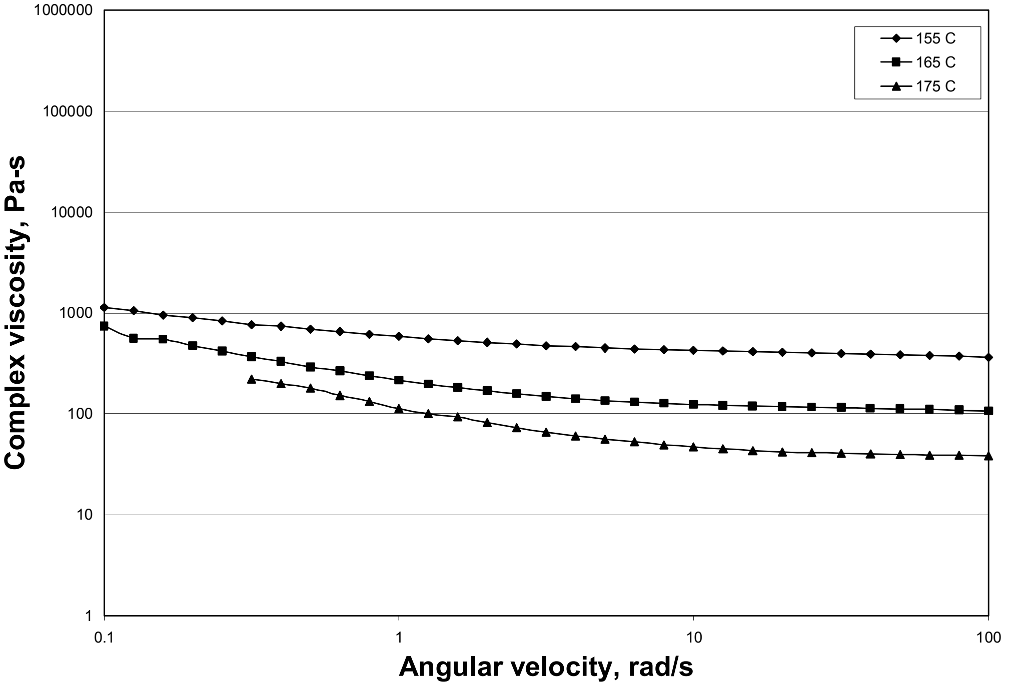

Figure 8. Complex viscosity against angular velocity for 95/05, OS/PET mixture

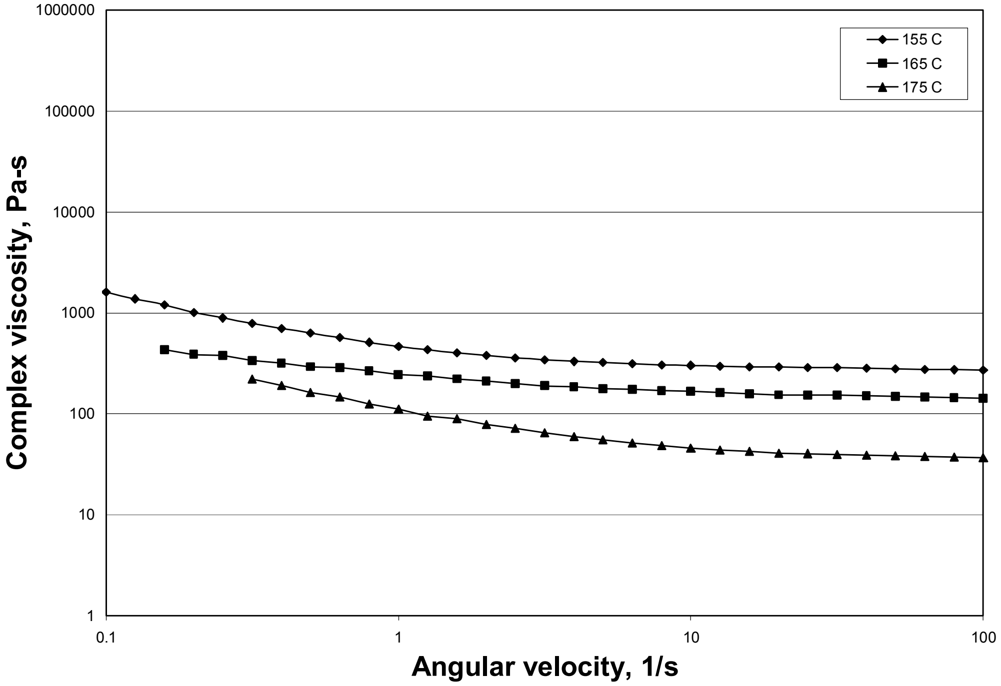

Figure 9. Complex viscosity against angular velocity for 100% OS

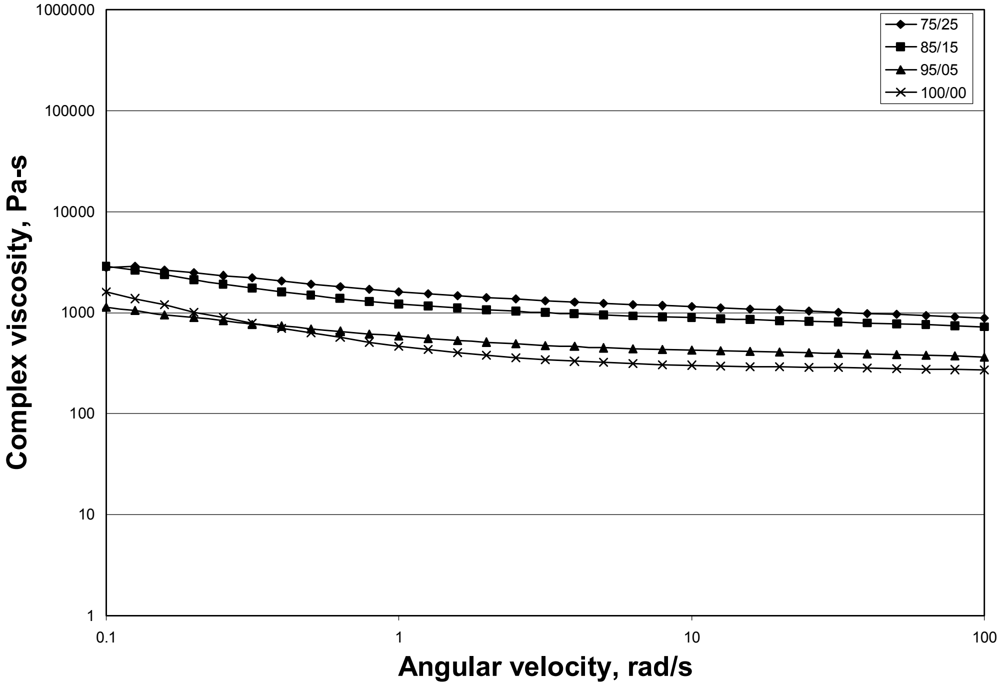

Figure 10. Complex viscosity against angular velocity for OS/PET mixtures at 155 C

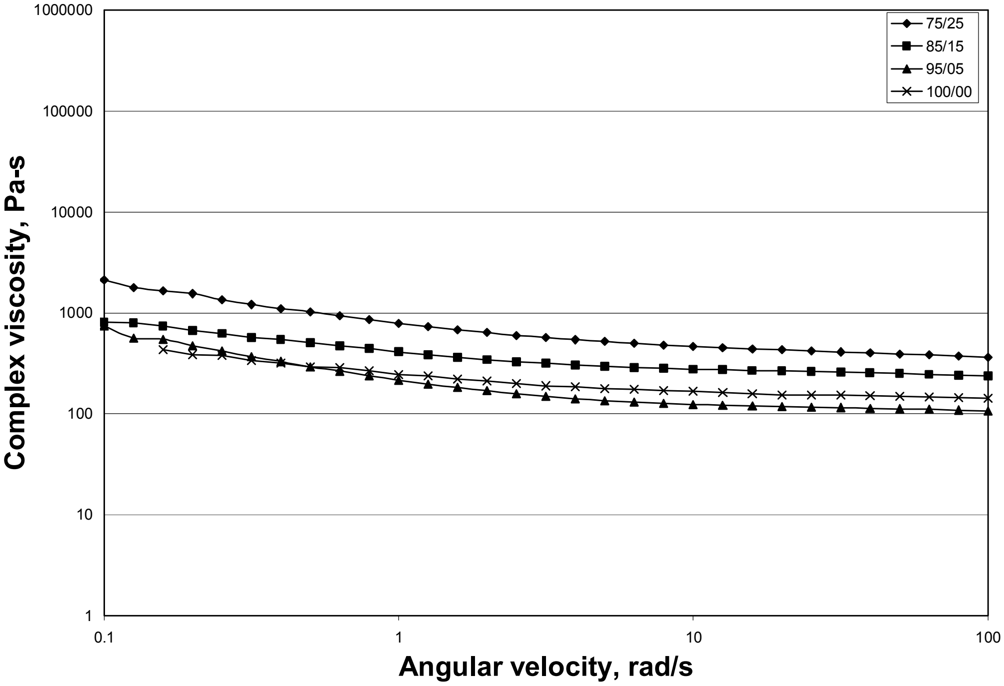

Figure 11. Complex viscosity against angular velocity for OS/PET mixtures at 165 C

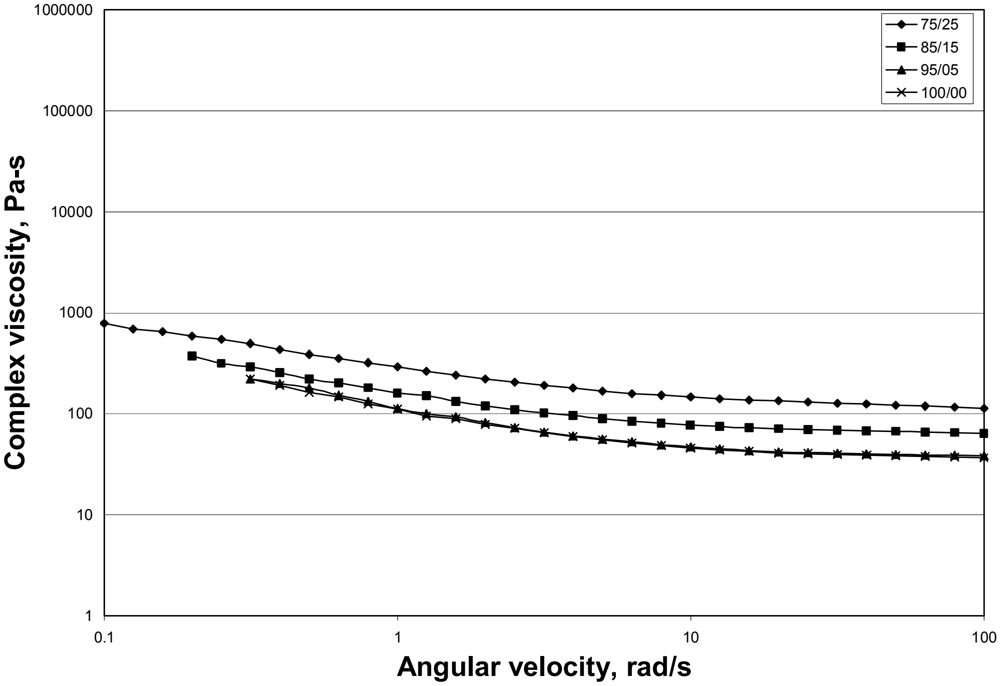

Figure 12. Complex viscosity against angular velocity for OS/PET mixtures at 175 C

