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I am submitting herewith a dissertation written by Zuopan Li entitled “Rheology of Lyocell Solutions from Different Cellulosic Sources and Development of Regenerated Cellulosic Microfibers”. I have examined the final electronic copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Human Ecology.

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Rheology of Lyocell Solutions from Different Cellulosic Sources and Development of Regenerated Cellulosic Microfibers

A Dissertation
Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Zuopan Li
August 2003

DEDICATION

This dissertation is dedicated to my parents, Guoxiao Li and Hongyun Zhang, my grandmother, Naimei Yang, my wife, Jihua Xiao, my brothers, Zuogao Li and Zuofeng Li, and the rest of the family, for always encouraging and supporting me to achieve my goals.

ACKNOWLEDGMENTS

I would like to thank all those who helped me achieve the Doctor of Philosophy degree in Materials Science and Engineering.

I am very thankful to Dr. Billie J. Collier for her precious guidance and suggestions. I wish to thank Dr. John R. Collier, Dr. Simioan Petrovan, Dr. Maureen Dever, Dr. Gajanan Bhat, Dr. Randall R. Bresee for their suggestions, Doug Fielden, Mike Neal, Greg Jones for their technical supports, and the USDA National Research Initiative for providing support for this work through contract number 00-35504-9357.

ABSTRACT

The primary goals of the study were to develop manufactured cellulosic fibers and microfibers from wood pulps as well as from lignocellulosic agricultural by-products and to investigate alternative cellulosic sources as raw materials for lyocell solutions. A protocol was developed for the lyocell preparation from different cellulose sources. The cellulose sources included commercial dissolving pulps, commercial bleached hardwood, unbleached hardwood, bleached softwood, unbleached softwood, bleached thermomechanical pulp, unbleached thermomechanical pulp, bleached recycled newsprint, unbleached recycled newsprint, bagasse and kudzu.

The rheological behavior of solutions was characterized. Complex viscosities and effective elongational viscosities were measured and the influences of parameters such as cellulose source, concentration, bleaching, and temperature were studied. One-way ANOVA post hoc tests were carried out to identify which cellulose sources have the potential to produce lyocell solutions having similar complex viscosities to those from commercial dissolving pulps. Lyocell solutions from both bleached and unbleached softwood and hardwood were classified as one homogenous subset that had the lowest complex viscosity. Kudzu solutions had the highest complex viscosity. The results showed the potential to substitute DP 1457 dissolving pulp with unbleached recycled newsprint pulps, to substitute DP 1195 dissolving pulp with bleached and unbleached thermomechanical pulps, to substitute DP 932 dissolving pulp with bleached thermomechanical pulps or bleached recycled newsprint pulps, to substitute DP 670 dissolving pulp with bagasse.

Lyocell fibers were produced from selected solutions and were treated to produce microfibers. Water, sulfuric acid solutions and sodium hydroxide solutions were used. The treatment of lyocell fibers in 17.5% NaOH solutions for five minutes at 20°C successfully broke the fibers into fibrils along fiber axis. The diameters of the fibrils were generally in the range of 2 to 6 μm, and there were also finer fibrils with diameters less than 1 μm.

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CHAPTER I

INTRODUCTION AND JUSTIFICATION

INTRODUCTION

The primary goal of this project was to develop lyocell fibers and microfibers from wood pulps and lignocellulosic agricultural by-products. Cellulose fibers are known for their eco-friendly characteristics as well as their other desirable properties. Agricultural commodities, by-products and residues are prospective alternative raw materials for fiber production. They are renewable resources and produced in large quantities. Significant efforts are required to develop the technologies to convert agricultural and industrial residues and by-products into textile products and also to enhance the technical performance in various applications.

Agricultural products and by-products of interest include sugarcane bagasse and kudzu. Sugarcane is an important agricultural crop in Florida and Louisiana. Currently, bagasse is used mostly in-house as fuel and in other low value applications such as land filling. Sugarcane rind, mechanically separated from the stalks, can be chemically and mechanically treated to extract the valuable cellulosic fibers (Romanoschi, 1998).

Kudzu, *Pueraria thunbergiana*, is a coarse-growing perennial legume that is native to Japan and China. Kudzu has threatened the existing ecosystem in the southeastern United States since the 1930s because it grows on top of and kills existing vegetation (Luo, et al., 2002). It would be a significant positive contribution to the environment if a value-added use could be found for kudzu.

Wood pulps are produced from wood raw materials through chemical and mechanical pulping processes. They dominate the industry of regenerated cellulosic fibers worldwide, and are also the raw material for paper products. Recycled newsprint pulps are reclaimed from old newsprints or magazines. The fibrous sources are deinked, turned into a slurry, and processed similarly to wood chip pulps. It is possible to produce newsprint from recycled newsprint pulps comparable to that from virgin fibers (Young and Rowell, 1986).

Lyocell fibers are a new type of rayon and were commercialized in the last decade. Lyocell fibers are produced from an environmentally benign, nontoxic two-component solvent, N-methyl morpholine N-oxide (NMMO) as shown in Figure 1.1, and water. Commercial lyocell fibers are Tencel® produced by Acordis and Lenzing Lyocell® fibers. Cellulose is dissolved in 87-90%w NMMO and 10-13%w water to produce commercial lyocell solutions. The solvent is essentially a NMMO monohydrate form ($NMMO{\cdot}H_2O$). The lyocell process is environmentally safe because the solvent is benign and is recycled during production (Meng et al., 1998, Murthy and Kuiti, 1999, Woodings, 2001).

Like other cellulosic fibers, lyocell fibers are biodegradable. Lyocell fabrics have much better wrinkle-resistance and abrasion-resistance than viscose rayon fabrics. They can be dyed and printed vibrantly (Burkinshaw and Gandhi, 1996, Burkinshaw and Gandhi, 1997b, Karypidis et al., 2001). Lyocell fibers can be used or blended with a wide variety of natural and manufactured fibers (Watkins, 1999, Zhang et al., 2000a) to produce fabrics that can be both washed and dry-cleaned. Lyocell fibers also have large potential in other industrial uses such as composites (Franko et al., 2001, Nef and Mall, 1996, Seavey et al., 2001, Seavey and Glasser, 2001), filters (Rose et al., 1998, Woodings, 1995b, Woodings and Edwards, 1995) and battery separators (Kelly and Woodings, 1996).

Microfibers are textile fibers with a linear density of one denier or less (Collier and Tortora, 2000). The direct spinning process and the bi-component process are two common techniques for producing microfibers. According to the definition above, common synthetic microfibers should have diameters of less than 11 μm and regenerated cellulosic microfibers should have diameters of less than 10 μm.

JUSTIFICATION

It is very important for the textile industry to develop new materials, composites and manufacturing technologies, which will allow the industry to produce textiles that are environmentally improved and that meet the customer requirements. Five main

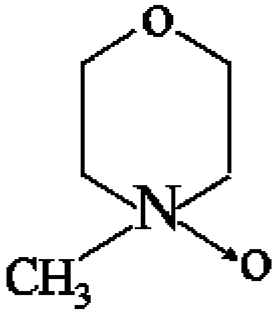

Figure 1.1. N-Methylmorpholine-Oxide (NMMO).

related issues are procuring raw materials, manufacturing products, meeting customer expectations, ensuring human health and environmental safety, and making profit. Environmental preservation and sustainable production systems play increasingly more important roles in the textile industry (Ortlepp et al., 1999, Perepelkin, 2000, Wolschner et al., 1995).

Microfiber products are commercially attractive because of their unique properties such as a soft and luxurious feel and high drapeability. Most of the microfibers in the market today are synthetic. Since the introduction of commercial nylon fibers in 1939, synthetic fibers have replaced natural fibers in many textile applications. But synthetic fibers are derived from petroleum that is not a renewable resource. Oil imports have been a heavy burden to the economy of oil importing countries (Perepelkin, 2000).

At the same time, there are great demands for natural fibers because of their aesthetics, comfort and biodegradability, which are not possessed by most synthetic fibers. Researchers are challenged to produce fibers that not only possess preferred properties but could also be produced in an environmentally friendly manner. The goal is minimal impact on the environment from the beginning source materials to the final product disposal. Biodegradability and reusability are very important because more than four million tons of textile wastes are generated annually (Negulescu et al., 1998), which are expensive to dispose of and increase environmental concerns. There is interest in producing environmentally improved textile products (EITP) using novel techniques and cheaper raw materials.

The lyocell process for manufactured cellulosic fibers has the practical potential to fulfill this objective. Cellulosic microfibers should gain more interest than general synthetic microfibers because of their comfort, good water absorbency and biodegradability. Obtaining fiber-forming cellulose lyocell solutions from reclaimed cellulosic materials and agricultural by-products could lower the cost of the resultant fibers and lower the environmental impact. The development of value-added products from agricultural products and other alternative raw materials will result in economic development at the local, national, and international levels.

Cellulosic sources for lyocell have been investigated and the results are promising (Collier et al., 2000, Collier, 1998, Romanoschi et al., 1997, Romanoschi, 1998, Zikeli, 2001). Work has been done on spinning lyocell fibers from solutions of kenaf and bagasse (Romanoschi, 1998). The objective of the research on the rheological properties of lyocell solutions from different cellulose sources was to evaluate the use of agricultural by-products to produce better-priced products.

A major limitation of the current application of lyocell fibers in general textile uses is the fibrillation tendency under wet abrasion conditions (Li et al., 1999, Micolai et al., 1996, Mortimer and Peguy, 1996a). In this project, however, the fibrillation tendency of lyocell fibers was utilized to explore the possibilities to produce microfibers.

RESEARCH OBJECTIVES

The primary objective of this project was to use current and developed techniques for producing cellulosic microfibers and to investigate alternative cellulosic sources as raw materials for lyocell solutions. The rheological behavior of solutions from lower cost raw materials was characterized and spinning conditions and aftertreatments were employed to induce formation of microfibers.

Specific objectives were:

1. To produce lyocell solutions from alternative cellulose sources;

2. To investigate the rheological and extrusion behavior of lyocell solutions from alternative cellulose solutions;

3. To produce lyocell fibers and microfibers.

CHAPTER II

LITERATURE REVIEW

CELLULOSE

Chemical Structure

Cellulose is among the most abundant polymers on the earth. It is an important structural element in plant cells and other living systems. The chemical structure of cellulose has been under continuous investigation since Anselme Payen discovered it in 1839 (Woodings, 2001).

Cellulose molecules are composed of repeating ring-structured units, "1,4-ß-D-linked polyanhydro glucopyranoses" (Nevell and Zeronian, 1985a), as shown in Figure 2.1. The units are aligned along the chains and every other unit rotates 180°. The symbol *n* is the average degree of polymerization. The degree of polymerization of native celluloses varies from about 1000 to more than 15000 glucose units (Nevell and Zeronian, 1985a).

As Figure 2.1 shows, cellulose can be expressed by $(C_6H_{10}O_5)_n$; more correctly it should be expressed by $C_6H_{11}O_6$-$(C_6H_{10}O_5)_n$-$C_6H_{11}O_6$ (Heuser, 1944). The two terminal units of the cellulose are different from those in the chain. These two terminals have four hydroxyl groups, but each repeating unit has three (Hermans, 1949).

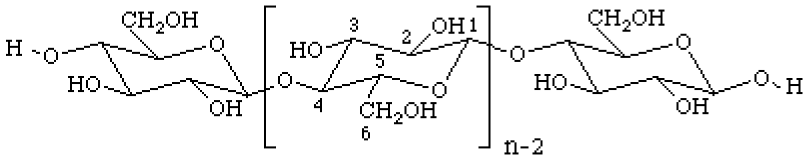

Figure 2.1. Chemical Structure of Cellulose.

Crystalline Structure

One of the key features of cellulose is that its repeating unit bears three hydroxyl groups. These hydroxyl groups and their hydrogen bonding ability play important roles in the crystalline structures and physical properties of cellulose materials. These hydrogen bonds between adjacent molecules result in strong intermolecular bonding (Lewin and Pearce, 1998).

There are at least four cellulose crystalline structures: celluloses I, II, III and IV (Hermans, 1949, Nevell and Zeronian, 1985a). In cellulose I, the cellulose chains are packed parallel while in cellulose II the chains are packed in an antiparallel fashion (Bayer et al., 1998, Hermans, 1949, Young and Rowell, 1986). Cellulose III can be obtained through treatments of cellulose I or cellulose II with liquid ammonia or amines or diamines (Hermans, 1949, Roche and Chanzy, 1981, Wada et al., 2001). Cellulose IV can be prepared from cellulose I or from thermal treatment of celluloses I, II or III in polar liquids (Buleon and Chanzy, 1980, Happey, 1979, Hermans, 1949). Both cellulose III and IV are seldom found in nature. Cellulose II is a more stable structure than cellulose I because it provides more extensive hydrogen bonding. Cellulose I occurs only in natural cellulose materials and can be converted to cellulose II irreversibly after being treated with strong sodium hydroxide solution and regenerated from solution (Young and Rowell, 1986).

Chemical Reactions of Cellulose and NMMO

The reactions of cellulose are related to its polysaccharidic nature and the characteristic of its large number of hydroxyl groups. The major chemical reactions include esterification, etherification, acetal formation, hydrolysis, and oxidative and thermal degradation (Hermans, 1949, Heuser, 1944).

Cellulose can react with water, alkalis and cuprammonium hydroxide as a polyhydric alcohol, and it can be used to form esters and ethers. A number of common alkylating agents can react with cellulose to produce cellulose ethers. The hydroxyl groups can be oxidized to aldehyde and carboxyl groups (Hermans, 1949, Nevell and

Zeronian, 1985b). As a polysaccharide, cellulose can be degraded to shorter chains through hydrolysis, acetolysis and oxidation. Cellulose is susceptible to hydrolysis in the presence of acids and alkalis. The hydrolysis from acids is much stronger than that from alkalis. Cellulose is biodegradable. In the presence of strong oxidizing agents, cellulose can be completely converted into CO_2 and H_2O (Hermans, 1949, Heuser, 1944).

Thermal degradation is closely related to the ageing, deterioration and degradation of cellulose materials. Lyocell fibers could be used as precursors of carbon fibers. At different temperatures, different kinds of thermal degradation reactions occur. At temperatures below 100°C cellulose shows slight signs of damage after a few hours of heating. At higher temperatures above 100°C, more pronounced degradation happens. When the temperature is above 200°C, tar appears and also gases are evolved (Heuser, 1944). At temperatures up to 300°C the cellulose can be finally degraded into a charred residue after the water elimination and degradation. Carbonyl, carboxyl and hydroperoxide groups, carbon monoxide and carbon dioxide are generated during the degradation at such a high temperature (Nevell and Zeronian, 1985b). At temperatures higher than 300°C, decomposition happens quickly. A variety of low molecular weight compounds and intermediate decomposition products are produced (Nevell and Zeronian, 1985b).

NMMO ($C_5H_{11}NO_2$) is a cyclic, aliphatic tertiary amine oxide as shown in Figure 1.1. The most frequent application of NMMO in organic synthesis is its use as an oxidant (Rosenau et al., 2001).

REGENERATED CELLULOSIC FIBERS

Rayon is the generic term for manufactured cellulosic fibers and the resulting yarns and fabrics manufactured of regenerated cellulose. Rayon fiber is defined by the Federal Trade Commission (FTC) as a manufactured fiber composed of regenerated cellulose, and this clarification of manufactured fibers includes those “composed of regenerated cellulose in which substituents have replaced no more than 15% of the hydrogens of the hydroxyl groups" (Kadolph and Langford, 1998). Rayon was initially called "artificial silk", and the name "rayon" was adopted by a committee formed by the U.S. Department of Commerce and various commercial associations (Lewin and Pearce, 1998). Rayon fibers include yarns and fibers made by the viscose, cuprammonium, saponification, polynosic, lyocell and the now obsolete nitrocellulose processes (Woodings, 2001).

Viscose Process

Viscose rayon was the first manufactured fiber (Lewin and Pearce, 1998, Woodings, 2001). In 1664, Robert Hooke proposed that artificial filaments might be spun from a substance similar to that which silkworms secrete to make silk. George Audemars was the first to make an artificial silk successfully by dipping a needle into a viscous solution of mulberry bark pulp and gummy rubber (Lewin and Pearce, 1998). Cross et al filed the patent on the viscose process in 1892 (Cross et al., 1894). Courtaulds Fibers produced the first commercial viscose rayon in 1905, and American Viscose Company produced the first rayon in the United States in 1910 (Lewin and Pearce, 1998).

Most rayon fibers today are produced by the viscose process. Rayon fibers are soft, absorbent, non-static, comfortable to wear and relatively inexpensive. Rayon fabrics are favored because they drape luxuriously and take dyes beautifully. But the colors of rayon fabrics can fade and deteriorate when exposed to light for a long period of time. Rayon fabrics wrinkle easily and can be damaged by hot irons (Collier and Tortora, 2000).

In the production of viscose rayon, cellulose is first purified, and then treated with carbon disulfide (CS_2) to form cellulose xanthate esters. The cellulose xanthate is dissolved in sodium hydroxide (NaOH) and passed through a spinneret to form filaments that are then regenerated into almost pure cellulose in a chemical bath (wet-spin) (Kadolph and Langford, 1998, Collier and Tortora, 2000, Woodings, 2001).