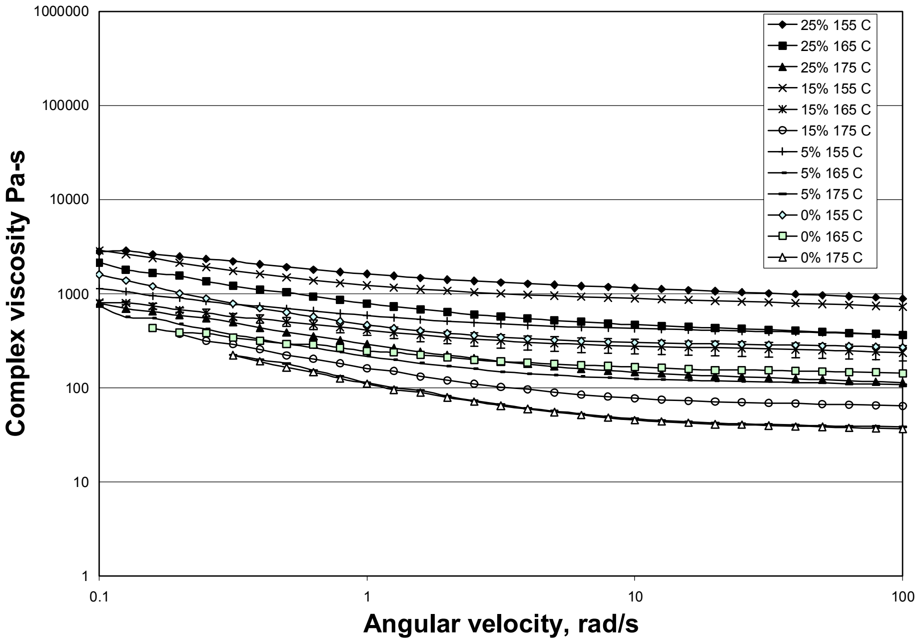

Figure 13. Complex viscosity against angular velocity for OS/PET mixtures

4.1.1 Organosolv dynamic moduli

G' and G" were also measured for this lignin sample. Figures 14 to 17 show G' and G" vs. angular velocity for OS and OS blends at 155, 165, and 175 C, respectively. The point in which they are equal is called the crossover point. This point serves as the division between the viscoelastic and viscous regions. The viscoelastic region of OS and OS blends occurs at low angular velocities. As temperature of OS and OS blends gets higher the crossover point shifts to higher angular velocities increasing the viscoelastic region. As lignin content increases from 75% to 100% the crossover point occurs at higher angular velocity extending the viscoelastic region. All samples show a decrease in G' and G" with increasing temperature. At 155 C, with the exception at 100% OS lignin, all OS blends behave as viscous fluids at low angular velocities. At 165 C all of the OS blends, except 75% OS, behave as viscoelastic fluids at low angular velocities. At 175 C, all of the OS lignin blends behave as viscoelastic fluids at low angular velocities.

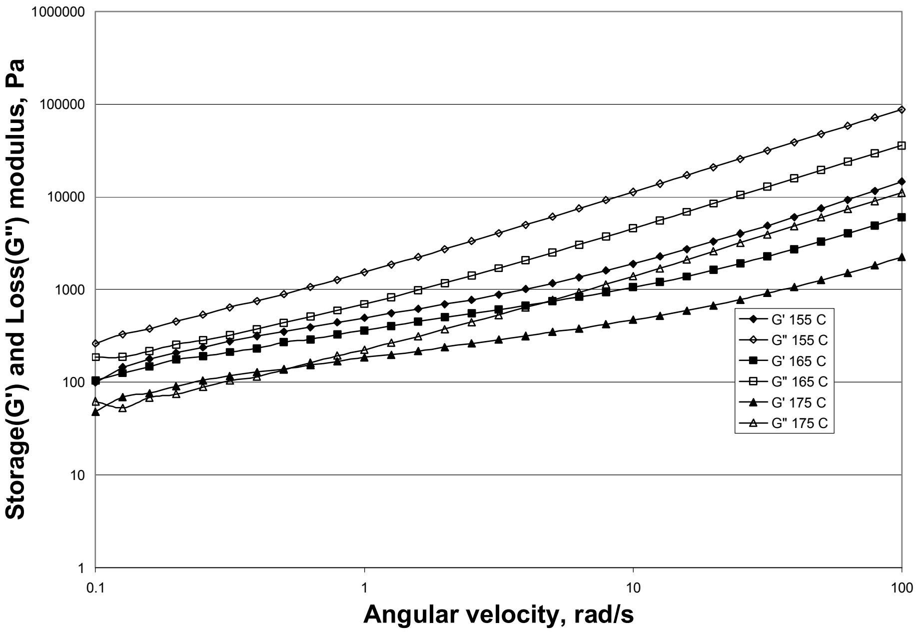

Figure 14. G’ G” against angular velocity of 75/25 OS/PET at 155, 165, and 175 C

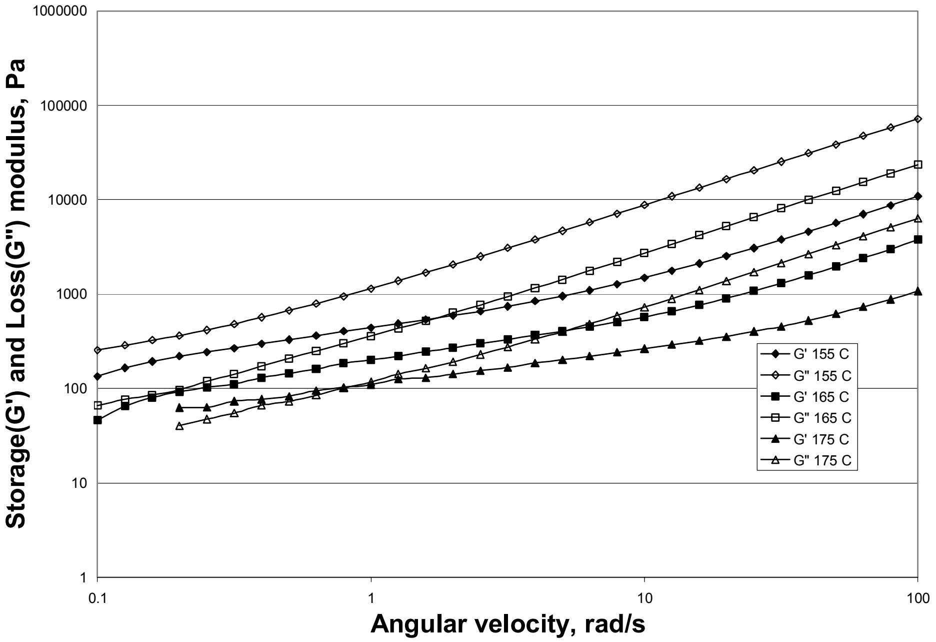

Figure 15. G’, G” against angular velocity of 85/15 OS/PET at 155, 165 and 175 C

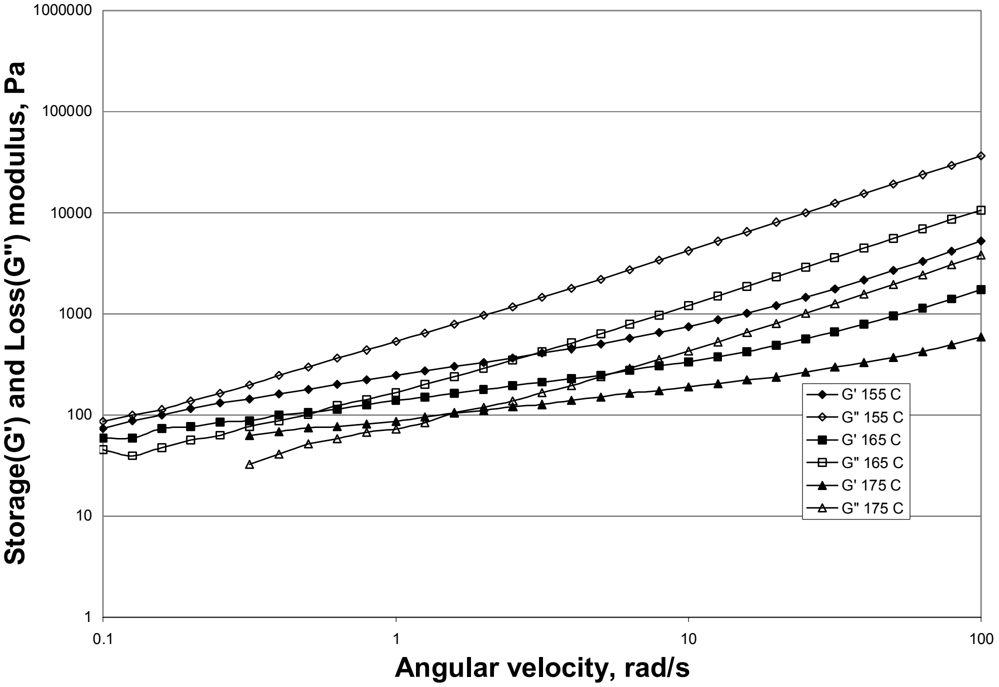

Figure 16. G’, G” against angular velocity of 95/05 OS/PET at 155, 165, and 175 C

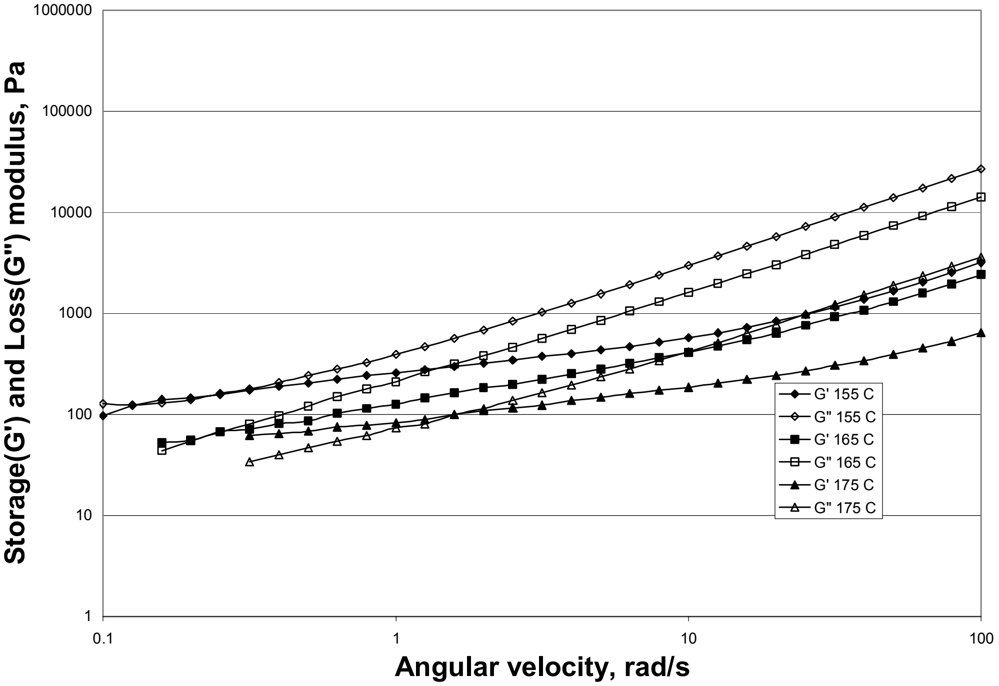

Figure 17. G’, G” against angular velocity of 100% OS lignin at 155, 165 and 175 C

4.1.2 Temperature shifting

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 viscosity curve to generate master curves and shift factors, from which activation energy for flow can be calculated. In the following, the method of reduced variables[30] was used in order to develop master curves by plotting the reduced complex viscosity η_r^* vs. reduced angular velocity ω_r. Because the complex viscosity curves for OS/PET blends show a trend to an infinity-shear-rate viscosity, this will be used to calculate the shift factor and not zero-shear-rate viscosity, as is the case for most of the melt or solution polymeric systems.

The shift factors are defined by the following equation

$$a_T = \frac{\eta_\infty(T)T_0}{\eta_\infty(T_0)T}, \tag{15}$$

where $\eta_\infty(T)$ and $\eta_\infty(T_0)$ are infinity-shear-rate viscosities of the solutions at temperature T and reference temperature T_0, respectively. Then, the reduced variables can be calculated with equations (16) and (17):

$$\eta_r^* = \eta^*(\omega,T)\frac{\eta_\infty(T_0)}{\eta_\infty(T)} = \eta^*(\omega,T)\frac{T_0}{a_T T} \tag{16}$$

$$\omega_r = \omega a_T. \tag{17}$$

Infinity-shear-rate viscosities of OS at different temperatures were determined by fitting the experimental data with a Carreau model given by equation (18):

$$\eta = \eta_0 + (\eta_0 - \eta_\infty)\left[1 + (\lambda\dot{\gamma})^2\right]^{(n-1)/2}, \tag{18}$$

where λ is a time constant η_0 is zero-shear-rate viscosity and n is the power-law exponent.