Additions of addictives such as zinc or glucose are used to control the rate of regeneration.

The viscose process can either be a continuous or batch process. The batch process is flexible in producing a wide variety of rayons, and the continuous process is the main method for producing rayon today because it is difficult to control the uniformity between batches for the batch process (Lewin and Pearce, 1998). The majority of acid and zinc employed during the spinning remain in the spinning bath circuit, and are carried to later process stages. It is important to recover the zinc and acid, but the later stages of the washing process result in dilute waste streams. It becomes increasingly costly to reuse them. It is also costly to meet the increasingly stringent environmental legislation that forces industry to recover CS_2 and hydrogen sulfide more and more effectively (Woodings, 2001).

Other Rayon Processes

In the nitrocellulose process developed by Chardonnet who set up the first company to manufacture nitrocellulose fiber, cellulose, usually cotton or wood pulp, is treated with nitric and sulfuric acids. The extent of nitration and degradation of the cellulose is carefully controlled. When most of the hydroxyl groups of the cellulose molecule are esterified, the nitrocellulose formed is called guncotton that resembles cotton in its appearance. The nitrocellulose process is now no longer of commercial importance mainly because of two factors. One is the fact that the process is of lower productivity than viscose and cuprammonium processes; the other is that the fiber produced has explosive properties. These two factors drove the nitrocellulose process to become obsolete (Woodings, 2001).

Cuprammonium rayon is produced by a solution of cellulosic materials in cuprammonium hydroxide at a low temperature in a nitrogen atmosphere, followed by extruding through a spinneret into a sulfuric acid solution to decompose cuprammonium complex to cellulose (Woodings, 2001). This is an expensive process with the environmental problem of copper in the waste stream. There is no cuprammonium rayon manufacturer in the United States.

The saponification process for rayon fibers involves with the production of cellulose acetate fibers. Cellulose acetate is produced by steeping purified cellulose in glacial acetic acid to acetylate the hydroxyl groups. The cellulose acetate is then dissolved in acetone, filtered and deaerated for extrusion through the spinneret to produce fine filaments of cellulose acetate into hot air that evaporates the solvents (Lewin and Pearce, 1998). The cellulose acetate fibers are heated, stretched and saponified with NaOH to regenerate cellulose fibers.

The polynosic process developed by Tachikawa (Tachikawa, 1956) includes several modifications of the viscose process resulting in higher modulus, higher strength fibers. Cellulose with a high degree of polymerization is used and the ageing process is omitted, maintaining a higher degree of polymerization in the cellulose. The cellulose is xanthated to a high degree with excess of CS_2 and the xanthate is dissolved in a dilute NaOH. The solution is then spun in a "cold low-acid low-salt zinc-free spinbath" and stretched to produce polynosic fibers. Polynosic rayon has very high a degree of orientation achieved by high stretching during the process. The fiber has fibrillar structures, high dry and high wet strengths, a low elongation rate, a relatively low water retention and a very high wet modulus (Tachikawa, 1956, Woodings, 2001).

Cellulose Sources for Regenerated Cellulosic Fibers

Cellulose sources for regenerated cellulosic fibers can be classified into two large categories, wood fiber sources and non-wood fiber sources. Wood fiber sources, both hardwood and softwood, are the main natural fiber sources worldwide. The main softwood species include pine, spruce and fir. The most important hardwood species include birch, aspen, oak, gum, maple and beech. These trees are obtained from both naturally grown forests and cultivated woods. Non-wood fibers such as cereal straws, sugarcane bagasse and bamboo are fiber sources with great potential, but are not fully utilized industrially (Woodings, 2001).

Wood raw materials for regenerated cellulosic fibers worldwide are predominantly chemically and mechanically pulped. The most common chemical pulping process is the Kraft pulping process in which NaOH and sodium sulfide (Na_2OH) are used as active delignification chemicals. In the pulping process most of the lignin is modified and dissolved. Subsequent bleaching removes the residuals and increases the pulp brightness and cleanliness. Dissolving pulp, depending on the pulping and bleaching processes, normally has 90 to 96% cellulose content (Woodings, 2001).

LYOCELL

Consumers are more ecology conscious today and they favor a fiber that is natural, biodegradable and non-toxic to the environment as well as breathable, comfortable, drapable, soft, wrinkle-resistant, shrink-resistant, and has other desirable properties. Researchers have been seeking new environmentally friendly processes for decades. The eco-friendly lyocell fiber became the first new generation of cellulosic fibers in recent decades. Courtaulds Fibers was the first to introduce lyocell commercially under the trade name Tencel in 1992. Lenzing AG is manufacturing lyocell under the trade name Lenzing Lyocell (He and Wang, 1999, Lee and Jo, 1999, Meng et al., 1998, Woodings, 1995a).

Lyocell Process

Lyocell is a relatively new type of regenerated cellulosic fiber that is produced by a direct solvent spinning process based on the ability of an amine oxide (particularly $NMMO \cdot H_2O$) to dissolve cellulose (Rosenau et al., 2001,Woodings, 2001). Although it was given a different generic name, lyocell is considered a sub-category of rayon according to the FTC.

In the commercial lyocell process, the pulp is wetted thoroughly with dilute aqueous amine oxide, and the excess water is removed to make a homogenous solution with a minimum of undissolved particles and air bubbles. The solution is spun through an air gap to a water/amine oxide bath. Then the fibers are washed and dried. The

NMMO in the washing solution and coagulation bath can be recovered, purified, concentrated and recycled (Woodings, 2001).

There are considerable differences between the lyocell process and other cellulose spinning methods. The lyocell process resembles the dry-wet spinning process in some aspects but there is essentially no mass transformation in the air gap and no chemical reaction in the coagulation bath (Liu et al., 2001). In comparison to conventional regenerated cellulose fibers, lyocell fibers have no apparent skin-core structure (Woodings, 2001). The lyocell process comprises fewer process steps, and uses less energy and less water. At the same time, this process mainly uses renewable resources, and has minimal environmental impact (Perepelkin, 2000, Rosenau et al., 2001).

A number of research efforts have concentrated on the preparation and characterization of lyocell solutions (Chanzy, 1982, Kim et al., 2001, Kosan and Michels, 1999, Petrovan et al., 1999) and fiber spinning (Chanzy et al., 1982, Fink et al., 2001, Liu et al., 2000, McCorsley, III, 1983, Mortimer et al., 1996, Mortimer and Peguy, 1996b, Zhang et al., 2000a). Work has been done on seeking alternative cellulose sources (Raheel et al., 1999, Dinand et al., 1999), fiber characterization (Kim et al., 2002), lyocell yarn spinning (Zhang et al., 2000a), and after-treatment on both lyocell fibers and fabrics (Alwis and Taylor, 2001, Scarborough and Mathews, 1998, Zhang et al., 2000b).

The typical starting compositions of industrial lyocell solutions are 50-60% NMMO, 20–30% water, 10-15 % cellulose pulp, and stabilizers. Excess water is subsequently evaporated under reduced pressure at a preset temperature until the dissolution of cellulose occurs to form a spinning dope. Thorough mixing and input of shear energy help to achieve dissolution in short times and to produce uniform lyocell solutions. Industrially, concentration, temperature, pressure and shear stress are controlled online through specially designed reaction vessels (Rosenau et al., 2001). The typical spinning dope composition is 14% cellulose, 10% water and 76% NMMO. The spinning temperature is between 100 to 120°C (Rosenau et al., 2001).

Theoretically the lyocell process system is an entirely physical process, and there is no chemical modification either of the NMMO or of the solute cellulose (Romanoschi, 1998, Rosenau et al., 2001, Woodings, 2001). In fact, the chemical problems in the NMMO/cellulose system sometime were the obstacles to industrial production in the 1980s. In the NMMO/cellulose system both the solvent and the cellulose undergo degradation during the process (Rosenau etal., 2001). The loss of NMMO in industrial production is an important economic issue, and the primary decomposition products can induce further decomposition.

Solvent

The solvent used in the commercial lyocell process is N-methylmorpholine-N-oxide that belongs to the family of cyclic, aliphatic, tertiary amine oxides. The chemical structure is shown in Figure 1.1 (Rosenau et al., 2001). NMMO has a white crystalline appearance, a density of $1.25 g/cm^3$, and a melting point of 184°C. It is a strong oxidant and thermally labile. It has a pronounced tendency to form hydrogen bonds and exhibits complete miscibility with water (Rosenau et al., 2001). Commercially NMMO is produced by oxidation of N-methylmorpholine (NMM) with aqueous hydrogen peroxide, and is primarily available as a concentrated aqueous solution (Rosenau et al., 2001).

NMMO has two stable hydrates, the monohydrate $NMMO \cdot H_2O$ with 13.3%(w/w) H_2O and the disesquihydrate $NMMO \cdot 2.5H_2O$ with 28%(w/w) H_2O. The two forms of NMMO hydrates are hygroscopic, and take up atmospheric moisture easily (Rosenau et al., 2001). Anhydrous NMMO cannot be obtained simply by heating the monohydrate or the disesquihydrate. The generation of NMMO requires azeotropic drying from organic solutions followed by crystallization or vacuum sublimation. It is possible to form the hydrates, but not neat NMMO, by simple evaporation of water in vacuum at temperatures above the melting point of the NMMO monohydrate (76-78°C) (Rosenau et al., 2001).

NMMO has been shown to dissolve polysaccharide materials such as starch, amylose, glycogen and cellulose (Chanzy et al., 1982). High concentrations up to 55% of cellulose solutions in NMMO were obtained with DP 600, DP 130 and DP 35 (Chanzy et al., 1980).

The physicochemical process of cellulose dissolution in NMMO/H_2O and the structure of the dissolved cellulose have been investigated intensively, but are still not comprehensively understood. Scientific methods employed include thermoanalysis, rheology, laser diffraction and other unconventional techniques (Fujii et al., 2001, Shen et al., 2000). The ability of NMMO/H_2O to dissolve cellulose is attributable to its ability to disrupt the hydrogen bond network of cellulose and its ability to form solvent complexes by establishing new hydrogen bonds between the macromolecules and the solvent (Rosenau et al., 2001). The chemical nature of the dissolution is commonly regarded as an acid-base (donor-acceptor) interaction that leads to a restructuring of the hydrogen bond network of the cellulose molecules and the solvent. The oxygen of the N-O bond in NMMO is able to form one or two hydrogen bonds with two hydroxyl groups. Details of the process and interactions between the cellulose hydroxyl groups and NMMO are still under study (Romanoschi, 1998).

Fiber Morphology

The difference between the structure and properties of lyocell and conventional viscose fibers derives from their different processing techniques (Achwal, 2001, Collier and Tortora, 2000, Woodings, 2001). The dry-wet spinning technique is used in the lyocell process. Lyocell fibers have a fibrillar structure in which microfibrils are parallel to the fiber axis (Mortimer et al., 1996, Mortimer and Peguy, 1996b). There is a possibility of causing the microfibrils to separate that could be used to produce lyocell microfibers, which is part of the subject of this dissertation.

The wet fibrillation propensity is characteristic of lyocell fibers, which is due to its special fiber structure. Wet fibrillation is the abrading of small fibrillar hairs from the fiber surface by subjecting water-swollen cellulose fibers to mechanical stress.

Lyocell fibers are particularly susceptible to such actions. This characteristic has been used to produce interesting fabric aesthetics such as peach-skin effects through fibrillation control on the fiber surface (Ortlepp et al., 1999, Ortlepp, 2001).

The fibrillation is primarily due to the high orientation of the microfibrillar cellulosic structure in the fiber and the lack of lateral cohesion between the microfibrils. Lyocell does not possess this marked propensity to fibrillate in a dry state. Only through the expansion of less-ordered interfibril zones after swelling in water, the fiber has the propensity to fibrillate because of the reduced interfibril cohesion. The intensity of the fibrillation is affected by processing parameters such as temperature, processing time, mechanical intensity and pH values (Boehnke, 1999, Li et al., 1999). There is no relationship reported between the swelling data and the different fibrillation behavior of cellulosic fibers. In contrast to the conventional viscose fibers, the proportion of larger pores in lyocell as well as the longitudinal extent of the pores between the microfibrils in the fiber direction is greater (Bredereck et al., 1997). Dye penetration studies might be helpful in the investigation of the pores in lyocell fibers.

The particular structure of the lyocell fiber is influenced by the conditions of the spinning process. The first orientation of lyocell fibers happens in the spinneret and the emergent filament stream is led to pass though a short air gap for cooling and then to the coagulation bath. The orientation in the air-gap is very high, and is maintained in the coagulation bath due to the rapid cellulose precipitation. The fibrillation control may be possible through varying different parameters of the spinning solution, spinning process and aftertreatments (Graveson et al., 1997, Graveson et al., 1998, Mortimer et al., 1996, Mortimer and Peguy, 1996c, Mortimer and Peguy, 1996a). The fibril cohesion is the key factor. Greater clustering of fibrils results in higher fibril cohesion and hence lower fibrillation (Bredereck et al., 1997).

Mortimer and Peguy (1996a, 1996c) conducted a series of experiments to study the effects of processing conditions on the fibrillation tendency of lyocell fibers. The results showed that the following conditions help to reduce fiber fibrillation: long, warm and humid air gaps, low line speeds, low cellulose concentrations, and coagulation baths of NMMO/water solution rather than pure water.

Enzyme treatment results in erosion to some extent and will affect the fibrillation propensity. Investigations have revealed that lyocell fibers exhibit a thin fiber sheath layer that swells to a greater extent than the core layer, and undergoes coarser fibrillation. Enzyme treatment can be used to produce controlled and even fibrillated effects or to reduce and avoid fibrillation permanently (Bredereck et al., 1997, Graveson et al., 1997, Kumar et al., 1994). The larger pore proportion and the longitudinal extent of the pores between the fibrils of lyocell promote fibrillation and also facilitate the diffusion of dye molecules. Dye constitution and dyeing method affect the dye influence on the fibrillation propensity (Bredereck et al., 1997).

Fiber Properties

Lyocell possesses many of the characteristics of other cellulose fibers. It has a soft hand, excellent drape, high absorbency, and excellent dyeability and printability just as rayon. Lyocell has numerous advantages over conventional rayon fibers while lyocell is classified as a subclass of rayon.

Lyocell fibers are much stronger than rayon fibers. Lyocell fibers are washable, shrink-resistant and wrinkle-resistant, overcoming most of rayon's disadvantages. Lyocell fiber has good strength in the wet and dry state. The water influence on the mechanical properties of lyocell fibers is considerably smaller than other kinds of regenerated cellulose fibers (Kreze et al., 2001). Lyocell fibers also have the natural absorbency and comfort of a cotton and ease of care of a synthetic. They can be blended easily with many other fibers (Watkins, 1999). The fiber looks like fine mercerized cotton and could be made into silk-like fabrics with the drape and fluidity and color richness of rayon. Lyocell fibers are biodegradable and the total lyocell process is environmentally friendly; the production does not cause chemical changes in the pulp or solvent (Rosenau et al., 2001).

Early lyocell had restricted applications in textiles because of its uncontrolled fibrillation. It was used mainly in woven products that were treated with gentle processes and garments requiring dry clean (Woodings, 2003). With improvements in the lyocell process, lyocell fibers have now been developed for various kinds of applications including textile products such as jeans, knits (Watkins, 1999), nonwovens (Macfarlane, 1997), reinforcement materials for composites (Seavey et al., 2001), and special papers such as cigar filters (Alwis and Taylor, 2001).

MICROFIBERS

Description

There is no exact definition of microfibers. Generally, microfibers refer to fibers having a fineness of less than 1 denier. Denier is “the weight in grams of 9000 meters of fiber or yarn” (Collier and Tortora, 2000). One denier lyocell fiber has a diameter of about 9.68 μm. The introduction of microfibers is an important event in the history of manufactured fibers. Microfiber technology originated in the early 1970s in Japan (Lewin and Preston, 1983).

There is a great demand for microfiber applications in fashion clothing. Microfiber fabrics have excellent softness, comfort, hand, drape, and easy-care properties. Tight woven microfiber fabrics have an exceptional property of obstructing water droplets from penetrating while allowing air and moisture vapor circulation (Horrocks and Anand, 2000). The water beads are much larger than the spaces between the yarns and are effectively locked out. This advantage makes the microfiber fabrics water repellent without the need for chemical treatments or coating, which increases comfort. Microfiber fabrics can be processed to have fancy effects such as peach-skin and leather-like appearances. Microfibers are also used to produce high quality wipes, bacteria barrier fabrics and other special products (Horrocks and Anand, 2000).

Chemical Composition

Most microfibers are polyester or nylon, although acrylic, viscose rayon and PP microfibers are available too (Horrocks and Anand, 2000). Polyester microfibers are easier to spin and provide finer filaments than other commercial microfibers. Consequently they have a larger share of the apparel and sportswear market (Lewin and Preston, 1983). Nylon microfibers give better cover, lower density, higher strength and greater abrasion resistance.

Production Processes

There are chiefly three routes for the production of microfibers: 1) chemical dissolution of one component in a bicomponent fiber, 2) physical splitting of a bicomponent fiber, and 3) direct spinning of the microfiber including the meltblown process (Horrocks and Anand, 2000; Lewin and Preston, 1983).

In the direct spinning, single component filaments are extruded through very fine spinnerets and drawn at high draw ratios. It requires high precision in engineering techniques and good production control (Horrocks and Anand, 2000). There is diameter limitation on this kind of microfiber production because of the filament breakage after extrusion. The meltblown process uses high-speed air to attenuate polymer extrudates from the spinnerets into microfibers with a diameter of several microns (Horrocks and Anand, 2000). This process produces nonwovens webs, not single filaments.

The chemical dissolution or physical splitting bicomponent process involves spinning of conventional bicomponent filaments and breaking them down into smaller components later. The main polymers in bicomponent fibers for microfiber production are PP, PET and nylon (Lewin and Preston, 1983). Microfibers of a linear density up to 0.001 denier can be produced from bicomponent fibers (Lewin and Preston, 1983).

Lyocell Microfiber

The meltblown process has the ability to produce fine fibers including microfibers. A series of studies have been conducted by Luo et al to produce lyocell microfibers from a series of compositions of hemicellulose, lignin and cellulose of low average degree of polymerization (Luo et al., 2001).

Solvent spinning is the common process to produce lyocell fibers industrially. The process can be divided into two parts: one part is similar to melt-spinning and the other part is like wet-spinning (Liu et al., 2001). Parameters such as concentration, jet hole size, draw ratio and air gap length, could be optimized to produce lyocell fibers having high fibrillation tendency for microfiber production (Woodings, 2003).

When lyocell solutions flow though a hyperbolic die, the elongational flow field could cause phase disengagement to produce microfibers at temperatures lower than that required to maintain the solution in an isotropic state (Collier et al., 1998). During phase disengagement, a solvent rich phase could be rejected in lyocell solutions of high concentrations, while a cellulose rich phase could be rejected in lyocell solutions of lower concentrations which results in independent microfibers (Collier et al., 2000). The formation of microfibrillar structure may be determined mostly by lyocell concentration and the flow field applied. Ideal lyocell concentrations for fibrillar structure formation should be of lower concentrations with the cellulose rich phase rejected from and surrounded by the solvent rich phase (Collier et al., 2000).

RHEOLOGY

Rheology is defined as the science of deformation and flow of matter, and deals primarily with the stresses generated during the flow of materials. Rheology plays a significant role in polymer processing, food processing, coating and printing, and many other manufacturing processes (Barnes et al., 1989, Morrison, 2001). Therefore, knowledge of the complete rheological properties of the lyocell solutions is required for better understanding, predicting and controlling lyocell production and final lyocell fiber properties.

Rheology of Solutions and Melts

Shear flow and elongational (or extensional) flow are the two primary flow modes in polymer processing operations. Knowledge of both shear and elongational rheology is required in polymer processing because either alone cannot fully describe the flow characteristics.

Shear Flow

For a Newtonian fluid, the viscosity is independent of shear rate and the shear stress is related to the shear rate through the equation (Barnes et al., 1989)

$$\tau = \eta \dot{\gamma}$$

where τ is the shear stress, η is the viscosity of the fluid and $\dot{\gamma}$ is the shear rate. For non-Newtonian fluids, viscosity changes with the variation of shear rate. It is often useful to describe non-Newtonian flow by an empirical power law (Barnes et al., 1989):

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

where k *and* n are constants, and n is the power law index. When $n = 1$ the expression reduces to the Newtonian law for Newtonian fluids. For shear thinning fluids n is less than one and for shear thickening fluids n is greater than one (Barnes et al., 1989, Morrison, 2001).

With viscoelastic polymer melts or solutions, some of the deformation is elastic, and will return to zero as a function of time when the force is removed. The remaining deformation, i.e. the viscous portion, will not return to zero when the force is removed. Under a constant force, the elastic displacement remains constant while the sliding displacement continues to increase.

If the force varies sinusoidally, the viscous dissipation energy is always positive and lost in the form of heat while the elastic energy may be positive or negative and is recouped (Barnes et al., 1989). The shear stress is a vector sum of elastic stress and viscous stress and the complex shear modulus G^* is defined as (Barnes et al., 1989):

$$G^* = G' + iG''$$

where G' is the in-phase storage modulus and G'' is the out-of-phase loss modulus with

$$\tan(\delta) = G''/G'$$

If the dynamic measurements are made in the linear viscoelastic region, the frequency where these parameter curves cross over (i.e. $G'=G''$) corresponds to the reciprocal of the average relaxation time for the material. A value for $\tan(\delta)$ greater than unity indicates the materials possess more viscous properties, whereas one value lower than unity means the materials possess more elastic properties (Barnes et al., 1989).

G' and G'' can be calculated by measuring the in-phase and out-of-phase components of the response of strain to an imposed stress or vice versa at different frequencies. The modulus may vary greatly with frequency/time scale of the experiment. The complex viscosity (η^*) measured is defined as

$$\left|\eta^*\right| = (\eta'^2 + \eta''^2)^{1/2} = \frac{\left|G^*\right|}{\omega}$$

$$\eta' = \frac{G''}{\omega},$$

$$\eta'' = \frac{G'}{\omega},$$

$$\left|G^*\right| = \sqrt{(G')^2 + (G'')^2},$$

and $$\omega = 2\pi f$$

where η' is the dynamic viscosity, η'' is the elastic part of the complex viscosity, ω is angular velocity and f is the frequency of oscillations.

Elongational Flow

Elongational flow is the dominant mode of fluid flow when a rapid change of shape such as stretching is involved in the operation. Extensional stretching flows are common in many polymer processing operations such as extrusion through converging profiles, injection molding, film stretching and fiber spinning.

The velocity field for uniaxial elongational flow in Cartesian coordinates is given by (Barnes et al., 1989)

$$\upsilon_x = \dot{\varepsilon}x \,, \upsilon_y = -\dot{\varepsilon}y/2 \,, \upsilon_z = -\dot{\varepsilon}z/2$$

where $\dot{\varepsilon}$ is a constant elongational strain rate, υ_x, υ_y and υ_z are the velocity components in *x*, *y*, and *z* directions respectively. The corresponding stress distribution is (Barnes et al., 1989)

$$\sigma_{xx} - \sigma_{yy} = \sigma_{xx} - \sigma_{zz} = \dot{\varepsilon}\eta_e(\dot{\varepsilon})$$

$$\sigma_{xy} = \sigma_{xz} = \sigma_{yz} = 0$$

where η_e is the elongational viscosity.

Trouton ratio (T_R) is defined as the ratio of elongational viscosity to shear viscosity (Barnes et al., 1989):

$$T_R = \frac{\eta_e(\dot{\varepsilon})}{\eta(\dot{\gamma})}$$

The elongational viscosity of a Newtonian fluid is usually three times the shear viscosity: $\eta_e = 3\eta$ (Barnes et al., 1989, Morrison, 2001).

Measurement

Mesurement of Shear Viscosity

Most rheological measurements are based on shear deformation because it is easier to measure. They are generally performed in one of four shear geometries: capillary flow, parallel-plate flow, cone-and-plate flow and Couette flow. The quantity measured is a force, pressure drop or torque that is directly related to the shear stress (Morrison, 2001).

Capillary rheometry is widely used in polymer processing particularly for viscosities at high shear rates. Flow through a capillary is a unidirectional flow. The viscosity measured is derived from the properties of the fluid near the wall and the derivation also assumes that the fluid at the wall is representative of the properties of the fluid in general (Morrison, 2001).

The parallel-plate rheometer and cone-and-plate rheometer are preferred for the study of small quantities of materials or for materials that would be adversely affected by the severe contractions at the inlet of a capillary die. Although there is the problem of radial dependence of the shear rate and shear strain in the parallel-plate experiment, a homogeneous flow can be produced in small angles (Morrison, 2001). Cone-plate rheometers are free of this problem but it is difficult to load highly viscous materials. Both static and dynamic methods are available to determine the viscoelastic behavior of materials (Barnes et al., 1989, Morrison, 2001). An example of a parallel plate instrument is the Advanced Rheometric Expansion System (ARES) by Rheometric Scientific (Figure 2.2) (Collier et al., 2000). The lower plate of the ARES rheometer is attached to a motor that is able to rotate in different modes (steady mode and oscillatory mode) and speeds. The upper plate is attached to a torque transducer and force transducers. There is a very efficient temperature control scheme on the ARES. The rheometer plates are enclosed in an oven with the ability to vent gases for cooling and heating.

The testing chamber of a Couette rheometer is of concentric-cylinder geometry, and the fluid to be tested is confined to the narrow space between the two cylinders. The gap must be small enough so that the assumption of a linear velocity profile holds (Morrison, 2001). The Couette geometry is limited to modest rotational speeds because of the instabilities that lead to three-dimensional flows. The instabilities are due to the high shear rate, inertia and the elasticity characteristics of the materials (Morrison, 2001).

Mesurement of Elongational Viscosity

It is generally agreed that it is far more difficult to measure elongational viscosity than shear viscosity. The basic problem is to maintain a uniaxial elongational

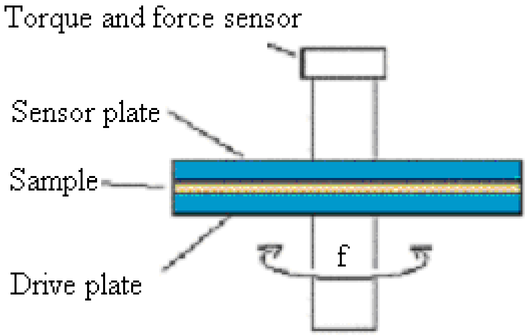

Figure 2.2. Schematic ARES with Parallel Plate Geometry.

flow for a sufficient time for the stress or the strain rate to reach a steady state, which enables the measurement of steady elongational viscosity (Burkinshaw and Gandhi, 1997a). In order to attain a constant elongational strain rate in the sample, the sample length must be increased exponentially with time (Barnes et al., 1989).

Existing methods to measure elongational viscosity include homogeneous stretching methods, constant stress devices, contraction flow devices, and spinning techniques. The homogeneous stretching method and the constant stress method are direct methods for the measurement of elongational viscosity (Barnes et al., 1989, Morrison, 2001).

Homogeneous Stretching Method

In one homogeneous stretching method the sample is held between a stationary block and a movable block. The velocity of the movable block increases exponentially with time to get a constant elongational strain rate in the sample. The overall deformation of the specimen is limited in the conventional stretching method. Meissner (Meissner, 1971, Meissner, 1969, Meissner, 1972) developed this method by using two sets of toothed wheels instead of end loading to provide constant stretching. The stress is measured by the deflection of a spring that is associated with one pair of rollers. Although the elongational strain rate can be accomplished in principle, a sufficient time is required for the stress to reach its steady state (Barnes et al., 1989).

The main problem of this method is the sagging of melt under its own weight. The method is restricted to high-viscosity materials and the sample is required to be extremely homogeneous because any small defect or weakness in the sample can cause necking and significantly affect the test results. It is also difficult to measure the stress of the sample held between the two ends while applying drawing to it (Barnes et al., 1989, Morrison, 2001).

Constant Stress Devices

The constant stress device was first introduced by Cogswell (Cogswell, 1968) and was developed later by Münstedt (Münstedt, 1975, Münstedt, 1979). In comparison to homogenous drawing devices, the specimen is stretched at a constant stress by adjusting the applied force as the sample elongates. Münstedt designed an apparatus that can be operated at constant stretching rate and constant stress. Smaller total deformation is required in constant stress devices to reach the steady-rate elongational flow than in the constant strain-rate devices.

The constant stress method has the same problems as the constant strain method. The method is restricted to high-viscosity materials and the sample is required to be extremely homogeneous.

Contraction Flows

The homogeneous stretching method and the constant stress method are direct methods for the measurement of elongational viscosity, and these two methods have their limitations. As stated above, the main problems with the Meissner type device (Meissner, 1971, Meissner, 1969, Meissner, 1972) are the sagging of the melt under its own weight and the requirement of extremely homogeneous samples. Completely molten polymers cannot be measured due to the experimental limitations of these two methods (Barnes et al., 1989).

Cogswell (1972a, 1972b) proposed an indirect method for the measurement of the elongational viscosity of polymer melts using converging flows to avoid the difficulties and the limitations of the direct measurement methods. A flow from a reservoir into a die having small diameter was interpreted as an extensional deformation superposed onto a simple shear flow. The shearing component and the extensional component were treated separately and added to give the total flow. Equations were derived for the elongational viscosity, the steady state shear viscosity, and the shear rate (Barnes et al., 1989).

Binding (1988) developed an approximate analysis of contraction flow with the assumption that the flow field is of least resistance; both shear and extensions were included in the formulation. The theory successfully predicts the phenomenon of vortex enhancement and provides estimates of the extensional viscosity (Barnes et al., 1989, Morrison, 2001).

Collier (Collier et al., 1998, Petrovan et al., 2000b) proposed that polymer melts could be elongationally characterized by using hyperbolic dies. The results showed that orientation-developing effects of the melt are so substantial that shearing gradients near the wall become comparatively insignificant. This discovery was theoretically justified by developing stream functions expressing the hyperbolic flow convergence and potential functions describing the pressure profiles as the driving force. The hyperbolic convergent dies have been explained.

The Advanced Capillary Extrusion Rheometer (ACER), is a state-of-the-art capillary rheometer, made by Rheometric Scientific Inc.. A schematic representation of the ACER is given in Figure 2.3 (Collier et al, 1998). The instrument has fully automatic control at precise strain rate operation and temperature. The ACER deforms a sample by forcing it through a capillary channel with a ram and the pressure is measured.

The Advanced Capillary Extrusion Rheometer uses constant diameter capillary dies of different sizes to measure the shear rheology. When a hyperbolic die is used with the ACER however, the effective elongational viscosity (η_{eff}) can be calculated as

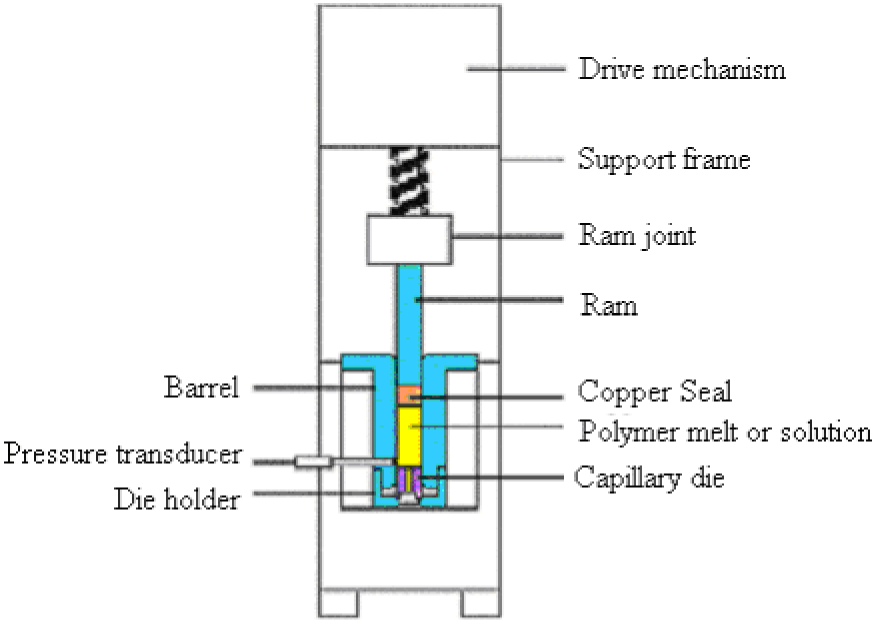

Figure 2.3. Rheometric Scientific Advanced Capillary Extrusion Rheometer (ACER).

a function of Hencky strain (ε_H) and elongational strain rate ($\dot{\varepsilon}$) (Collier et al., 1998, Petrovan et al., 2000b):

$$\eta_{eff} \equiv \frac{\Delta P}{\dot{\varepsilon}\varepsilon_H}$$

$$\dot{\varepsilon} = (v_0/L)(\exp \varepsilon_H - 1)$$

$$\varepsilon_H = \ln\left(\frac{D_0^2}{D_e^2}\right)$$

where v_0 is the ram speed, D_o is the inlet diameter, D_e is the outlet diameter, L is the centerline length of the hyperbolic die (Figure 2.4).