The temperature dependence of a_T is often found to be an "Arrhenius dependence" of the following form:

$$a_T = \exp\left[\frac{\Delta H}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right], \tag{19}$$

where ΔH is the activation energy of flow and R is the ideal gas constant.

A temperature shift was performed for the 95/05 OS/PET lignin blend. Figure 18 shows Carreau parameters η_∞, λ, n, and the shift factors at the three temperatures. These values were used to create a master curve. Data points for the complex viscosity of 95/05 OS/PET are shifted and fitted to the master curve in Figure 19. The coefficient of determination ($R^2 = 0.99$) shows that the shifting procedure is very accurate. The Arrhenius plot in Figure 20 shows the activation energy ΔH for the lignin blend to be 45.5 Kcal/mol with a correlation coefficient of 0.99. This activation energy for shear flow of 95/05 OS/PET is higher that that of some polymeric melts, such as low density or high density polyethylene.

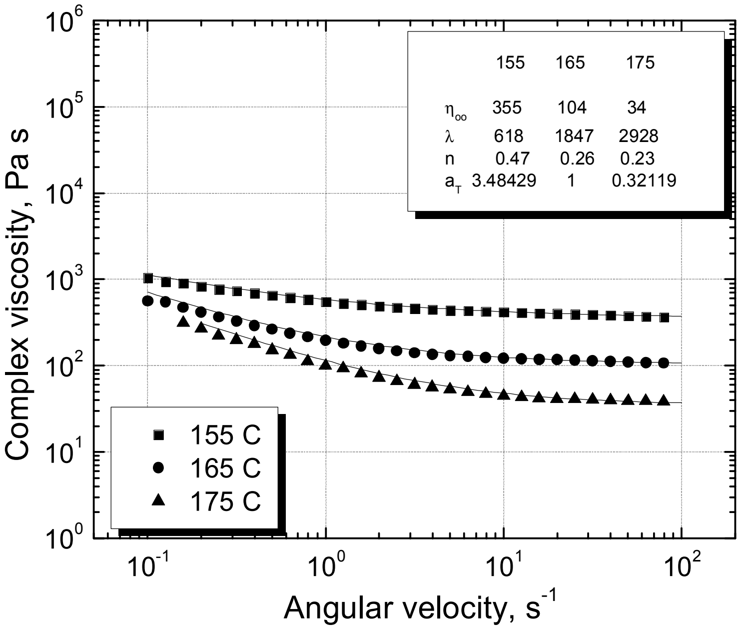

Figure 18. Complex viscosity against angular velocity for 95/05 OS/PET

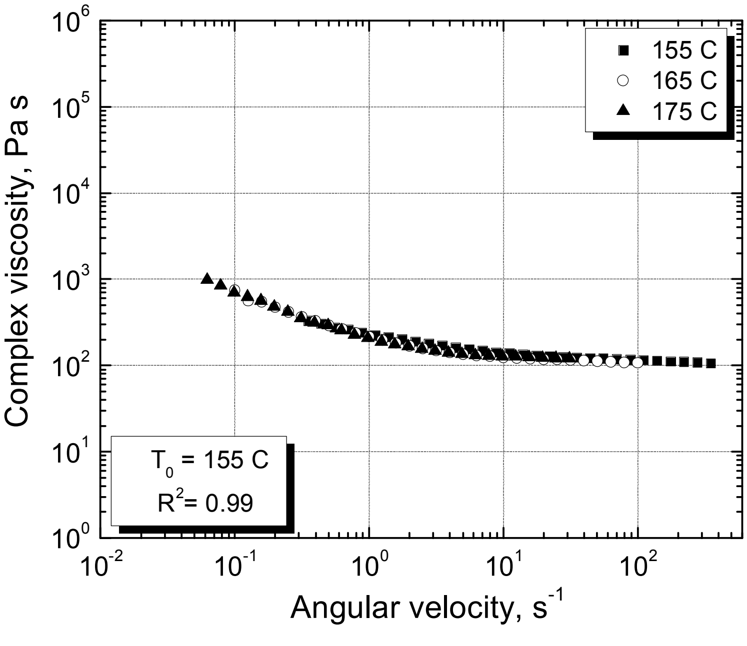

Figure 19. Temperature shifted complex viscosity against angular velocity.

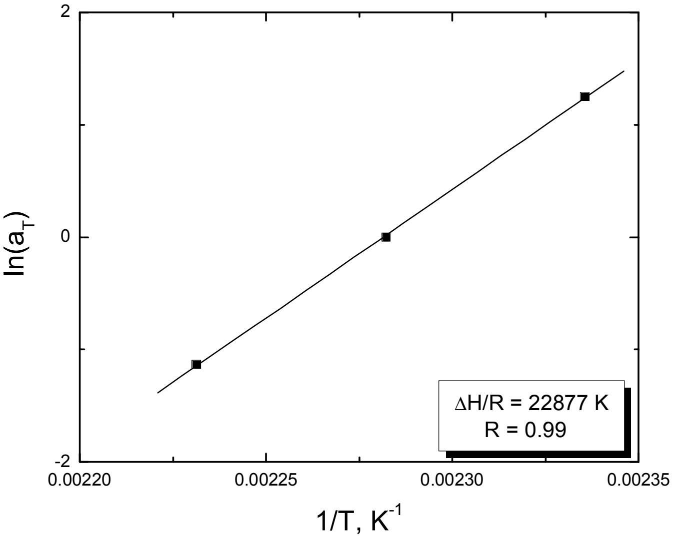

Figure 20. Arrhenius plot for the shift factors of 95/05 OS/PET lignin blend

4.2 Washed 1369 complex viscosity

The viscosity of 1369 and 1369 blended with 5, 15, and 25% PET was measured at 190, 200, and 210 C (Figures 21-24). Multiple runs were performed on 85/15 1369/PET at 200 C to check experimental errors. The error bars are shown in Figure 22. At low angular velocities there is a slight increase in viscosity, as displayed in Figure 20. A slight Newtonian plateau is shown at some of the higher temperatures in Figures 21 and 22. After the slight increase all samples show a shear thinning trend at all temperatures and concentrations. All compositions show a decrease in complex viscosity with an increase in temperature. When the plates of the ARES were pulled apart at 210 C all samples produced fibers. Only the higher percentage PET produced fibers at the lower temperatures. The fibers were fine and brittle, on both top and bottom plates, about an inch long, and numbered around 10-15.

Figures 25 to 27 show the complex viscosity against angular velocity of lignin and lignin blends at the different compositions. The difference in complex viscosity between 0, 5, and 15% PET, at all temperatures, is very small showing no effect on the viscosity. However, upon increasing the percentage of PET to 25% there is a significant increase in the complex viscosity at all three temperatures. This trend indicates a change in the blends characteristics within this range of composition.

A graph showing washed 1369 at all mixtures, at all temperature is shown in Figure 28. The highest viscosities are found in the 25% blends at all three temperatures. The three lowest viscosities are 0% at 210 C, 5% at 210 C, and 15% at 210 C. Temperature shifting was not done because a trend towards infinity-shear-rate or zero-shear-rate viscosity is not seen in 1369 blends. With the exception of the 75% 1369, the viscosity of 1369 blends at 200 and 210 C is comparable to that of melt blowing grade of PPs.

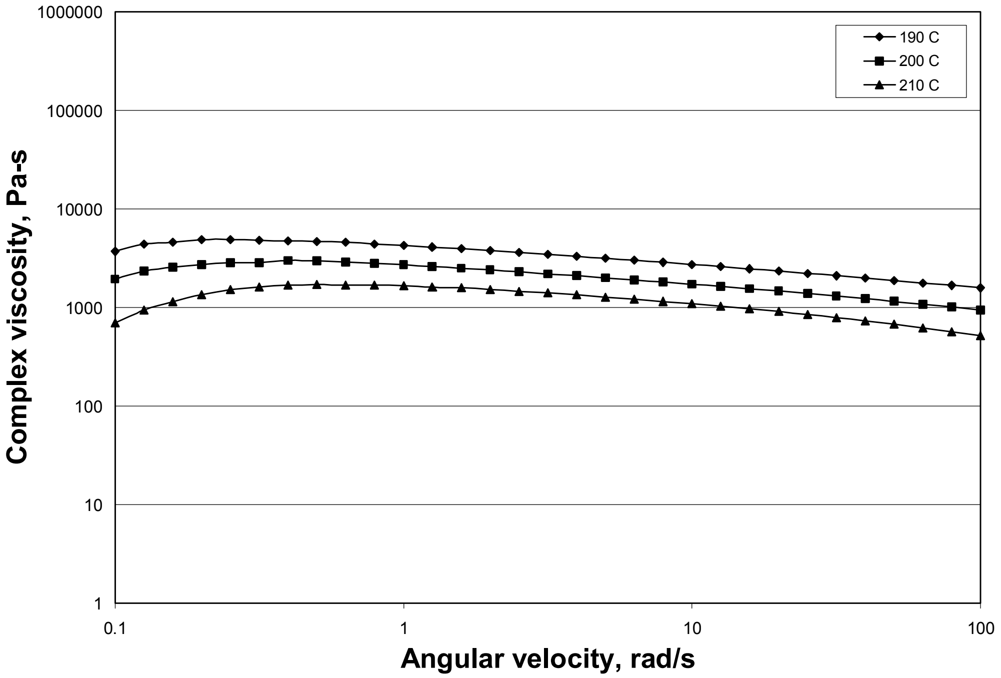

Figure 21. Complex viscosity against angular velocity for 75/25, 1369/PET mixture

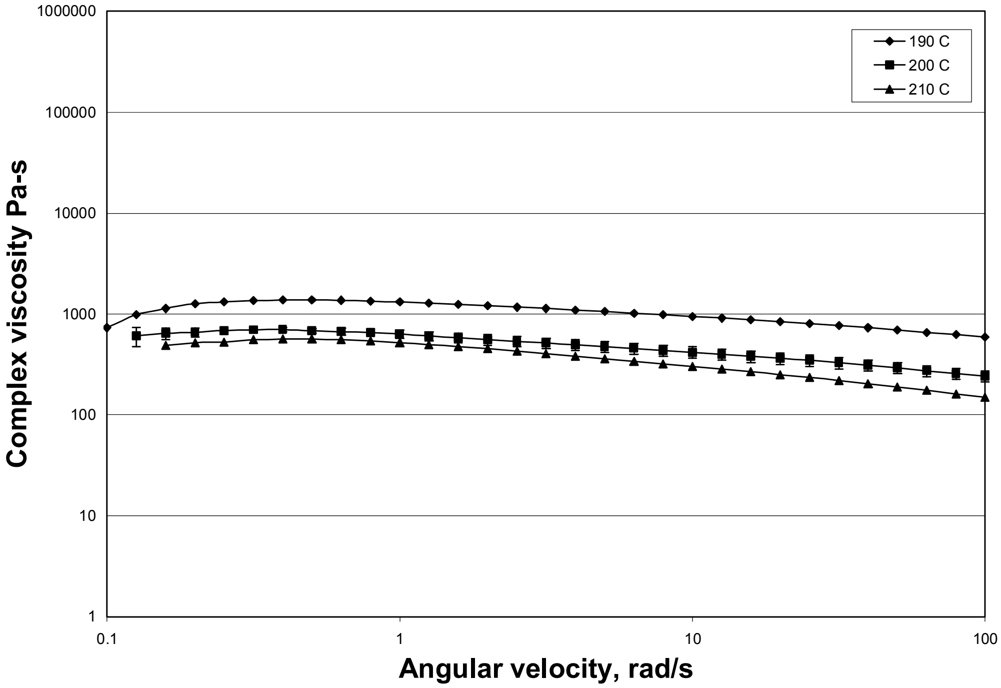

Figure 22. Complex viscosity against angular velocity for 85/15, 1369/PET mixture

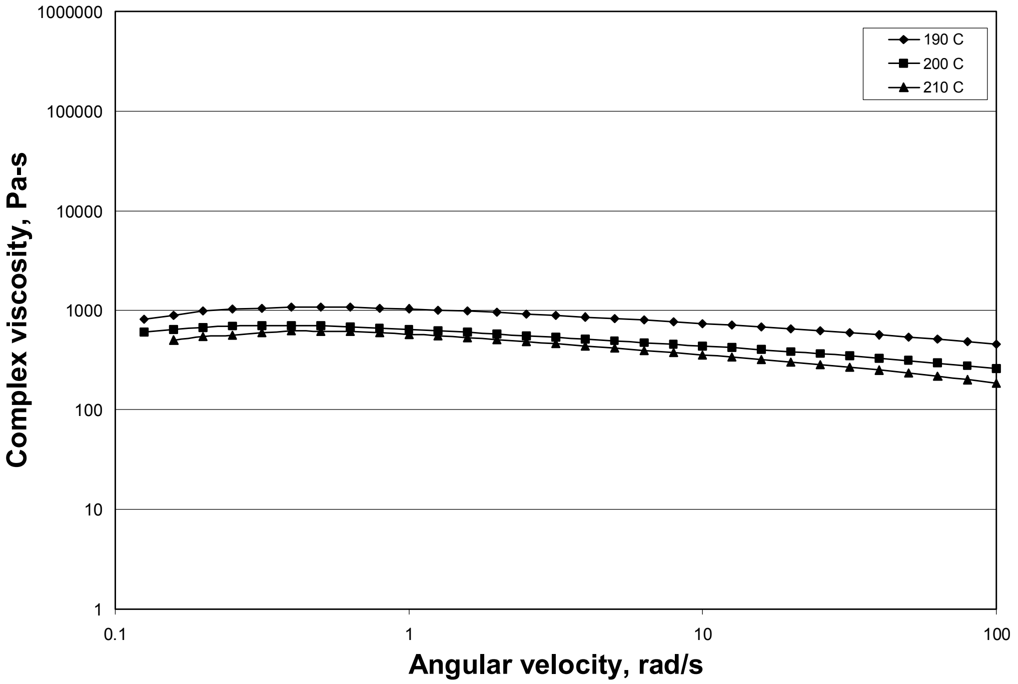

Figure 23. Complex viscosity against angular velocity for 95/05, 1369/PET mixture

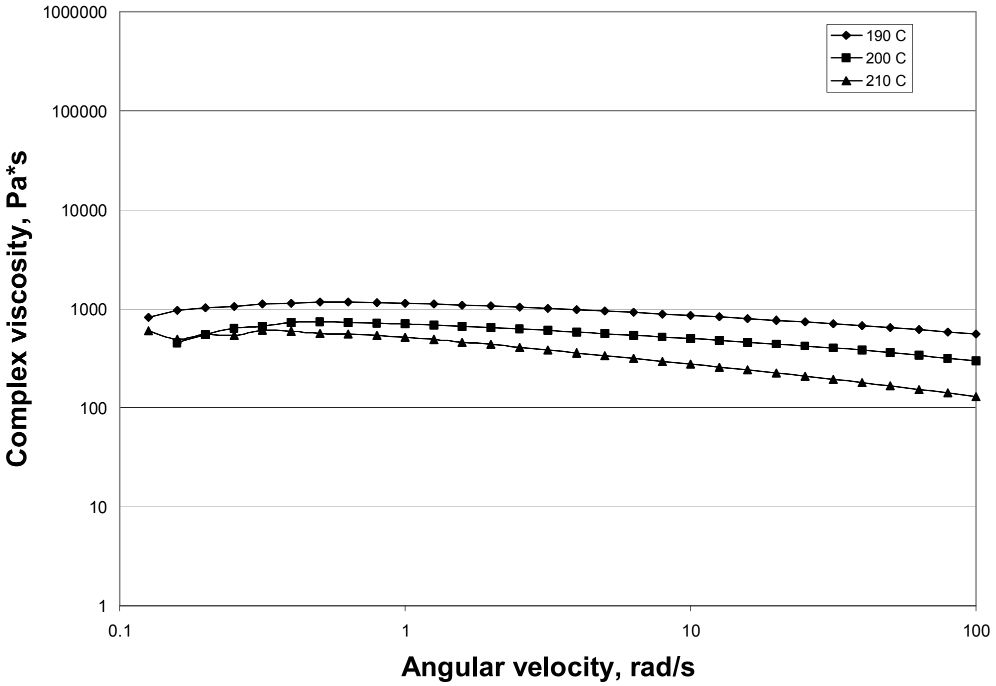

Figure 24. Complex viscosity against angular velocity for 100% 1369

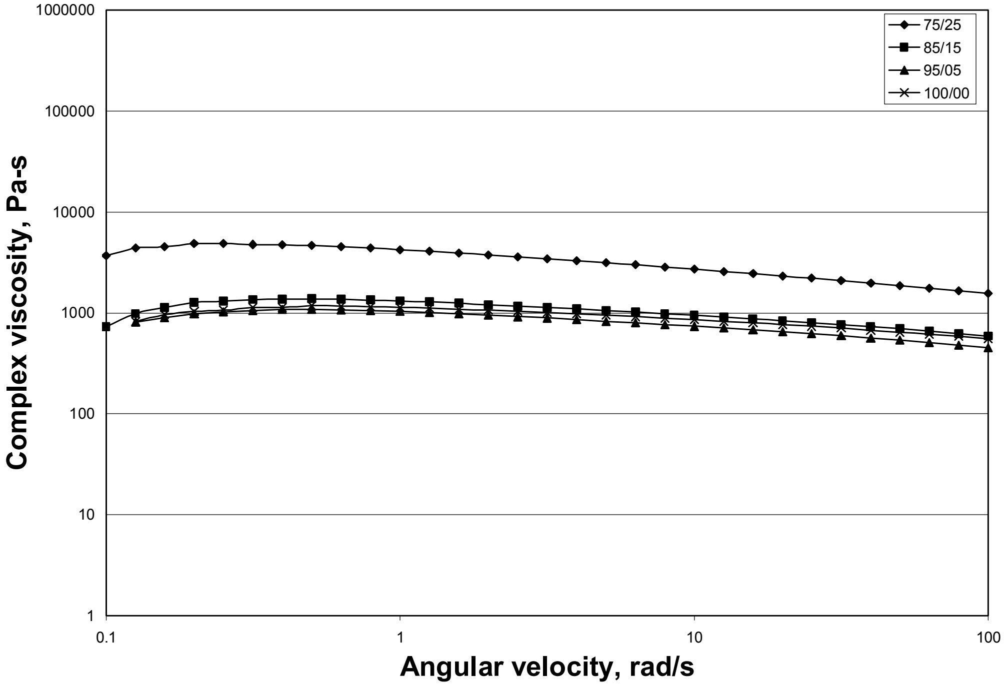

Figure 25. Complex viscosity against angular velocity for 1369/PET mixtures at 190 C

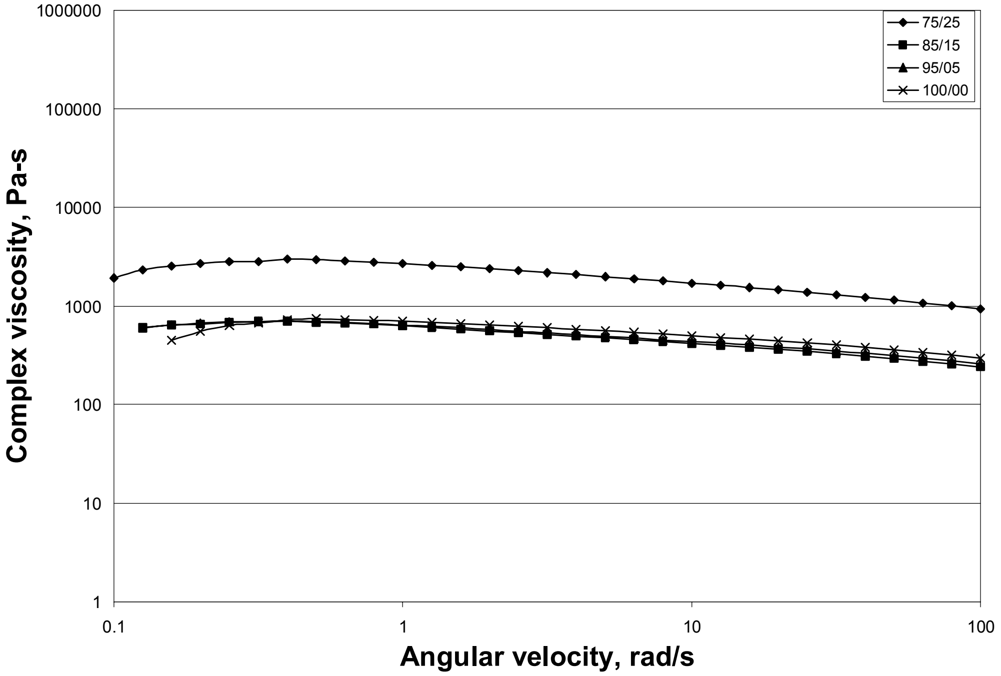

Figure 26. Complex viscosity against angular velocity for 1369/PET mixtures at 200 C

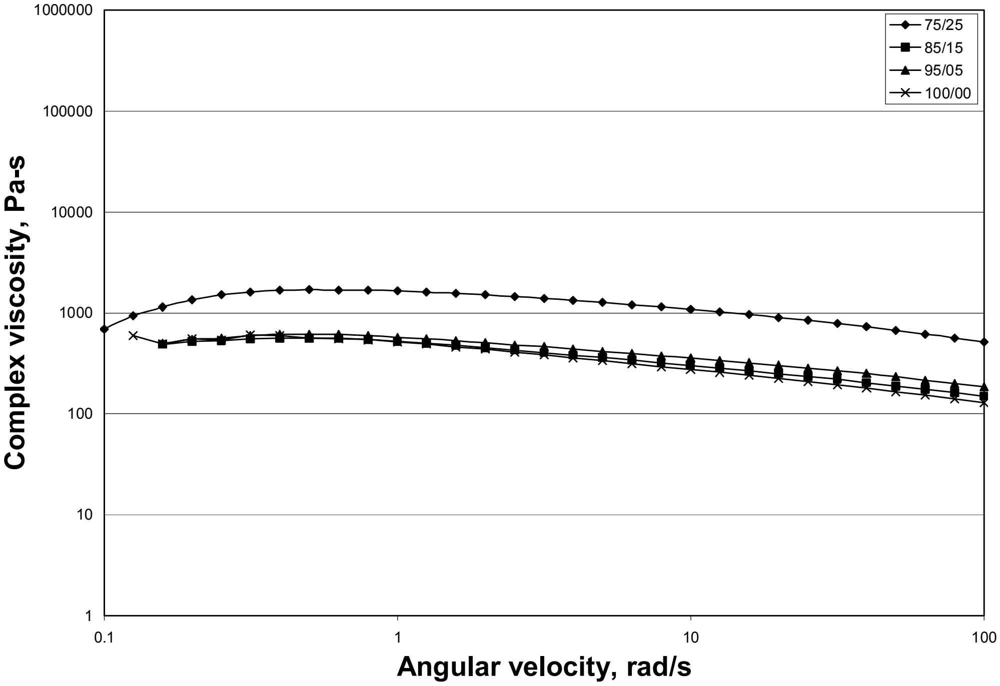

Figure 27. Complex viscosity against angular velocity for 1369/PET mixtures at 210 C