Increasing the Hencky strain brings about an increase in the elongational viscosity, and the orientation of the fiber produced is higher. Body forces, enthalpy of orientation, and entropy of orientation were reported to be high at low temperature and

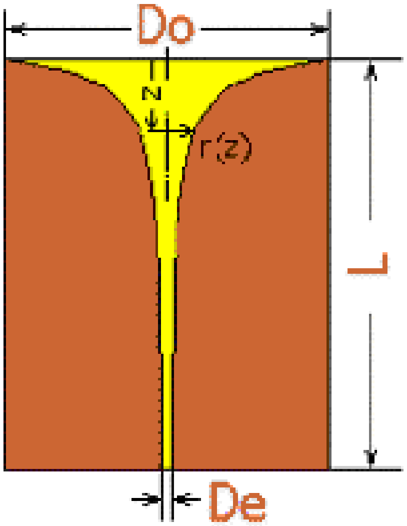

Figure 2.4. Convergent Hyperbolic Die.

high deformation rates (Petrovan et al., 2000a, Romanoschi, 1998). Temperature, Hencky strain, and deformation rates could be used as parameters to control the rheological and orientation behavior of lyocell solutions, and therefore the characteristics of the lyocell fiber properties. As the lyocell solution flows through hyperbolic convergent conical dies (Collier et al., 1998a), the cellulose molecules are forced to extend and become nearly parallel to the fiber axis inducing crystallization. The dies were designed to generate a constant elongational strain rate throughout the core. The die channel decreases as $R^2z = C$, where C is a constant, z is the flow direction and R is the radius of the flow channel (Collier et al., 1998a). As found by light scattering experiments aggregates of molecules were present even in the dilute cellulose-NMMO solutions (8%) (Fink et al., 2001). Phase separation and microfiber formation occurred in the convergent die (Collier et al., 1998a, Romanoschi, 1998). Cellulosic chains of higher DP can increase the elongational viscosity (Petrovan et al., 1999) and enhance the orientation induced by the convergent flow (Petrovan et al., 2000b).

Other Techniques

The spinning method is relatively easy to perform and the general kinematics can be determined with relative ease (Hudson and Ferguson, 1976, Jones et al., 1987). But it is not possible to quantitatively interpret the experimental data in terms of the definition of elongational viscosity. This method can be used for polymer melts and for low viscosity liquids (Barnes et al., 1989).

The lubricated flow method provides a flow close to the ideal elongational flow by the use of lubrication to eliminate the unwanted shearing at the rheometer walls. However, the interpretation of experimental data is complicated, and the technique itself is far from easy to use because the interface boundary condition between the sample and the lubricant is dependent on the rheological properties of the sample (Jones et al., 1987, Williams and Williams, 1985, Mieck et al., 1997).

CHAPTER III

METHODS, INSTRUMENTS AND PROCEDURES

Objectives of this research include: a) preparation of lyocell solutions from different cellulose sources; b) study of the rheological properties of the prepared solutions; c) study of the spinnability of lyocell solutions; and e) exploration of the feasibility of making lyocell fibers and microfibers. To accomplish the objectives, lyocell solutions were made from different agricultural and waste cellulosic sources and commercial dissolving pulps, including commercial dissolving pulps of different degrees of polymerization (DP 760, DP 1720), commercial bleached and unbleached hardwood, softwood, thermomechanical, and recycled newsprint pulps, bagasse and kudzu. Lyocell solutions were first produced, and the rheology of these solutions was studied including the complex viscosities of all lyocell solutions and the effective elongational viscosities of selected lyocell solutions.

PREPARATION OF LYOCELL SOLUTIONS

The preparation of lyocell solutions may be divided into three steps: a) grinding the cellulose into a fine powder; b) preparation of $NMMO \cdot H_2O$; and c) mixing of cellulose powder and $NMMO \cdot H_2O$ in a Brabender mixing head to make lyocell solutions.

Preparation of Cellulose Powder

Bagasse and kudzu were provided in the form of treated pieces. Bagasse was extracted from mechanically separated sugar cane rind and kudzu was extracted from mechanically separated kudzu stems. They were partially delignified with NaOH. The commercial dissolving pulps of DP 670 and DP 1720 and other pulps were provided in the form of paper sheets. Dissolving pulps are different from common paper pulps in that they are chemically refined and purified pulps composed of more than 90% pure cellulose fiber while paper pulps are less pure (Woodings, 2001). The paper sheets, bagasse pieces and kudzu pieces were first broken into small pieces, then put into a grinder to make the ground powder. Other cellulosic sources were received in the form of pulps. They were first put on screens, washed with water for 30 minutes and allowed to dry in the air at room temperature. The final pulps in the form of papers were then broken and ground. All the cellulose powders were kept in an oven at 105°C for at least 24 hours. They were then put into plastic bags and sealed with a vacuum sealer.

Preparation of NMMO·H_2O

Fifty weight percent NMMO solutions were distilled to 87%w solutions in a rotary evaporator under vacuum. The molecular weight of NMMO is 117 and that of NMMO monohydrate is 135. The 87%w NMMO solutions are essentially the monohydrate form (Macfarlane, 1997). The silicone oil bath in which the solution was heated was set at 100°C.

Preparation of Lyocell Solutions

Cellulose powder, NMMO·H_2O and 1% (by weight on pulp) propyl gallate as an anti-oxidant were mixed and dissolved in the mixing chamber of a Brabender. The mixture was mixed until the solution was transparent. Different concentrations of lyocell solutions required different preparation times. More preparation time was required for higher concentrations (Table 3.1).

The temperature of the mixer was set at 90°C, and the mixing speed was held constant at 80 rpm. A filter device was designed to filter the lyocell solutions immediately after the preparation. The amount of undissolved particles filtered from the solutions was insignificant, and bagasse solutions had the largest amount of undissolved particles. The solutions were cooled to a solid and stored in sealed bags.

RHEOLOGICAL CHARACTERIZATION OF LYOCELL SOLUTIONS

In the realm of lyocell processing, it is important to consider the factors that affect viscosity. The major factors include temperature, concentration, molecular weight, molecular weight distribution, and shear rate. Both dynamic complex viscosities and elongational viscosities were measured on selected solutions.

Table 3.1. Mixing time of lyocell solutions.

Concentration (%)	Time (hour)
4	1
6	1.5
8	3
14	4

Measurement of Effective Elongational Complex Viscosity with the ACER

The effective elongational viscosities of lyocell solutions were all studied with the ACER rheometer using a hyperbolic die of Hencky 7, which has an entrance diameter of 19.95 mm, an outlet diameter of 0.6 mm and a length of 25 mm.

The lyocell solids were broken into small pieces before they were charged into the heated barrel of the ACER and allowed to melt. After the temperature stabilized, the effective elongational viscosity of lyocell solutions was measured according to the ram speed, pressure drop and the die shape.

Measurement of Complex Viscosities with the ARES

Like polymer melts, lyocell solutions exhibit a time-dependent visco-elastic behavior, which is a combination of elasticity and viscosity. The combined viscoelastic behavior can be examined by determining the effect that an oscillating force has on the response of the solution. Dynamic complex viscosities of all lyocell solutions were characterized with the ARES.

The lyocell solid was contained in sealed bags and pressed flat by compression molding at 90°C. The thickness of the lyocell solid was about 1.5 mm. The re-solidified solution was cut circularly to a diameter of 25 mm for use in the ARES.

Parallel plates were used for all the lyocell solutions in complex viscosity measurements. Compressed air was used as the vent gas for cooling and heating of the lyocell solutions. The oven temperature was first set to 90°C and the circularly-cut sample was put between the two plates. The computer-controlled upper plate was set to move downward to the lower plate from a gap of 2 mm to 1.2 mm with a maximum normal force set at 10 gf. When it was completed, any solution that compressed out of the plate edge was removed. The gap was then set from 1.2 mm to 1.05 mm. After quick removal of the solution compressed out at the edge, a thin layer of silicone oil was applied to prevent moisture uptake and coagulation of the sample. The oven was then closed. The gap was set to 1.00 mm and the temperature stabilized.

Dynamic strain sweep tests were first conducted at an angular velocity of 1 rad/s, and the linear viscoelastic range of the strains was determined. Dynamic frequency sweep tests were then made from 0.1 rad/s to 100 rad/s at a strain (2% for all the solutions) within the linear range.

LYOCELL FIBER SPINNING

Lyocell solutions of selected concentrations and sources were spun from the ACER to produce lyocell fibers by a dry-jet process. The lyocell solution was heated to different temperatures in the range of 80 to 110 °C and extruded at elongational rates of 1/s, 5/s and 500/s. A Hencky 7 hyperbolic die with an outlet diameter of 0.6 mm was used. The air gap was set at 10 cm and the coagulation bath was a water bath at room temperature.

A drawing device was set up, and fiber drawing was applied when it was possible (Figure 3.1). SEM and optical microscopy were the main techniques used to characterize the fiber morphology.

FIBER TREATMENT TO MAKE MICROFIBERS

Lyocell fibers produced were subjected to different treatments to produce microfibers. Tap water, 2%w H_2SO_4, 14%w and 17.5%w NaOH solutions were used to treat the lyocell fibers. Fibers were cut into lengths of 30 mm and treated with 50 mL solutions in a flask of 150 mL. Mechanical forces were provided by a magnetic stirring

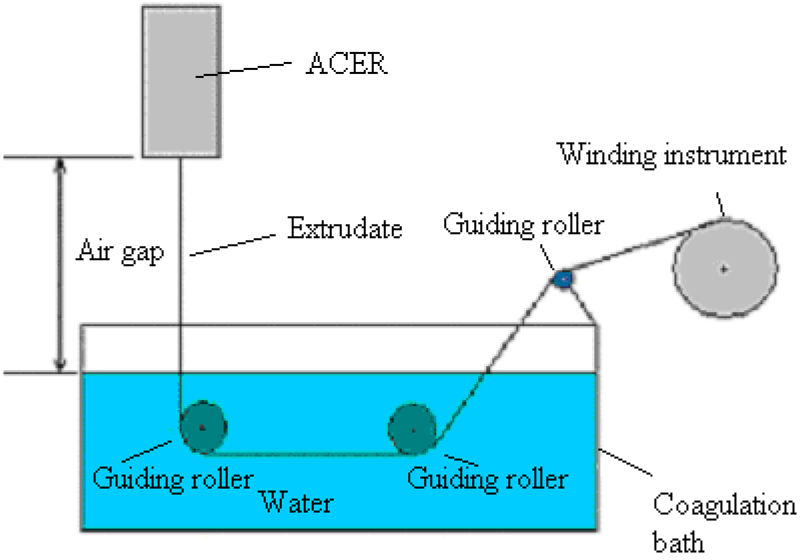

Figure 3.1. Dry-jet spinning of Lyocell fibers.

bar. The lyocell fibers were treated for different time periods to explore the feasibility of producing microfibers.

The first method was the stirring-in-water treatment, stirring the fibers in tap water for 1.5 hours. The fibers were observed and optical micrographs obtained. The second method used 14%w NaOH solution to treat the fibers for 1.5 hours followed by washing with water and treatment with 2%w H_2SO_4 solution for different time periods. The fibers were washed again and observed under a microscope. The third method used 17.5% NaOH solutions to treat lyocell fibers. The fibers were first treated in the solution for a period of time, washed, and then pressed lightly with a cover glass on the microscope slide to break them axially. The sample was observed under optical microscopy.

CHAPTER IV

RESULTS AND DISCUSSIONS

The primary goals of the study were to develop manufactured cellulosic fibers and microfibers from wood pulps as well as from lignocellulosic agricultural by-products and to investigate alternative cellulosic sources as raw materials for lyocell solutions. The rheological behavior of solutions was to be characterized, and spinning conditions and treatments were employed to induce formation of microfibers .

REPEATABILITY OF LYOCELL PREPARATION AND MEASUREMENTS

Lyocell solutions were produced according to the same protocol for all cellulosic sources as described in Chapter III. Lyocell solutions were prepared from different cellulosic sources: commercial dissolving pulp (DP 670, DP 1720), bleached hardwood, unbleached hardwood, bleached softwood, unbleached softwood, bleached thermomechanical pulp (TMP), unbleached TMP pulp, bleached recycled newsprint, unbleached recycled newsprint, bagasse and kudzu. Dissolving pulp blends of DP 670 and DP 1720 were also studied. The blends included DP 932, a blend of DP 1720 and DP 670 at a ratio of 1:3, DP 1195 at a ratio of 1:1 and DP 1457 at a ratio of 3:1.

In order to determine the repeatability of the lyocell preparation protocol, a series of lyocell solutions were made and the complex viscosities were compared. Five batches of 14% lyocell solutions from DP 670 dissolving pulp were prepared. From each batch, five complex viscosity measurements on five specimens were carried out at 90°C. Figure 4.1 shows the floating error bar graph of the complex viscosity measurements of each batch. The repeatability of all the measurements of the five batches is demonstrated in the Figure 4.2.

The coefficient of variance (CV) of the twenty-five measurements decreased with increasing angular velocity. The CV value is 19.21% at 0.1 s^{-1}, 13.53% at $1 s^{-1}$, 9.07% at $10 s^{-1}$, and 6.83% at 100 s^{-1}. The reproducibility of the lyocell preparation and measurement is good, although CV values are higher at lower angular velocities.

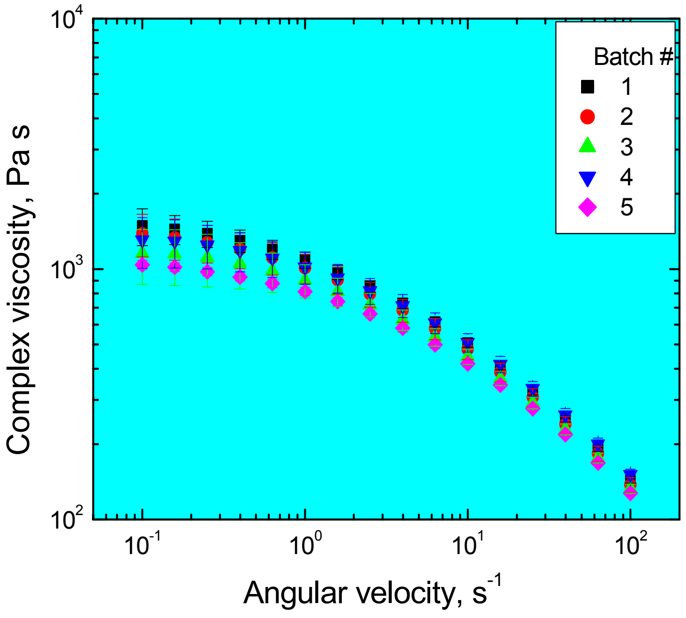

Figure 4.1. Complex viscosity measurements for separate batches of lyocell solutions of DP 670 dissolving pulp.

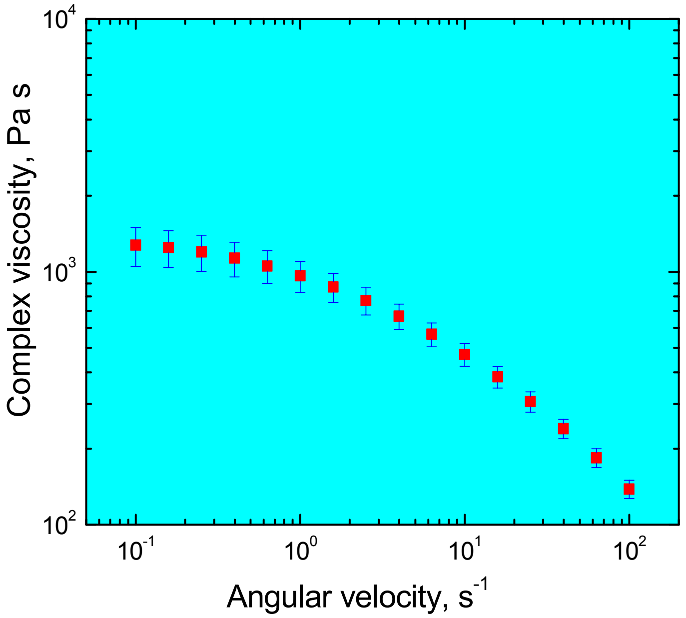

Figure 4.2. Complex viscosity of five batches of lyocell solutions of DP 670 dissolving pulp.

COMPLEX VISCOSITY OF LYOCELL SOLUTIONS FROM DIFFERENT SOURCES

Effects of Source, Concentration and Bleaching

Cellulose source, concentration and bleaching can affect the complex viscosity of lyocell solutions. A series of complex viscosity measurements were made on the lyocell solutions from different sources at 90°C (Figures 4.3 – 4.14).

All lyocell solutions exhibited shear-thinning behavior. The complex viscosity decreased with the increase of angular velocity. With the increase of concentration, complex viscosities increased except the 14% solutions of hardwood and softwood at lower angular velocities. The long preparation time for the 14% solutions probably changed the molecular weight distribution of the cellulose. However this needs to be further investigated. The viscosities of low concentration lyocell solutions are comparable to those of polymers used for meltblowing; and they could be used for meltblowing.