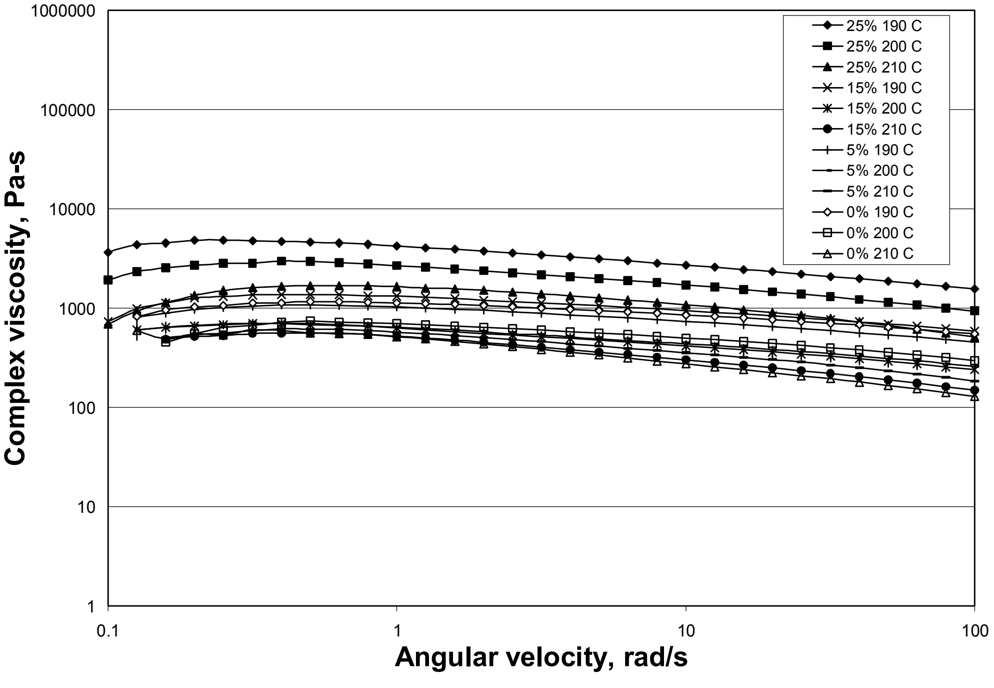

Figure 28. Complex viscosity against angular velocity for 1369/PET mixtures

4.2.1 Washed 1369 dynamic moduli

The storage modulus and the loss modulus for 1369 and 1369 blends were also measured. Figures 29 to 32 show G' and G" vs. angular velocity for 1369 and 1369 blends at 190, 200, and 210 C, respectively. The viscoelastic region for 1369 and 1369 blends occurs at very low (<1) angular velocities. As temperature increases the crossover point occurs at higher angular velocity increasing the viscoelastic region. As lignin content increases from 75% to 100% the crossover point occurs at higher angular velocity slightly extending the viscoelastic region. The blend of 75/25 1369/PET behaves as a viscous fluid at every temperature. The blend of 85/15 1369/PET at 210 C behaves as a viscoelastic fluid at very low angular velocities, all other temperatures behave as a viscous fluid. The blends of 95/05 1369/PET and that of 100% washed 1369 lignin at 200 C and 210 C both had viscoelastic regions at very low angular velocities.

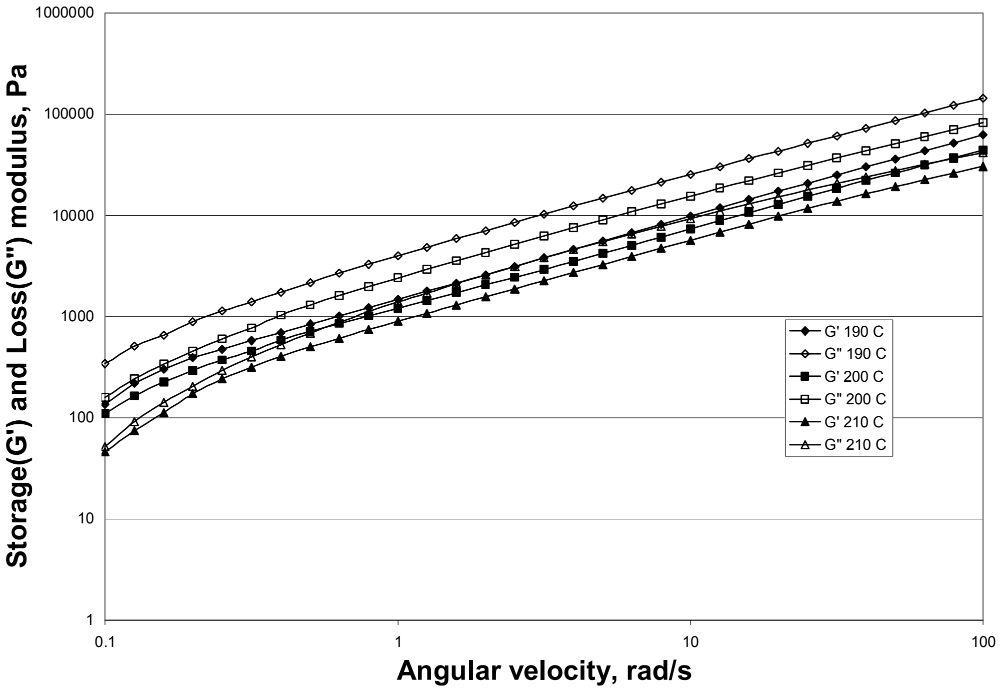

Figure 29. G', G" against angular velocity of 75/25 1369/PET at 190, 200, and 210 C

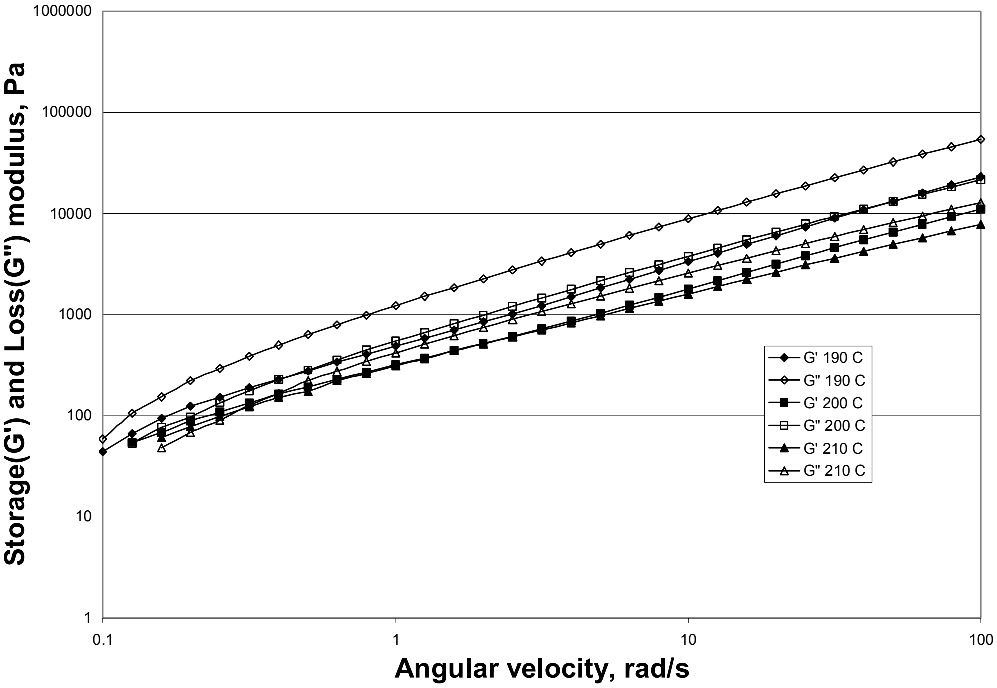

Figure 30. G’, G” against angular velocity of 85/15 1369/PET at 190, 200, and 210 C

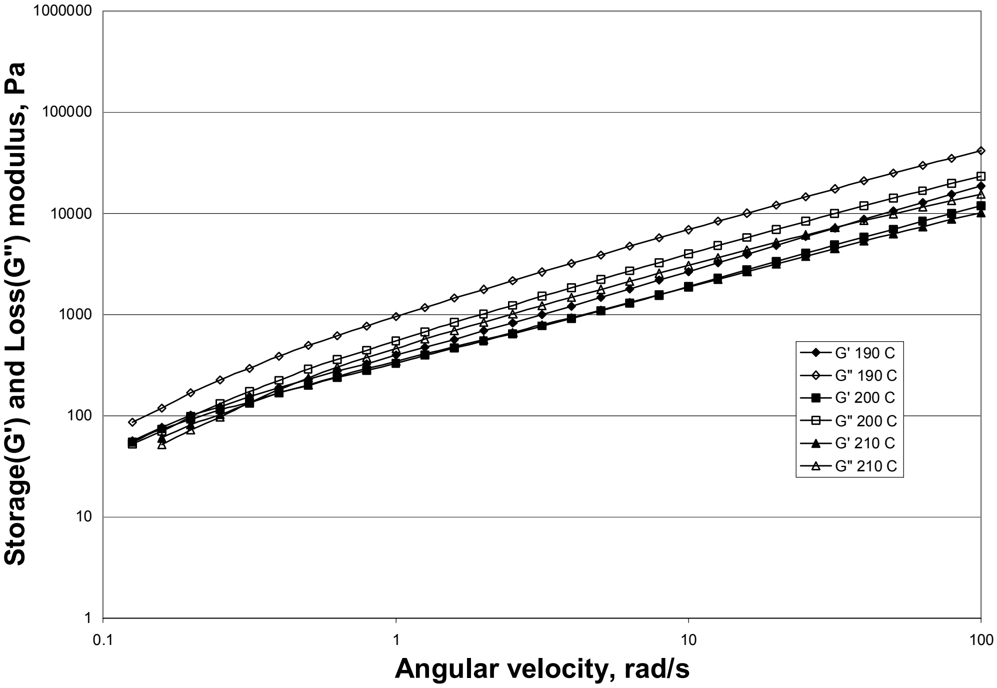

Figure 31. G’, G” against angular velocity of 95/05 1369/PET at 190, 200, and 210 C

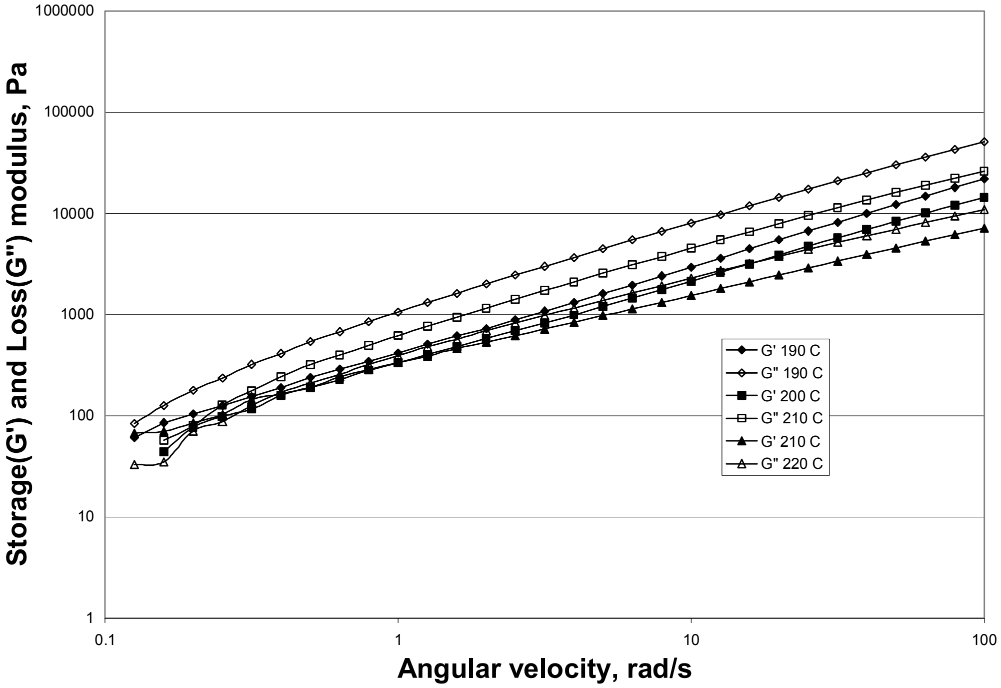

Figure 32. G’, G” against angular velocity of 100/00 1369/PET at 190, 200, and 210 C

4.3 MWIAT complex viscosity

The complex viscosity of MWIAT and MWIAT blended with 5, 15, and 25% PET was measured at 200, 210, and 220 C (Figures 33-36). Multiple runs were preformed on 85/15 MWIAT/PET at 210 C to check experimental errors. The errors are so small that error bars are not seen in Figure 34. As angular velocity increases, there is a large increase in complex viscosity at low angular velocities. Such increases suggest crosslinking of lignin segments or condensations of different lignin segments. The harsh kraft pulping process would produce different types of lignins from softwoods and hardwoods showing better opportunity for crosslinking and condensation. This is supported by the fact that this behavior also occurs on a smaller scale in the 1369, but does not occur in OS, which is obtained by much milder pulping procedures. After this increase shear thinning occurs for all compositions and temperatures. All compositions show a decrease in complex viscosity with an increase in temperature, although at 85 and 100% lignin there is little change seen between 210 and 220 C. The complex viscosity of MWIAT at all temperatures and blends is significantly higher than that of the other two lignins. None of the temperatures or blends produced fibers when the plates were pulled apart. Samples appeared more like a baked brownie.

Figures 37 to 39 show the complex viscosity against angular velocity of lignin and lignin blends at the different temperatures. The higher the percentage of PET in the blend, the higher is the viscosity. The difference in complex viscosity between 15% and 25% PET, at all temperatures, is very small, although it does increase slightly in all instances. An increase in complex viscosity is seen when PET is increased from 0 to 5% and again in the increase from 5 to 15%.

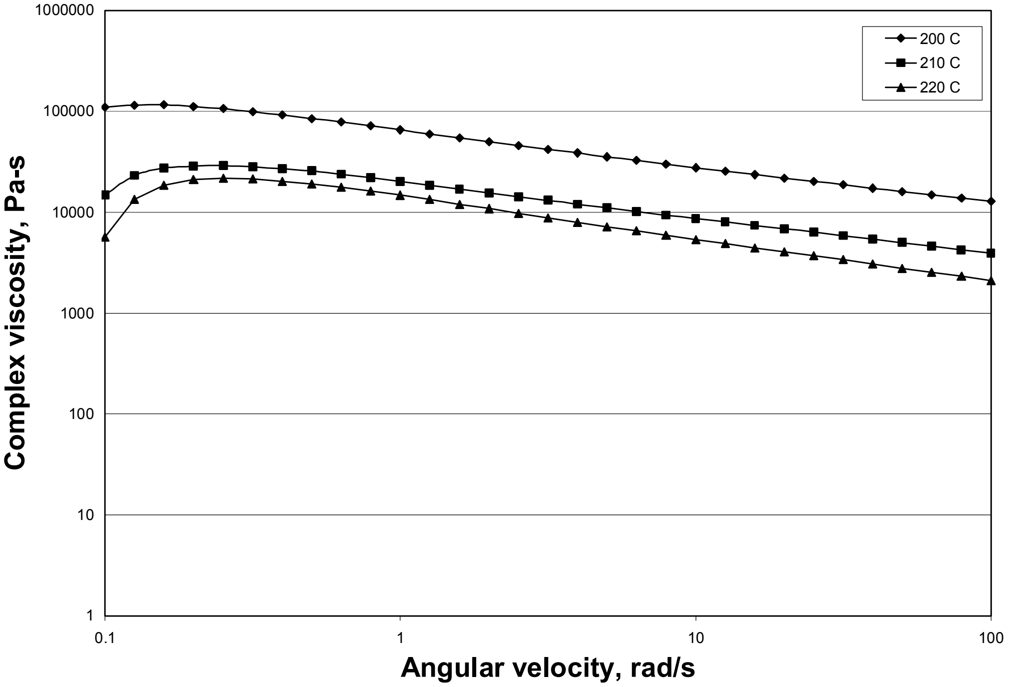

Figure 33. Complex viscosity against angular velocity for 75/25, MWIAT/PET mixture

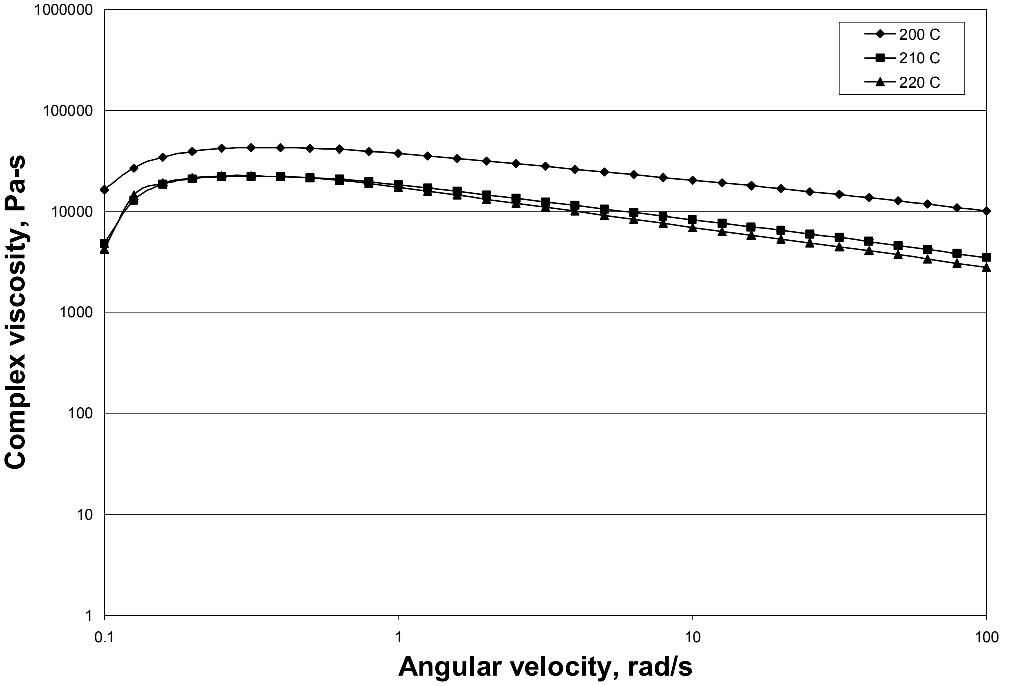

Figure 34. Complex viscosity against angular velocity for 85/15, MWIAT/PET mixture

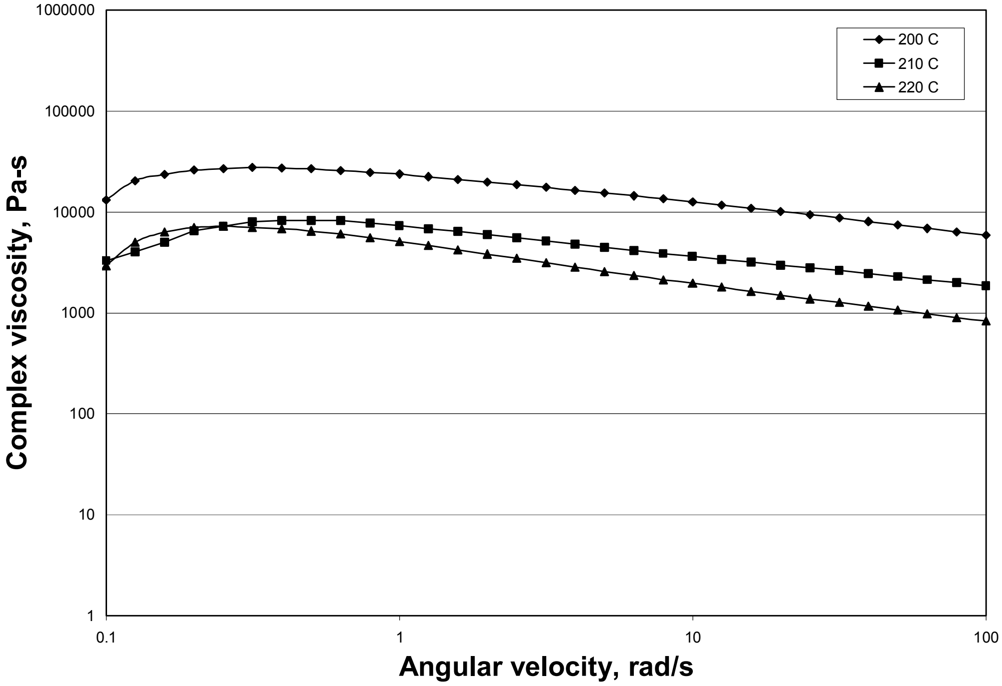

Figure 35. Complex viscosity against angular velocity for 95/05, MWIAT/PET mixture

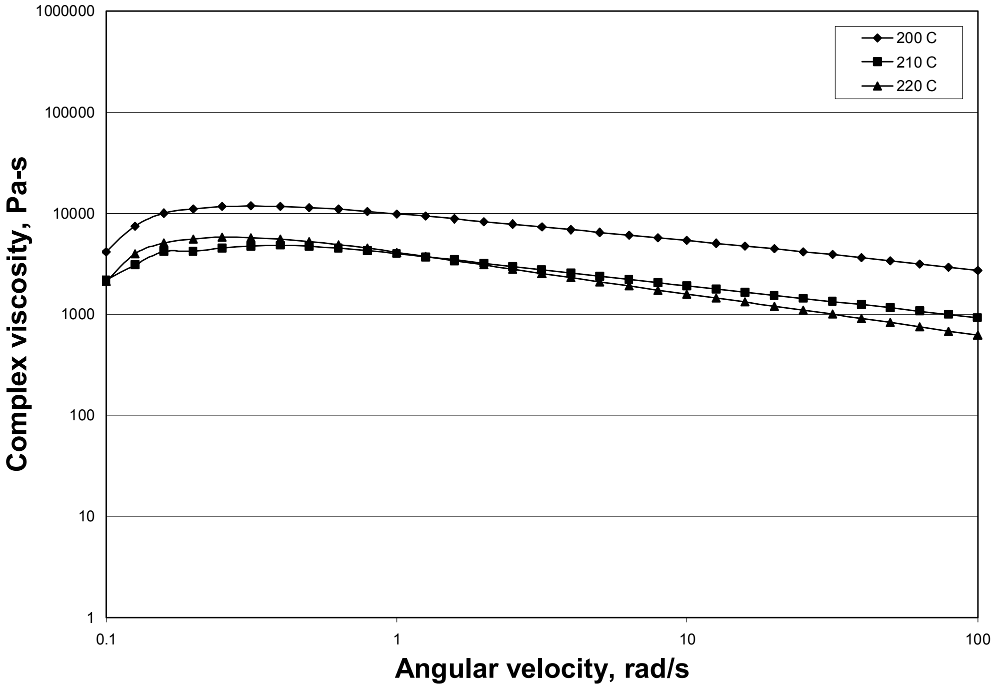

Figure 36. Complex viscosity against angular velocity for 100% MWIAT

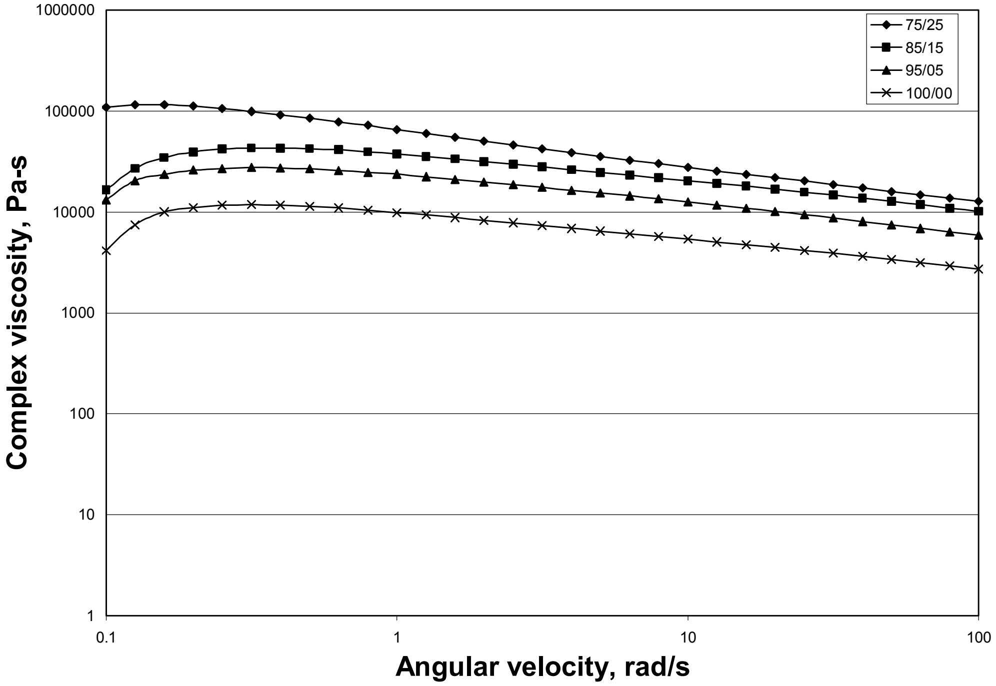

Figure 37. Complex viscosity against angular velocity for MWIAT/PET mixtures at 200 C