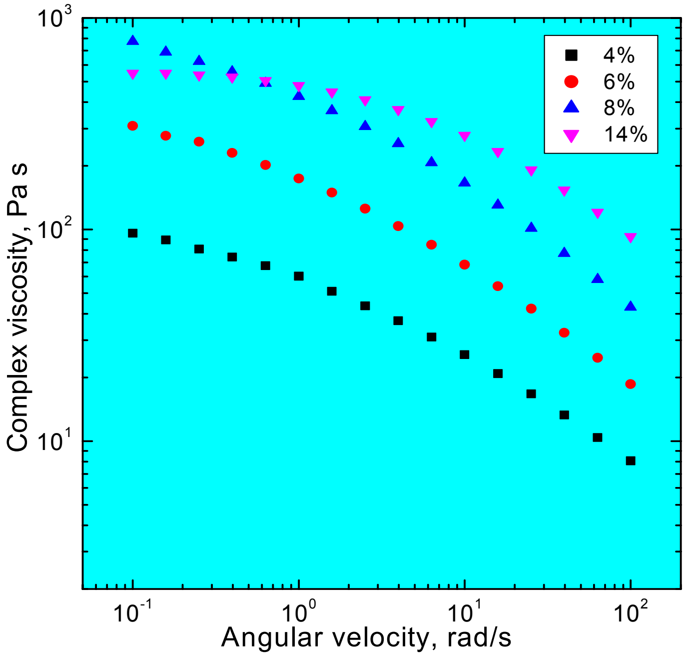

Figure 4.3. Complex viscosity of lyocell solutions prepared from bleached softwood.

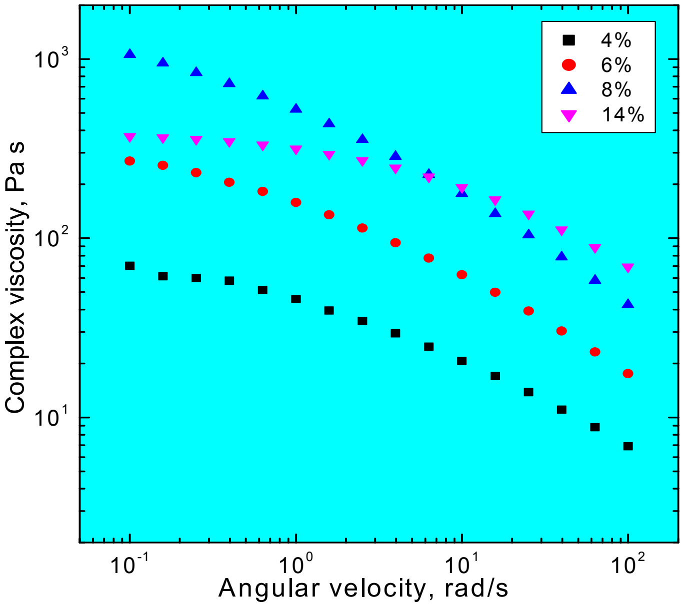

Figure 4.4. Complex viscosity of lyocell solutions prepared from unbleached softwood.

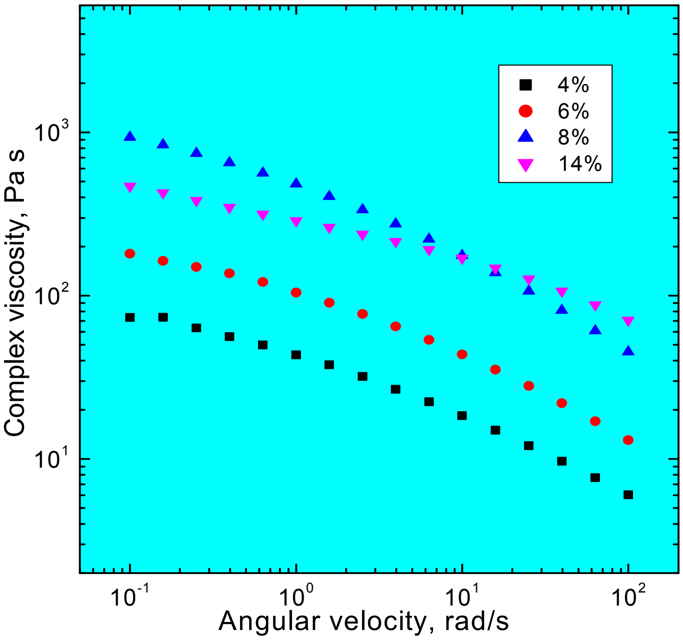

Figure 4.5. Complex viscosity of lyocell solutions prepared from bleached hardwood.

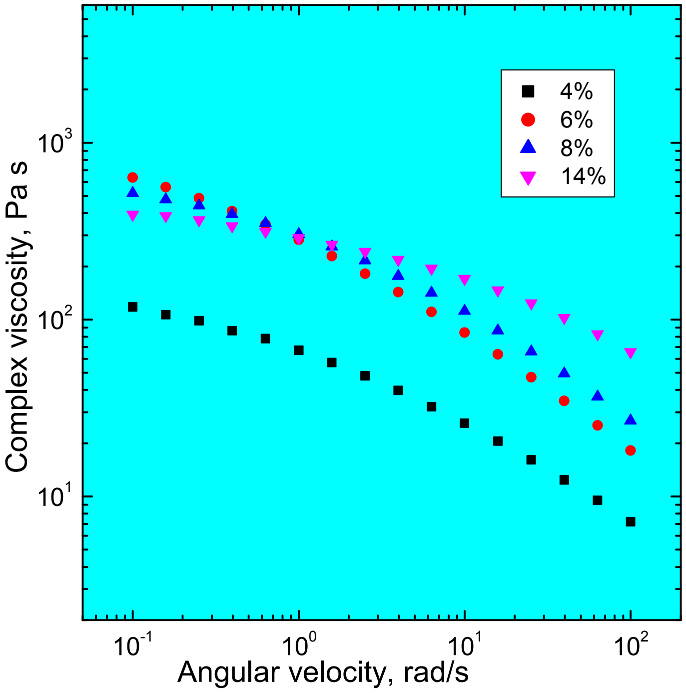

Figure 4.6. Complex viscosity of lyocell solutions prepared from unbleached hardwood.

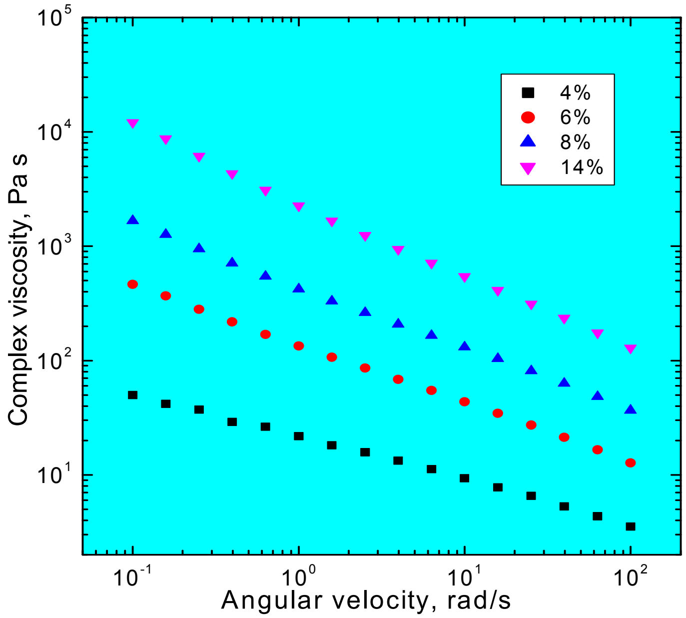

Figure 4.7. Complex viscosity of lyocell solutions prepared from bleached recycled newsprint.

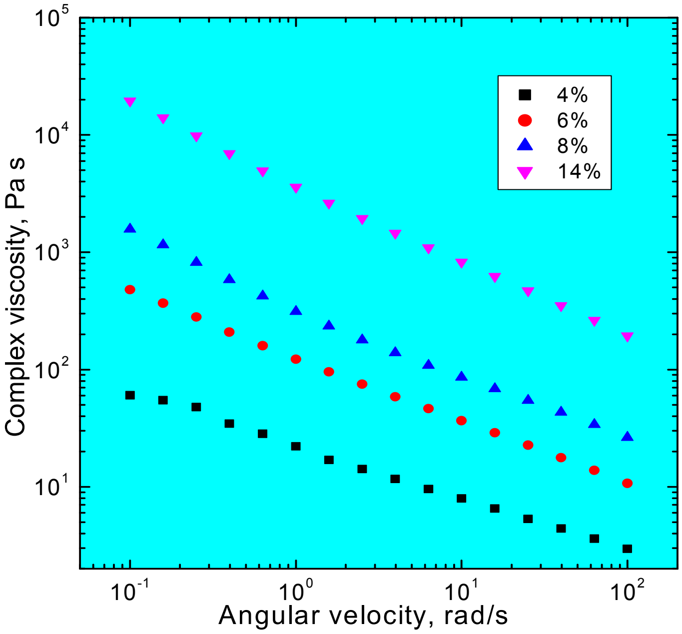

Figure 4.8. Complex viscosity of lyocell solutions prepared from unbleached recycled newsprint.

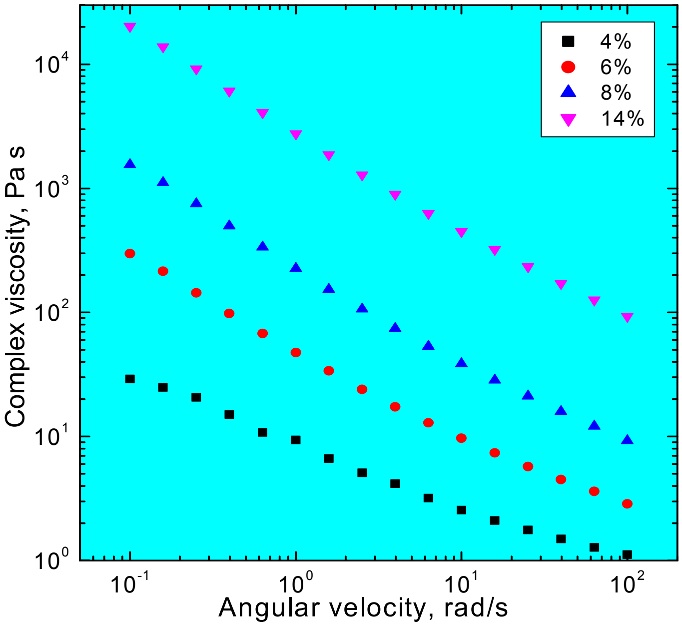

Figure 4.9. Complex viscosity of lyocell solutions prepared from bleached TMP.

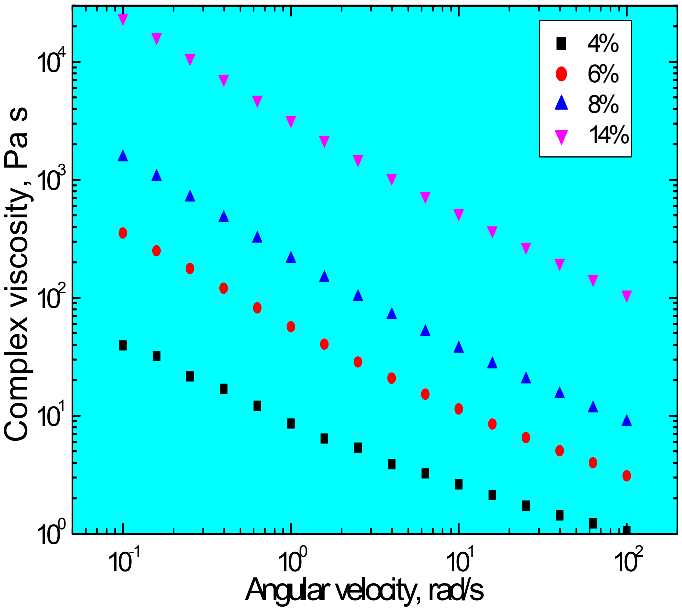

Figure 4.10. Complex viscosity of lyocell solutions prepared from unbleached TMP.

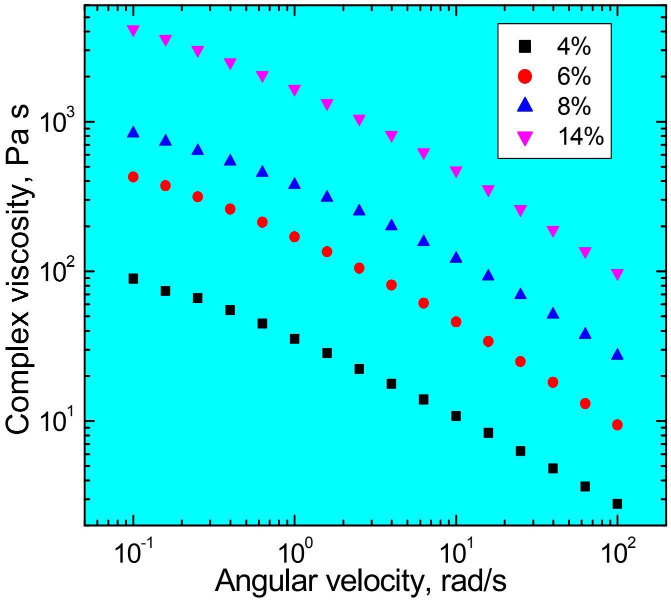

Figure 4.11. Complex viscosity of lyocell solutions prepared from bagasse.

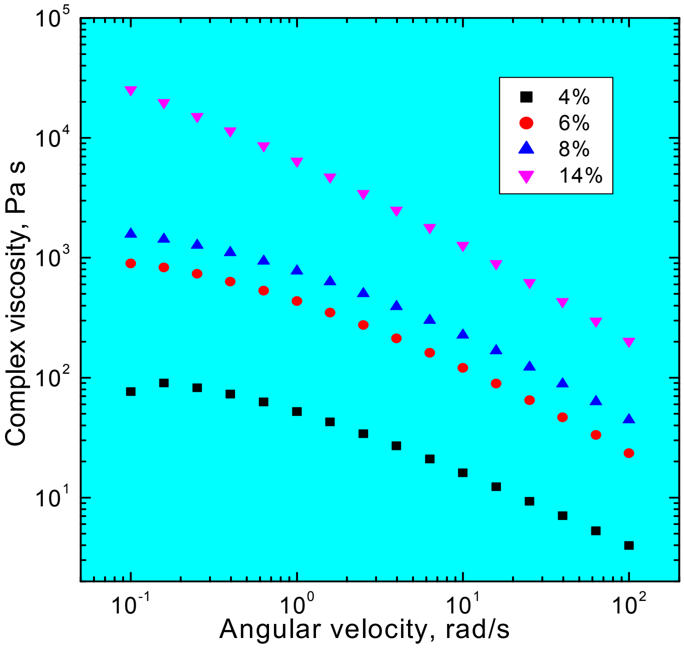

Figure 4.12. Complex viscosity of lyocell solutions prepared from kudzu.

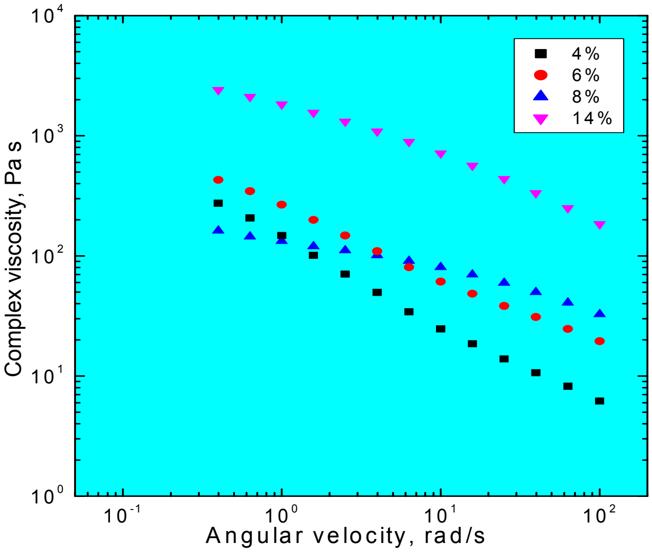

Figure 4.13. Complex viscosity of lyocell solutions prepared from DP 670.

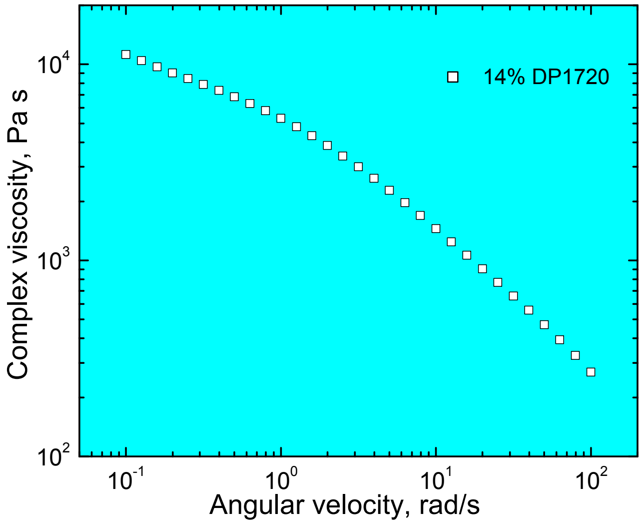

Figure 4.14. Complex viscosity of a 14% lyocell solution from DP 1720 (Measured by Xiaoling Wei, The University of Tennessee).

Univariate analysis of variance (ANOVA) was carried out on the complex viscosities to determine the effects of source, concentration, and bleaching. The viscosity values at an angular velocity of 1 rad/s were selected because this data point was representative of the complex viscosities of different lyocell solutions: a solution having a higher complex viscosity than another solution at 1 rad/s usually also had higher ones at other angular velocities except 8% and 14% hardwood and softwood solutions. ANOVA results are shown in Table 4.1.