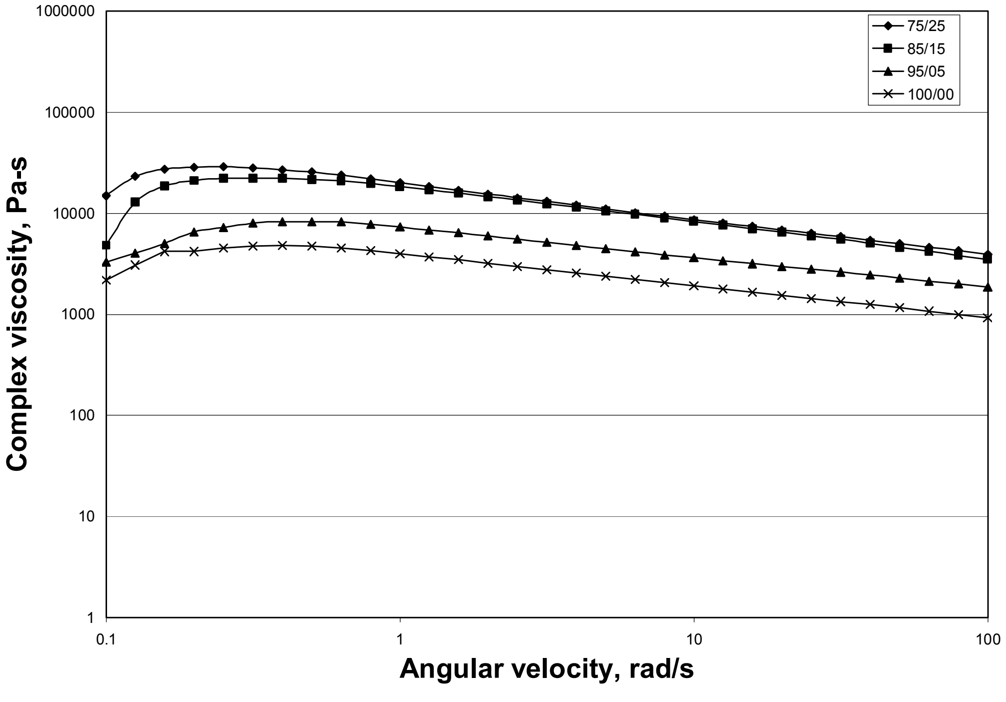

Figure 38. Complex viscosity against angular velocity for MWIAT/PET mixtures at 210 C

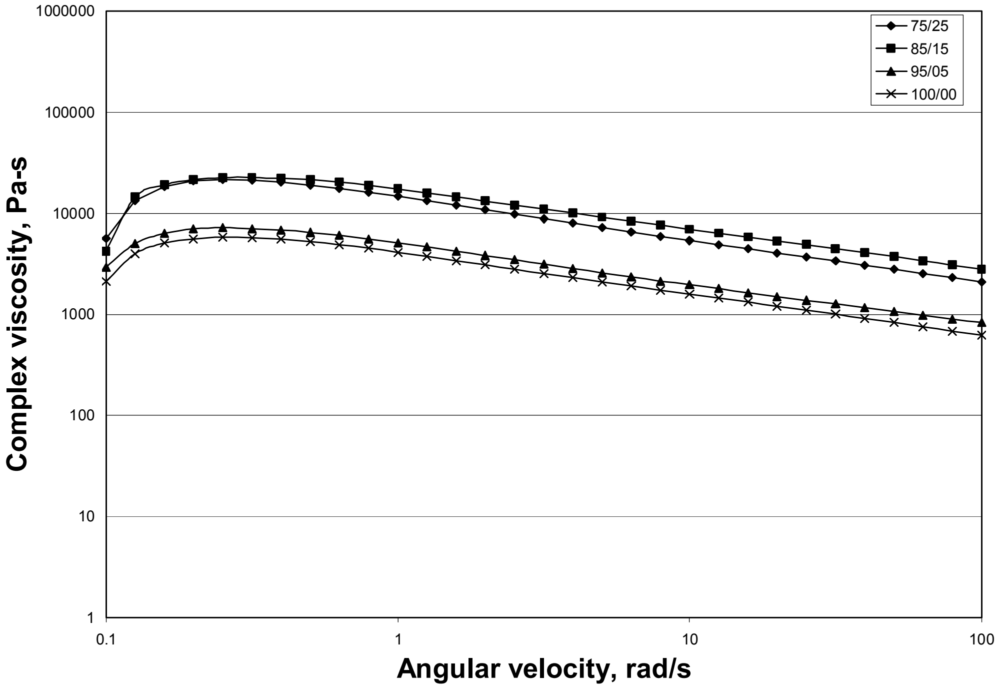

Figure 39. Complex viscosity against angular velocity for MWIAT/PET mixtures at 220 C

A graph showing all MWIAT mixtures, at all temperatures is shown in Figure 40. The highest viscosities are found in the blends at 200 C. The three lowest viscosities are 0% at 220 C, 0% at 210 C, and 5% at 220 C. This suggests that for the MWIAT temperature is a more important parameter than percentage of PET. Temperature shifting was not done because there was no trend towards infinity-shear-rate viscosity or zero-shear-rate viscosity. All viscosities of MWIAT and MWIAT blends are much higher than that of melt blowing grades of PPs(~35-720 Pa*s) at the same angular velocities. A dramatic difference in complex viscosity is shown between MWAIT and the other two lignins, as shown in Figure 41, for the lignins at 85/15 lignin/PET. This difference could be the results of higher molecular weight or crosslinking caused by the different lignins extracted from the mixed woods. The higher viscosity may also be the influence of impurities found in the unwashed lignin. Figure 41 also shows OS and 1369 at similar complex viscosities, this may be the results of washing on the kraft lignin.

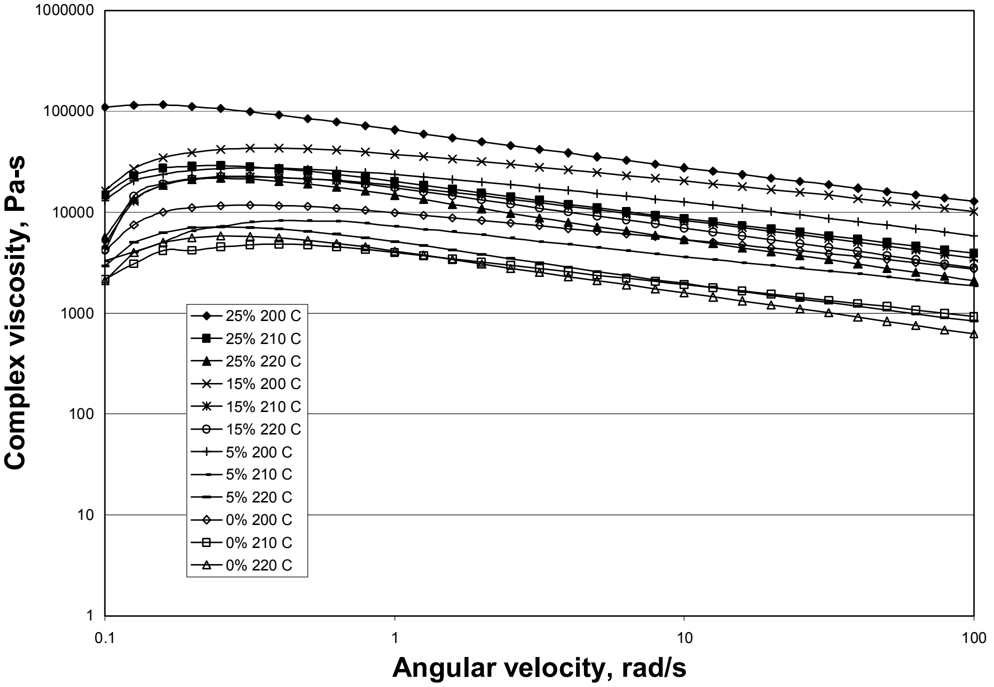

Figure 40. Complex viscosity against angular velocity for MWIAT/PET mixtures

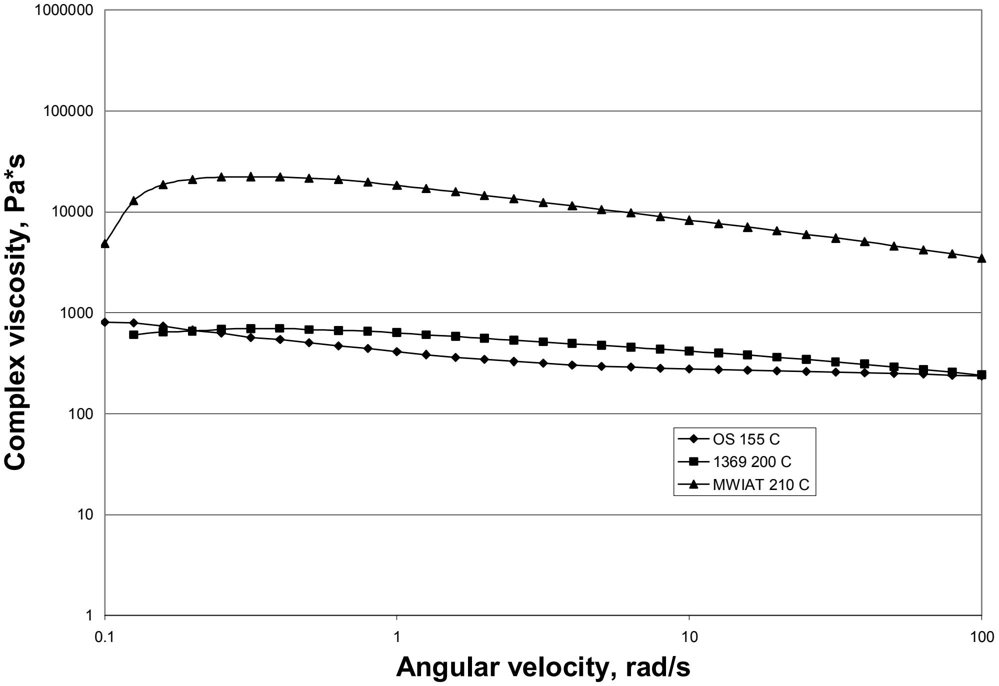

Figure 41. Complex viscosity against angular velocity for 85/15 OS, 1369, and MWIAT at 165, 200, and 210 C respectively

4.3.1 MWIAT dynamic moduli

The storage modulus, G', and the loss modulus, G", were also measured for this lignin sample. Figures 42 to 45 show G' and G" vs. angular velocity for MWIAT and MWIAT blends, at 155, 165 and 175 C, respectively. The viscoelastic region of MWIAT and MWIAT blends occurs at low angular velocities. For 75/25 blends, as temperature increases the crossover point occurs at higher angular velocity increasing the viscoelastic region. Blends of 85 and 95 % lignin content, as well as pure mixed wood lignin melt, show crossover points that are less affected by the change in temperature, except 85/15 blend at 200 C, which behaves as a viscous fluid. All samples exhibited a decrease in G' and G" with increasing temperature. The blend of 75/25 MWIAT/PET at 200 C behaves as a viscoelastic fluid at low angular velocities. Blends of 85/15, 95/05, and 100/00 MWIAT/PET behave as viscous fluids at 200 C but have viscoelastic regions at the other two temperatures at low angular velocities.