The main variables, concentration, source, and bleaching, as well as all interactions, were significant. The two-way interactions were plotted to further examine the results (Figures 4.15-4.18).

There were four concentrations and four cellulose sources; sixteen t-tests were carried out to further analyze the bleaching effects on the complex viscosities of different lyocell solutions. The t-test results are shown in Table 4.2. The results confirm the significance of the differences shown in the Figures 4.15 – 4.18.

Table 4.1. Effects of concentration (C), source (S) and bleaching (B) on the complex viscosity of lyocell solutions.

Dependent Variable: Viscosity(Pas)

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	84979592[a]	31	2741277	642	<0.0001
Intercept	28623952	1	28623952	6700	<0.0001
B	236672	1	236672	55	<0.0001
C	40426317	3	13475439	3154	<0.0001
S	8306439	3	2768813	648	<0.0001
B*C	774453	3	258151	60	<0.0001
B*S	393310	3	131103	31	<0.0001
C*S	33103228	9	3678136	861	<0.0001
B*C*S	1739174	9	193242	45	<0.0001
Error	273435	64	4272		
Total	113876980	96			
Corrected Total	85253028	95			

a. R Squared = .997 (Adjusted R Squared = .995)

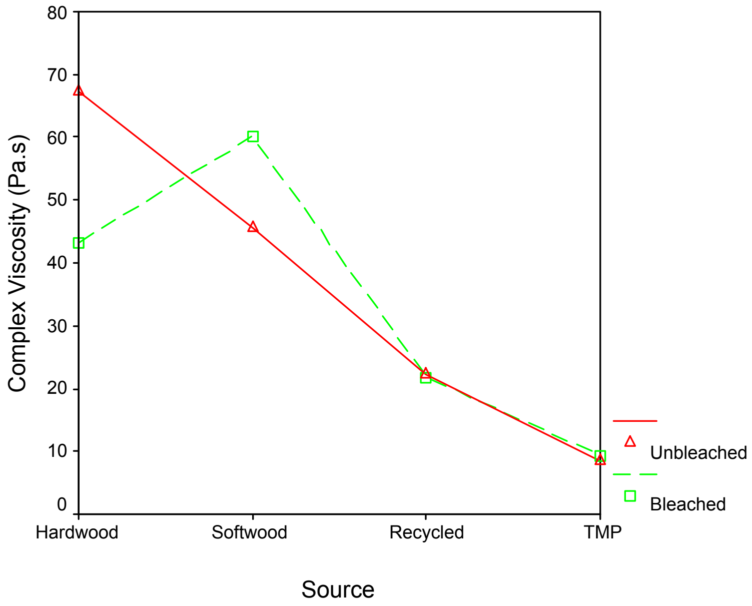

Figure 4.15. Interaction of source and bleach treatment for 4% lyocell solutions.

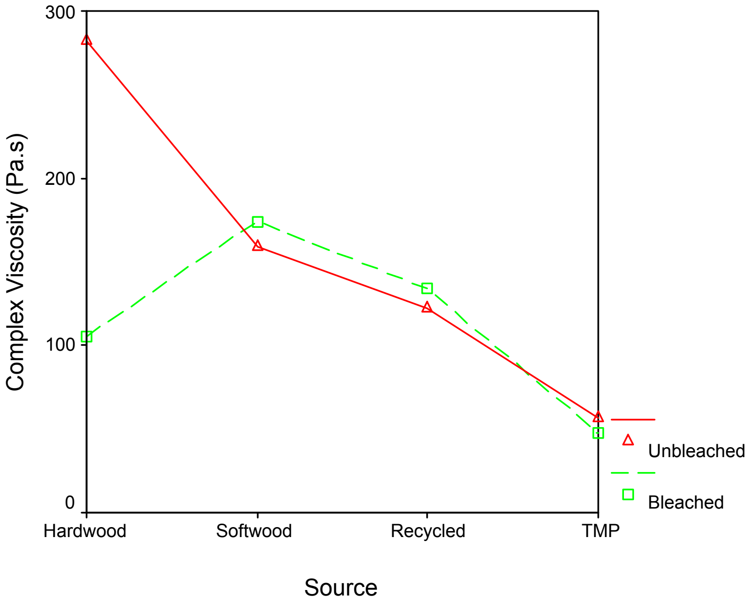

Figure 4.16. Interaction of source and bleach treatment for 6% lyocell solutions.

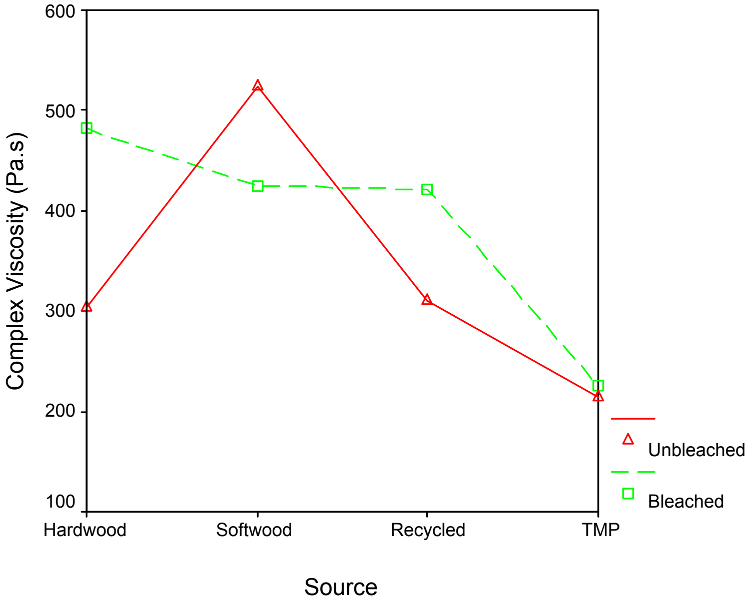

Figure 4.17. Interaction of source and bleach treatment for 8% lyocell solutions.

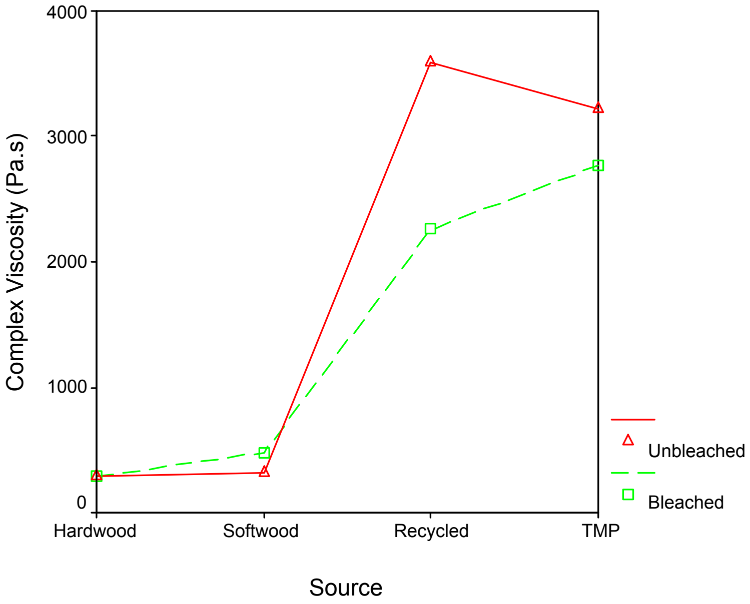

Figure 4.18. Interaction of source and bleach treatment for 14% lyocell solutions.

Table 4.2. p-values of t-test (two-tailed) for equality of means of complex viscosities of bleached and unbleached lyocell solutions.

Concentration / Source	4%	6%	8%	14%
Hardwood	0.002	<0.0001	0.001	0.858
Softwood	0.007	0.002	0.018	0.001
Recycled newsprint	0.775	0.260	0.004	0.002
Thermomechanical	0.654	0.009	0.492	0.007

For 4% solutions, bleaching affected the hardwood and softwood, but not the recycled and TM pulps. Unbleached softwood had a higher viscosity than bleached pulp; whereas the opposite was true for hardwood. For 6% solutions, the effect of bleaching was most apparent in the hardwood pulp. Bleaching also affected the viscosities of the softwood and TM pulps but only slightly. The bleaching effects were also different: it increased the viscosity of the solution from the softwood pulp, but decreased those from the hardwood and TM pulps. For 8% solutions, bleaching had effects on the hardwood, softwood and recycled newsprint pulps, but not on the TM pulp. Bleaching decreased the viscosity of the softwood solutions, which was contrary to the effects presented at 4% and 6%. For 14% solutions, bleaching had significant effects on the softwood, recycled newsprint and TM pulps. There was no significant effect on the hardwood pulp.

In general, bleaching decreases the molecular weight and purifies the cellulose. The decrease in molecular weight should result in lower complex viscosities, but the purification may result in fewer impurities and relatively high percentage of cellulose in the solution, which might result in a higher complex viscosity. In addition, degradation of the cellulose may have occurred during solution preparation, decreasing the complex viscosity. The lyocell solutions of unbleached pulps would be expected to suffer more severe degradation because of the higher percentage of impurities, such as alkaline residuals (Woodings, 2001).

The thermal degradation effect on lyocell solutions was demonstrated on 6% DP 670 solutions. The complex viscosities of lyocell solutions were measured before and after two hours' heating treatment at 90°C. The decrease of viscosity is apparent (Figure 4.19).

For hardwood pulps, bleaching had significant effects on the complex viscosity of 4%, 6% and 8% solutions, but no significant effect on that of 14% solutions. The bleaching effects were also different. The complex viscosities of 4% and 6% bleached hardwood lyocell solutions were lower than those of unbleached. This might have been due to the fact that bleaching decreased the molecular weight, and hence the complex

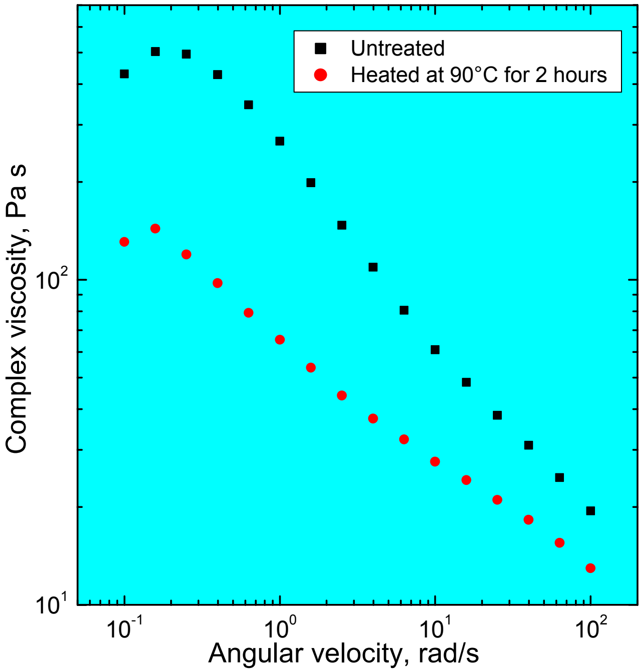

Figure 4.19. Complex viscosities of 6% DP 670 lyocell solutions before and after two-hours' heating treatment at 90°C.

viscosity. The complex viscosities of 6%, 8% and 14% unbleached hardwood solutions were similar.

For softwood pulps, the complex viscosities were affected significantly by the bleaching. Bleaching generally increased the complex viscosities of softwood lyocell solutions, although the 8% data did not follow this pattern. For softwood solutions, the effects of fewer impurities and higher percentage of cellulose seemed to be dominant; the complex viscosities of bleached softwood solutions were higher than those of unbleached. The complex viscosity of 14% bleached softwood was higher than that of 8% bleached softwood, but that of 14% unbleached softwood was lower than that of 8% unbleached softwood.

The effects of bleaching on recycled newsprint pulps and TM pulps were more complicated because of their high content of impurities. TM pulps are produced by refining steam-softened wood chips in a pressurized refiner (http://www.utipulp.org/pages/wood.html). The lignin content and other impurities are higher than that in the Kraft pulps. This is also true for recycled newsprint pulps.

For recycled newsprint pulps, the complex viscosities of 8% and 14% lyocell solutions were significantly affected by the bleaching. Bleaching increased the viscosities of 8% solutions. However, the long preparation time of 14% solutions caused much more degradation, resulting in lower viscosity than that of 14% unbleached recycled newsprint. The complex viscosity increased with the increase of concentration.

For TM pulps, there were significantly decreasing effects in the complex viscosities of the 6% and 14% lyocell solutions, but no significant effects in those of the 4% and 8% solutions. As with the recycled newsprint pulps, the complex viscosity increased with the increase of concentration. Neither bleached nor unbleached thermomechanical pulps were dissolved well, and there were undissolved particles found in the solutions. The same was true for the bleached and unbleached recycled newsprint pulps.

According to Table 4.2, the differences between bleached and unbleached sources are more apparent for hardwood and softwood at lower concentrations, yet more apparent for thermomechanical and recycled newsprint pulps at higher concentrations.

One-Way ANOVA Post Hoc Tests

There exist differences among the means of complex viscosity of lyocell solutions from different cellulose sources. It is beneficial to identify homogeneous subsets of means that are not different from each other among the lyocell solutions from different sources, especially to find which agricultural cellulose could have the potential to produce lyocell solutions having similar complex viscosity to that from commercial dissolving pulps.

Post hoc range tests and pairwise multiple comparisons can determine which means differ. Pairwise multiple comparisons test the difference between each pair of means. One-way ANOVA post hoc tests were carried out on the complex viscosity data of lyocell solutions. The complex viscosity data are compared and grouped into subsets as shown in Table 4.3.

Lyocell solutions from both bleached and unbleached softwood and hardwood could be classified as one homogenous subset. This group had the lowest complex viscosities. Lyocell solutions from kudzu had the highest complex viscosity, and was different from all other sources. Solutions from DP 1720 had the second highest complex viscosity, and was significantly different from other sources.

Solutions from unbleached recycled newsprint pulps were similar to solutions from DP 1457 and those from unbleached TM pulps. Solutions from bleached TMP were similar to solutions from unbleached TMP and DP 1195 and to those from bleached recycled and DP 932. Solutions of DP 670 and bagasse were similar.

The results showed the potential to substitute DP 1457 with unbleached recycled newsprint pulps, to substitute DP 1195 with bleached and unbleached TM pulps, to substitute DP 932 with bleached TM pulps or bleached recycled newsprint pulps, and to substitute DP 670 with bagasse.

Effects of Concentration on Dynamic Moduli

Dynamic moduli (storage modulus *G’* and loss modulus *G”*) of the lyocell solutions of different concentrations from all the cellulose sources are shown in Figures 4.20 - 4.31. The storage modulus gives information about the elastic character of the fluid or the energy storage that takes place during the deformation. The loss modulus gives information about the viscous character of the fluid or the energy dissipation that occurs in flow.

The dynamic moduli increased with concentration except for 14% bleached and unbleached softwood and hardwood lyocell solutions at low angular velocities. This may be due to the longer preparation time of 14% lyocells, but the mechanism of this

Table 4.3. Post Hoc analysis of complex viscosities at 1/s (Pa·s).

Tukey HSD[a,b,c]

Source	N	Subset							
		1	2	3	4	5	6	7	8
Bleached Hardwood	3	288							
Unbleached Hardwood	3	290							
Unbleached Softwood	3	314							
Bleached Softwood	3	479							
DP 670	5		1223						
Bagasse	3		1662						
DP 932	3			2256					
Bleached Recycled	3			2260					
Bleached TMP	3			2766	2766				
DP 1195	3				2901				
Unbleached TMP	3				3218	3218			
Unbleached Recycled	3					3594	3594		
DP 1457	2						3777		
DP 1720	2							5395	
Kudzu	3								6413
Significance		.98	.156	.052	.130	.347	.988	1.00	1.00

Means for groups in homogeneous subsets are displayed.
Based on Type III Sum of Squares
The error term is Mean Square(Error) = 27831.139.

[a] Uses Harmonic Mean Sample Size = 2.885.

[b] The group sizes are unequal. The harmonic mean of the group sizes is used. T I error levels are not guaranteed.

[c] Alpha = .05.

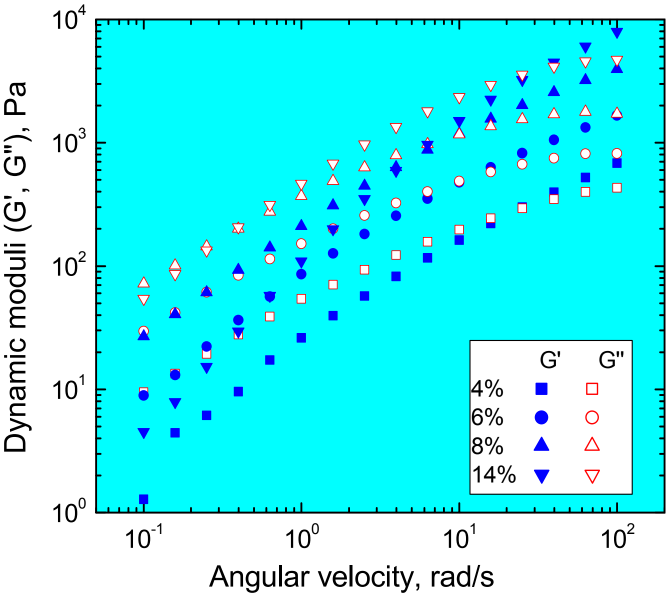

Figure 4.20. Dynamic moduli of lyocell solutions prepared from bleached softwood.

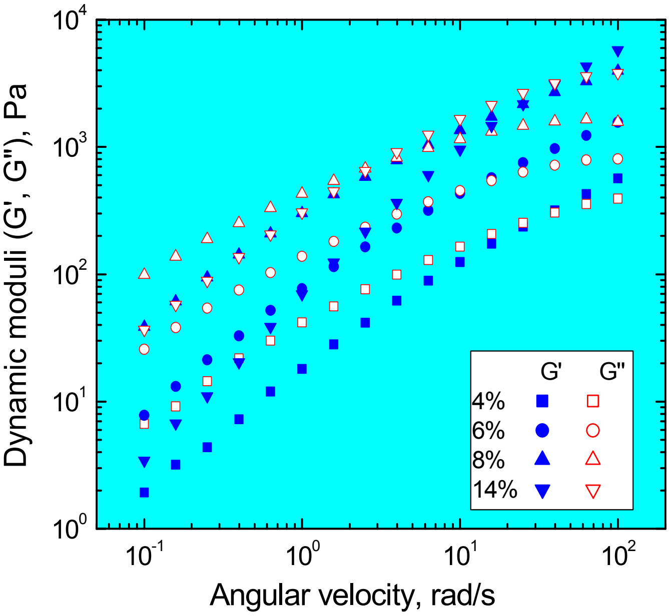

Figure 4.21. Dynamic moduli of lyocell solutions prepared from unbleached softwood.

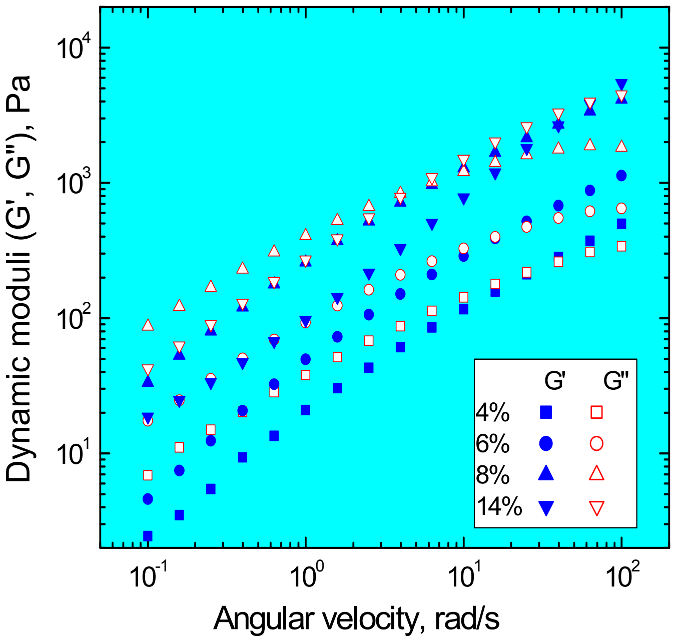

Figure 4.22. Dynamic moduli of lyocell solutions prepared from bleached hardwood.

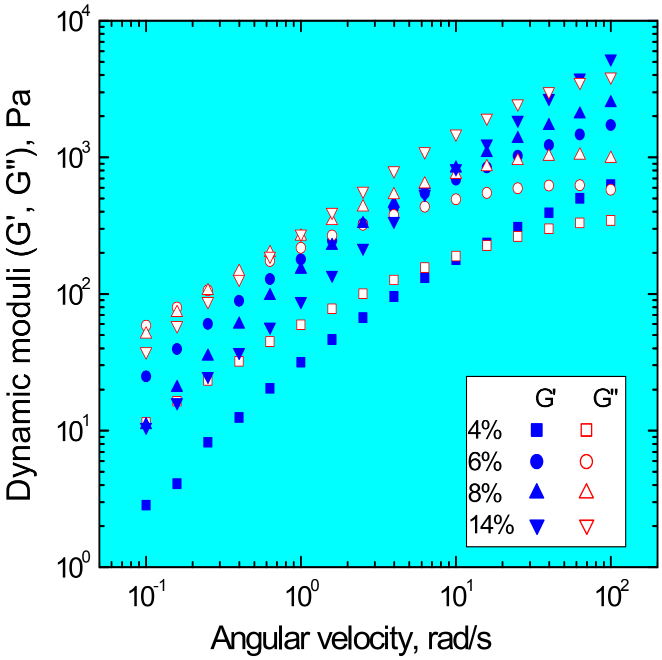

Figure 4.23. Dynamic moduli of lyocell solutions prepared from unbleached hardwood.

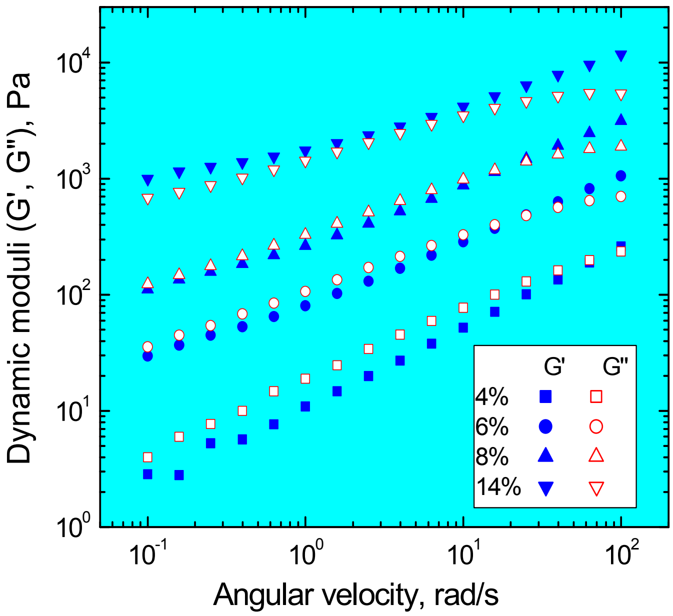

Figure 4.24. Dynamic moduli of lyocell solutions prepared from bleached recycled newsprint.

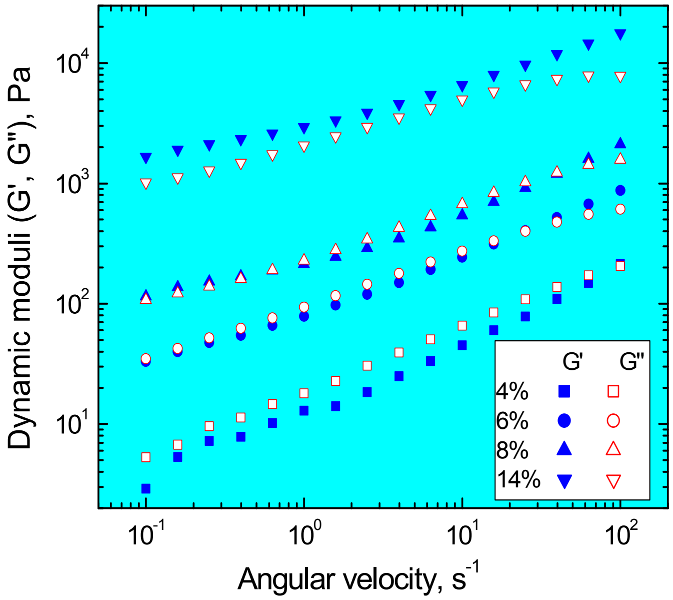

Figure 4.25. Dynamic moduli of lyocell solutions prepared from unbleached recycled newsprint.

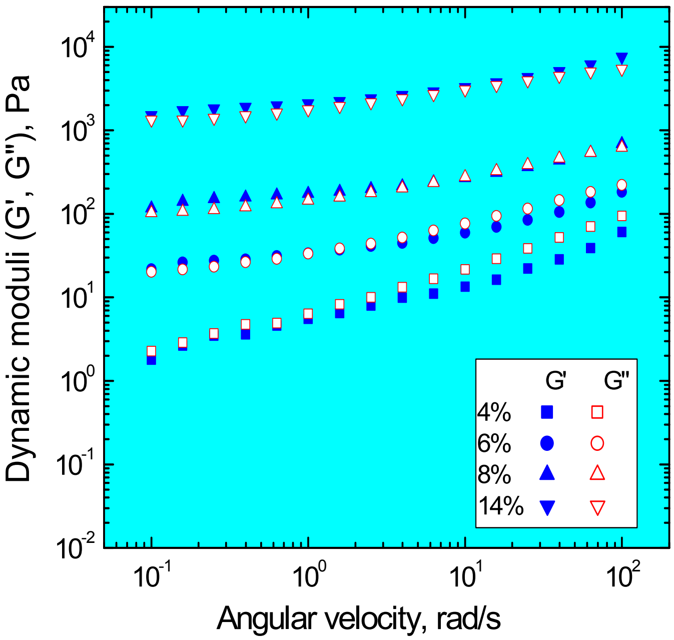

Figure 4.26. Dynamic moduli of lyocell solutions prepared from bleached TMP.

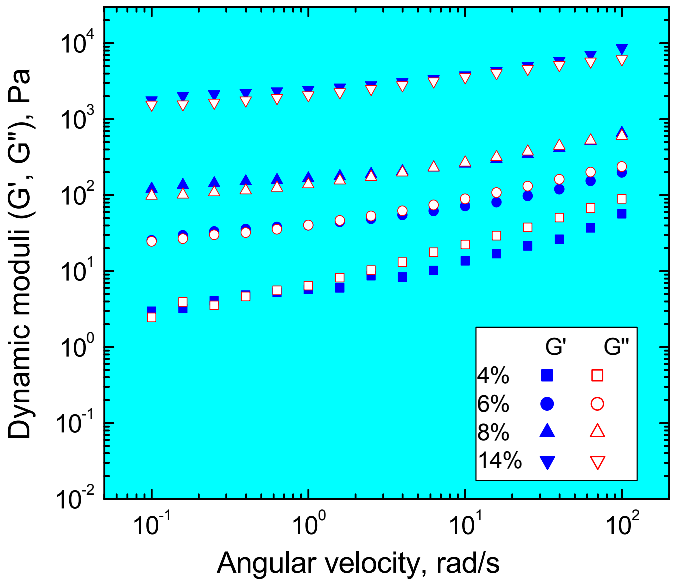

Figure 4.27. Dynamic moduli of lyocell solutions prepared from unbleached TMP.

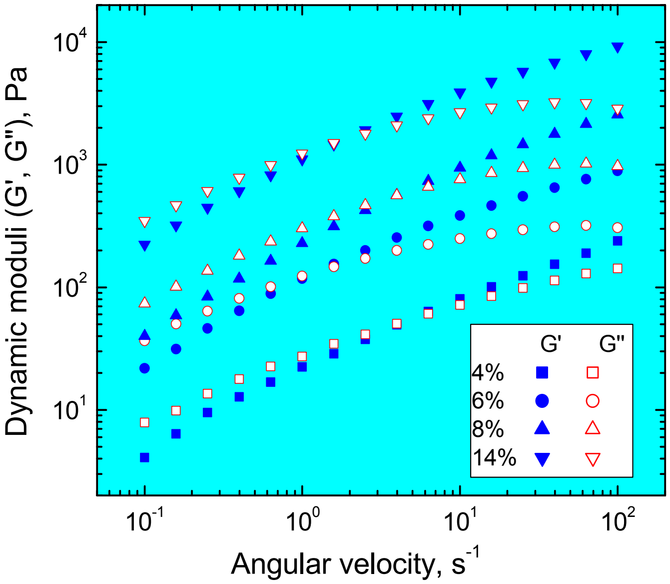

Figure 4.28. Dynamic moduli of lyocell solutions prepared from bagasse.

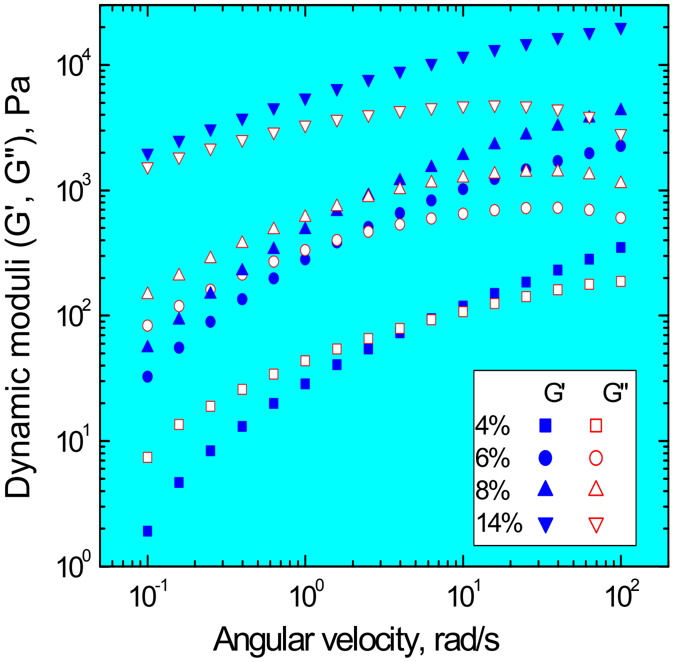

Figure 4.29. Dynamic moduli of lyocell solutions prepared from kudzu.

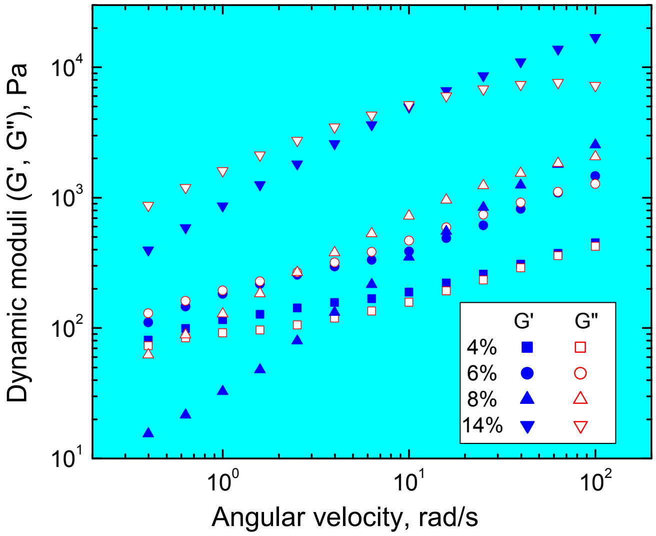

Figure 4.30. Dynamic moduli of lyocell solutions prepared from DP 670.

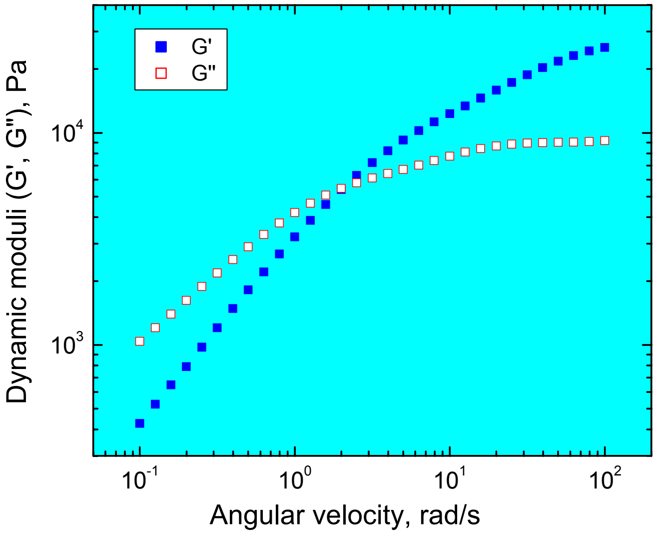

Figure 4.31. Dynamic moduli of the 14% lyocell solution prepared from DP 1720 (Measured by Xiaoling Wei, The University of Tennessee).

phenomenon is uncertain. There could have been degradation of the cellulose chains that resulted in lower viscosity at low angular velocities. At higher angular velocity, lyocell solutions of higher percentage demonstrated higher complex viscosities and higher dynamic moduli.

At low frequencies, the storage and loss moduli G’ and G” of the lyocell solutions were small. This is because the low frequencies allow enough time for the molecules to untangle and significant relaxation occurs. When the lyocell solution is deformed at high frequencies the entangled chains do not have enough time to relax and the moduli go up. The curve pattern of DP 670, DP 1720, softwood, hardwood, kudzu and bagasse is different from that of recycled and TMP.