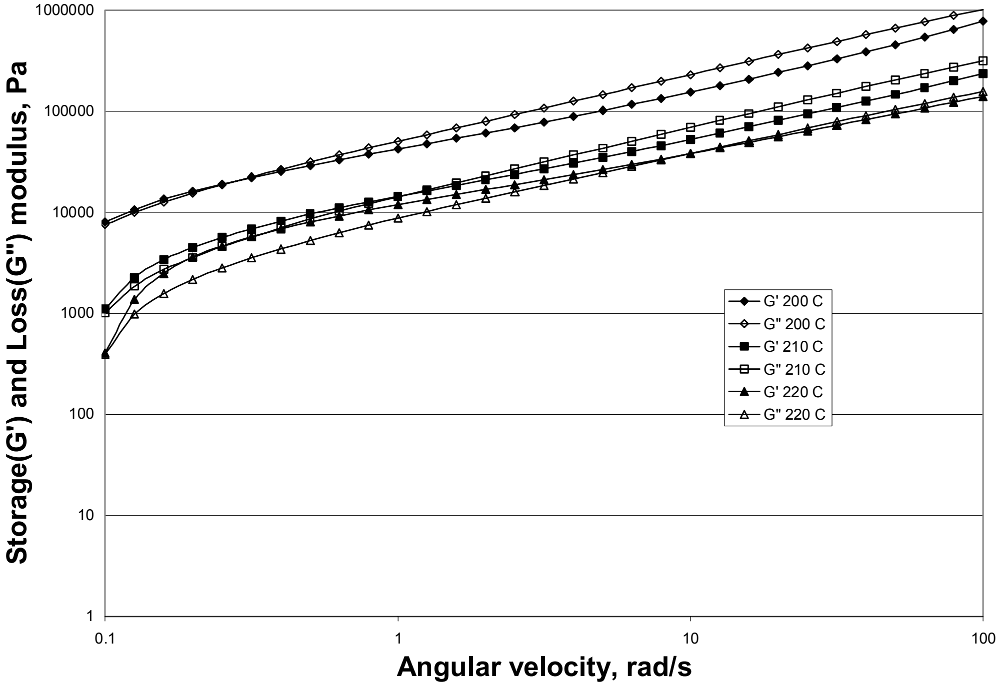

Figure 42. G', G" against angular velocity of 75/25 MWIAT/PET at 200, 210, and 220 C

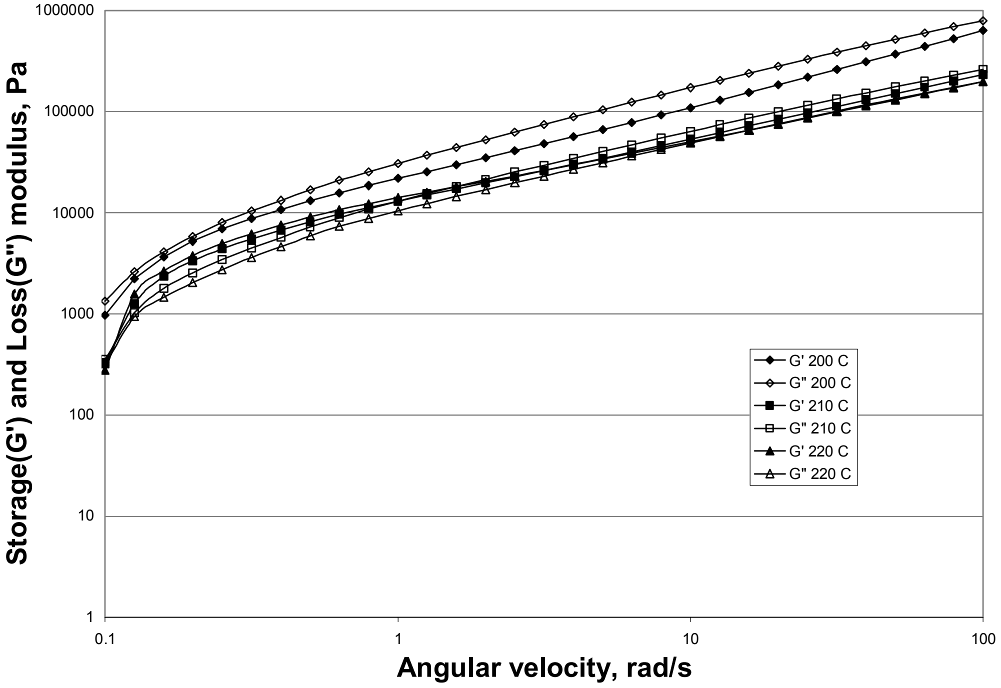

Figure 43. G’, G” against angular velocity of 85/15 MWIAT/PET at 200, 210, and 220 C

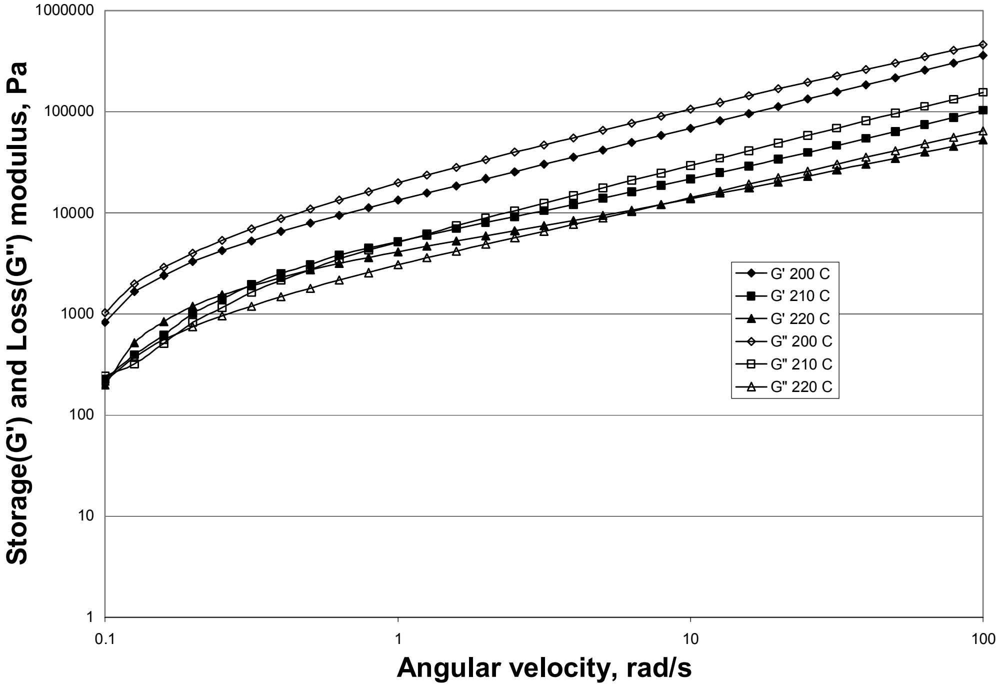

Figure 44. G’, G” against angular velocity of 95/05 MWIAT/PET at 200, 210, and 220 C

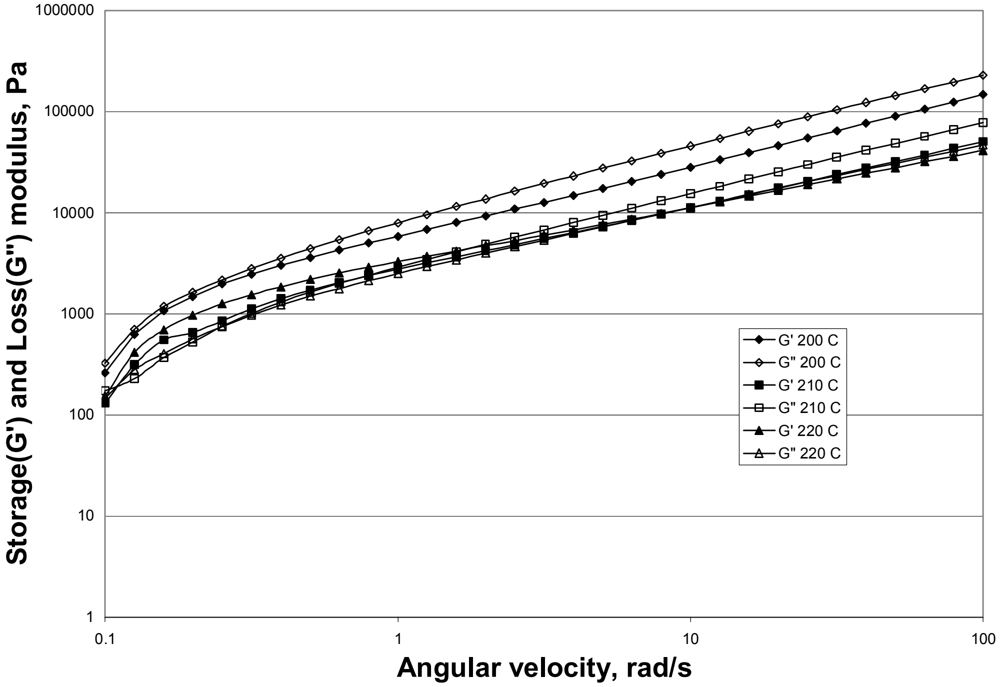

Figure 45. G’, G” against angular velocity of 100/00 MWIAT/PET at 200, 210, and 220 C

CHAPTER 5. CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Three different lignins (organosolv, kraft, and washed kraft) were blended at different percentages with a polyester to enhance the processability of the lignin for manufacturing carbon fiber precursors by melt spinning. The effect of polyester addition on rheological characteristics of the lignins, complex viscosity and dynamic moduli, were determined at different temperatures.

The lignin blends displayed shear thinning behavior for all compositions and temperatures. However, both the kraft lignins, 1369 and MWIAT, showed increases in complex viscosity at very low angular velocities. Such increases suggest crosslinking of lignin segments or condensations of different lignin segments. A dramatic difference in complex viscosity is shown between MWAIT and the other two lignins. Both OS and some compositions of 1369 have complex viscosities similar to that of melt blowing grades of PPs.

The lignins blends behave as viscous or viscoelastic fluids, depending on the percentage of lignin and temperature. At high temperatures, high percentage lignin, and low angular velocity the lignin blends feature a viscoelastic character. Lower percentage lignin blends and blends at high angular velocities behave as viscous fluids.

A master curve for the complex viscosity of the OS was generated and activation energy calculated from the Arrhenius plot of the shift factors. The activation energy for shear flow of OS blends is higher that that of some polymeric melts, such as low density or high density polyethylene.

Mixed wood indulin AT lignin and corresponding lignin blends show higher viscosities, as compared to those for melt blowing grade PPs and this suggests that this lignin may not be a good candidate for processing into nonwovens by melt blowing. But by adjusting the processing parameters, such as temperature, this lignin may be a good candidate for spinning fibers. Washed 1369 lignin and lignin blends rheological characteristics had some similarities to those of melt blowing grade PPs and should be examined more closely to determine if it would be a good candidate for fiber productions. Rheological characteristics for Organosolv lignin and PET blends are similar with that of melt blowing grade PPs suggesting it would be a good candidate for fiber manufacturing.

5.2 Recommendations

1. Test the kraft lignins for crosslinking or condensation by consecutive dynamic frequency sweeps on the ARES
2. Wash MWIAT and run rheological tests to study the effects of washing
3. Run rheological test on other polymers mixed with these three lignins
4. Run rheological tests on other varieties of lignins mixed with PET and other polymers
5. Develop master curves for shifting with respect to temperature and calculate activation energy for all tested blends, showing zero-shear-rate or infinity-shear-rate viscosity.

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VITA

Jesse Daniel Bush, born in January of 1977, grew up in the small town of Dandridge, TN. Jesse graduated from high school in 1995 then attended Pellissippi State Community College where he obtained an Associate of Science Degree in 1997. After which he enrolled in the University of Tennessee Knoxville Chemical Engineering department. Upon graduating from UTK in 2004 with a BS in Chemical Engineering and a minor and Material Science Engineering, Jesse enrolled in the graduate program at UTK. In May of 2006, Jesse earned a Master of Science degree in Chemical Engineering.