Crossover data of selected solutions is listed in Table 4.4. The crossover points of G’ and G” curves of wood pulp solutions shift from higher angular velocity and lower modulus to lower angular velocity and higher modulus with the increase of lyocell concentration except for 14%. The trend is also true for kudzu, bagasse and recycled. TMP solutions show a different trend of the crossover points. Bleached TMP (6%, 8%, and 14%) and unbleached TMP (6%, 8% and 14%) have higher G’ than G” at lower angular velocities (Figures 4.26 and 4.27), which is contrary to the results for other sources.

G’ is related to the elastic response, and G” to the viscous response of these materials which demonstrated viscoelastic behavior. At strain rates lower than the cross over strain rate G’ values are lower than G” values, indicating the viscous response dominates; at strain rates higher than the cross over strain rates G’ values are higher than G” values, indicating the elastic response dominates. The cross over strain rate is the reciprocal of the average relaxation time, which can be related to the weight average molecular weight for the solution (Collier et al., 2000).

Table 4.4. Crossover points of lyocell solutions.

Source	4%		6%		8%		14%	
	ω (rad/s)	G’,G” (Pa.s)	ω (rad/s)	G’,G” (Pa.s)	ω (rad/s)	G’,G” (Pa.s)	ω (rad/s)	G’,G” (Pa.s)
Bleached Softwood	23.67	288.50	10.94	504.23	9.50	1141.80	32.56	3906.20
Unbleached Softwood	33.50	284.13	12.64	499.32	4.86	890.35	42.04	3233.30
Bleached Hardwood	28.37	228.38	17.55	415.18	7.69	1094.00	67.13	4052.30
Unbleached Hardwood	13.04	209.69	2.32	311.15	6.68	649.86	52.02	3337.00
Kudzu	5.74	89.93	1.84	421.57	2.21	836.58	N/A	N/A
Bagasse	4.73	54.26	1.25	134.65	3.87	554.09	1.80	1586.20
Bleached Recycled	73.14	210.70	23.82	472.02	19.27	1271.50	N/A	N/A
Unbleached Recycled	89.65	194.42	23.83	393.02	0.60	185.95	N/A	N/A
Bleached TMP	N/A	N/A	1.13	34.50	7.79	252.36	N/A	N/A
Unbleached TMP	0.12	2.96	1.07	40.72	6.31	228.66	N/A	N/A

Temperature Effects on Complex Viscosities

The complex viscosities of lyocell solutions at different temperatures were measured with the ARES rheometer. Typical temperature effects on complex viscosities and dynamic moduli of 14% lyocell solutions from DP 670 are shown in Figure 4.32. The measurement temperature varied from 55°C to 120°C. With the increase of temperature, the complex viscosity and dynamic moduli decreased. When the temperature was above 100°C, the solutions demonstrated more viscous characteristics as demoinstrated by the viscous modulus *G”* being higher than the elastic modulus *G’*. At temperatures below 100°C, the solutions were more elastic than viscous.

EFFECTIVE ELONGATIONAL VISCOSITIES OF LYOCELL SOLUTIONS

Effective elongational viscosities of selected lyocell solutions were measured on the ACER with a semi-hyperbolic Hencky 7 die. Both concentration effects and temperature effects were studied.

Concentration Effects on Effective Elongational Viscosities

The elongational viscosities of 6%, 8% and 14% lyocell solutions from DP 670 are shown in Figure 4.33. The elongation rate varied from 1/*s* to 700/*s*.

Strain rate thinning is apparent in the results. With the increase of strain rate, the effective elongational viscosity of the solutions decreased.

Lyocell solutions of higher concentrations demonstrated higher elongational viscosities. In lyocell solutions of lower concentrations, the cellulose molecules are less likely to get entangled with each other than those in higher concentrations. With the increase of concentration, the probability of molecular entanglement increases and hence the elongational viscosity increases.

Temperature Effects on Effective Elongational Viscosities

Temperature effects on elongational viscosity were studied with ACER using a Hencky 7 hyperbolic die. The temperature effect on the effective elongational viscosity

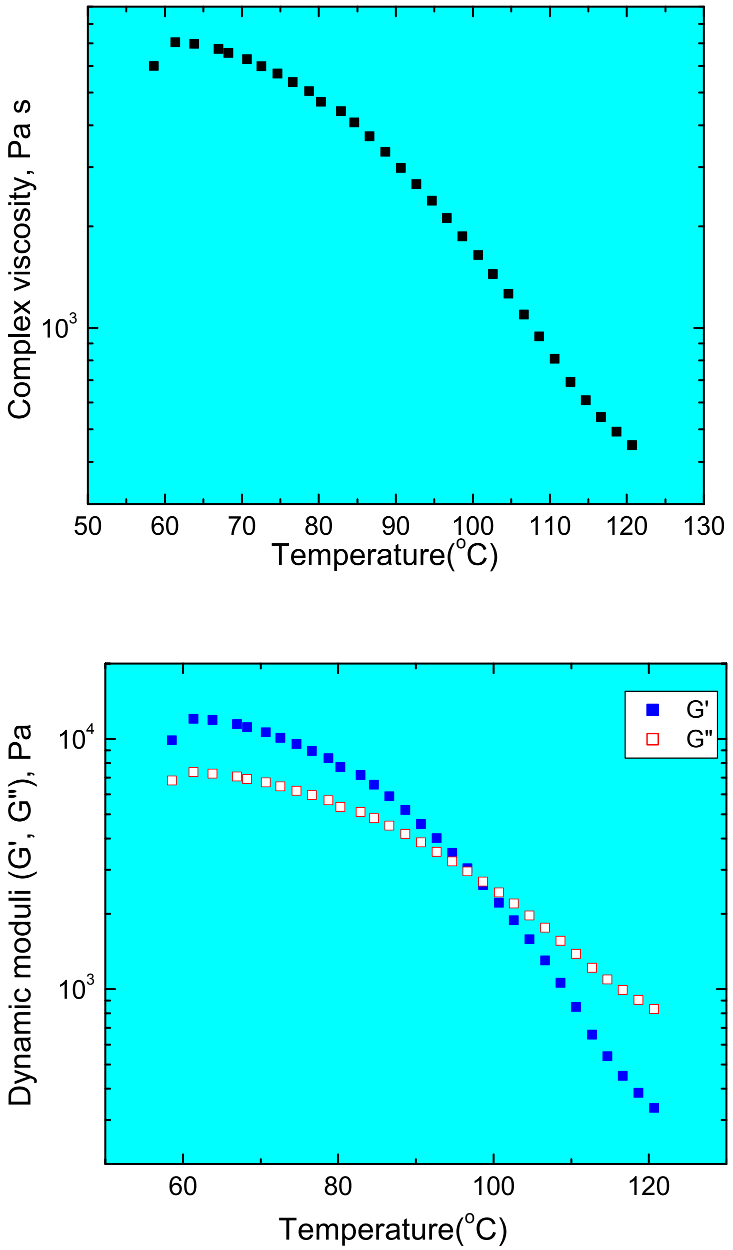

Figure 4.32. Temperature effects on complex viscosities and dynamic moduli of 14% lyocell solution prepared from DP 670.

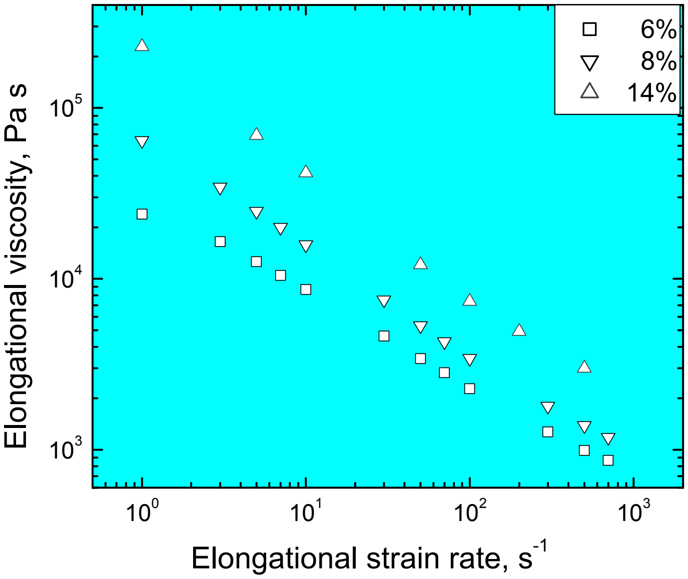

Figure 4.33. Elongational viscosities of lyocell solutions prepared from DP 670.

of lyocell solutions is demonstrated in Figure 4.34. The data exhibited are effective elongational viscosities of 10%, 14% and 18% lyocell solutions from DP 670. The results were measured at temperatures from 80 – 115°C. The strain rate was set as 1/*s*.

With the increase of solution temperature, a decrease of effective elongational viscosity occurred for all the lyocell solutions. With the increase of temperature, the cellulose molecules in the solutions become more active and flow more easily, decreasing the viscosity. The decrease of the effective elongational viscosity was exponential with the temperature increase from 80°C to 115°C. The complex viscosity decreased more rapidly with increasing temperature than the elongational viscosity as shown in Figures 4.32 and 4.34.

Besides the decreasing effects of the temperature on the effective elongational viscosities, there was a general increasing effect of concentration. With the increase of the concentration, the effective elongational viscosities increased.

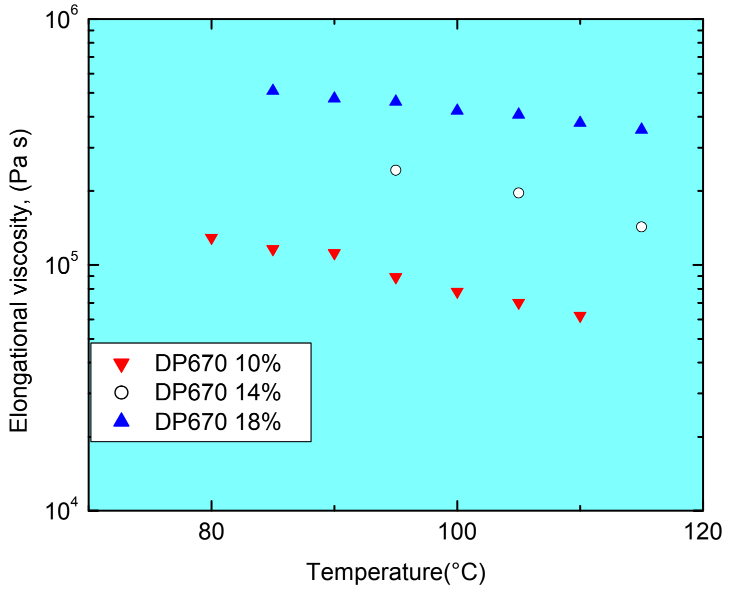

Figure 4.34. Elongational viscosities of lyocell solutions from DP 670.

LYOCELL FIBER SPINNING

The spinnability of the lyocell solutions was explored. Experiments were carried out to form filaments by extruding lyocell solutions through a Hencky 7 die in the ACER at different temperatures. The extrudates were passed through an air gap of 10 cm and a water bath before being wound and washed to remove the NMMO completely.

Phase separation was expected to occur during the spinning process. The decrease of temperature, the dilution of the NMMO monohydrate with additional water and the developing orientation decrease the ability of NMMO to dissolve cellulose. The decrease of solubility of cellulose would result in the precipitation of a cellulose rich phase and also a solvent rich phase. The disengagement of the two phases during spinning was postulated to be important in microfiber formation. It is influenced by the phase equilibrium and the cooling and dilution rates. The hyperbolic convergent die was expected to orient the resultant cellulosic fibers in the flow direction.

Bagasse Extrudate

Attempts were made to extrude fiber from 8%, 12% and 14% bagasse lyocell solutions at temperatures from 80°C to 110°C with an air gap of 10 cm. A continuous bagasse extrudate was formed but the fibers were not able to be drawn. Whenever drawing was applied, the extrudate broke.

Bagasse extrudates were successfully collected at 90°C and washed with tap water to remove NMMO. The extrudate was air-dried. SEM pictures of longitudinal and cross-sectional direction of fibers are shown in Figures 4.35 and 4.36. The dry surface of the 8% bagasse fiber was rough. There is some indication of a fibrillar structure in the longitudinal views. But the cross sections show these are only on the fiber surface. Similar results were obtained from 10%, 12% and 14% bagasse lyocell fibers.

DP 670 Lyocell Fiber

DP 670 lyocell solutions demonstrated much better spinnability, although the complex viscosities of lyocell and bagasse solutions were classified into one group. Both 8% (90°C) and 14% (90°C or 100°C) lyocell fibers were spun with a Hencky 7 die and an air gap of 10 cm. The fibers were successfully drawn into small diameters in the range from 10 μm to 30 μm.

Both drawn and as-spun lyocell fibers were collected and examined with SEM or optical microscopy. SEM pictures of the 14% DP 670 lyocell fiber are shown in Figure 4.37. In comparison with bagasse lyocell fibers, the 14% DP 670 lyocell fibers have very smooth fiber surface. No fibrillation phenomena were observed on the fiber surface.

Fibers from Bleached Softwood

Lyocell solutions from bleached softwood also demonstrated good spinnability at 90°C with a Hencky 7 hyperbolic die and an air gap of 10 cm. The diameters of bleached softwood lyocell fibers are in a range of 10 to 20 μm. Figure 4.38 shows two

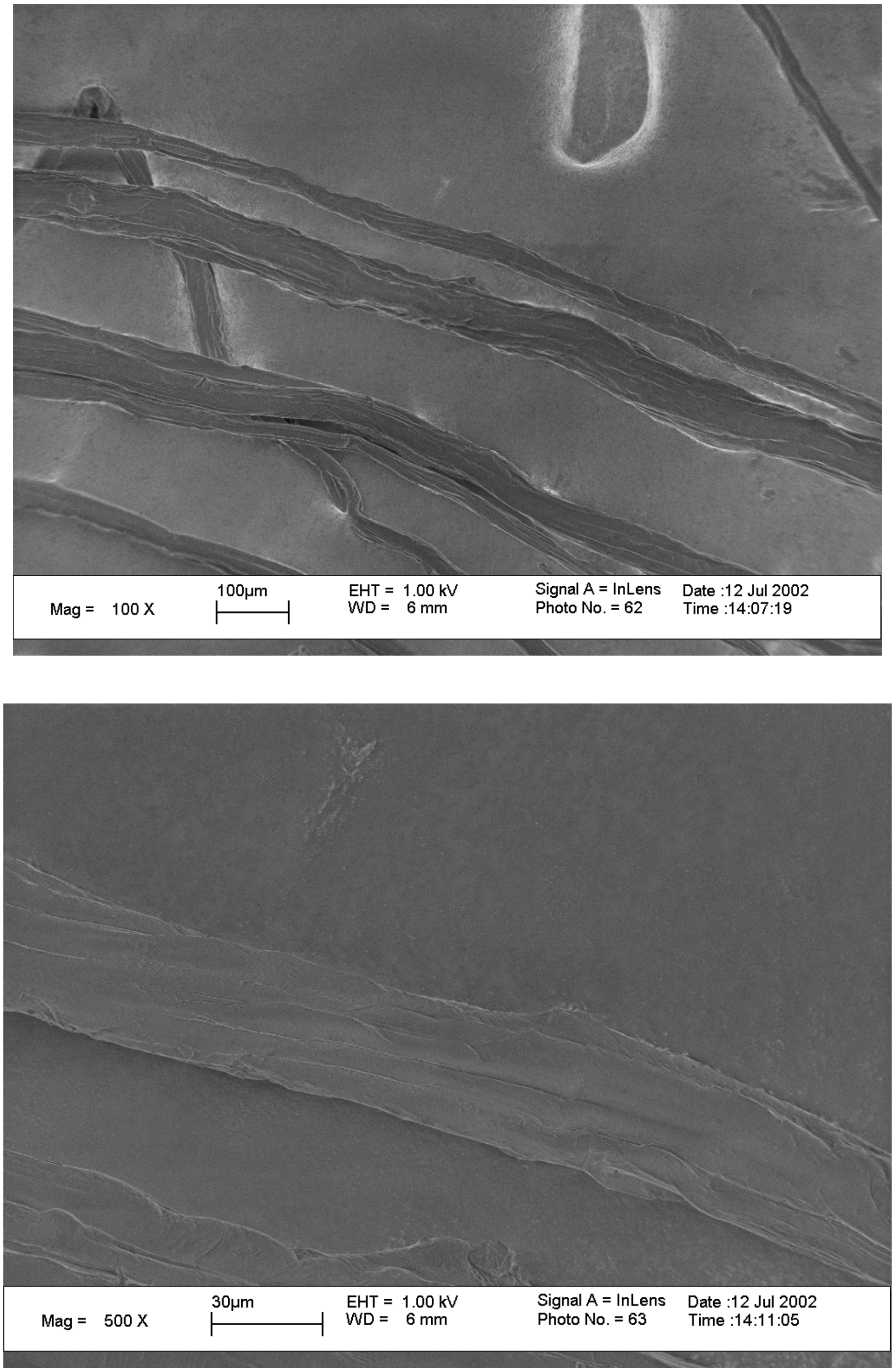

Figure 4.35. SEM of lyocell fiber from 8% bagasse solution (90°C, air gap 10 cm, Hencky7 die, elongation rate 5/s).

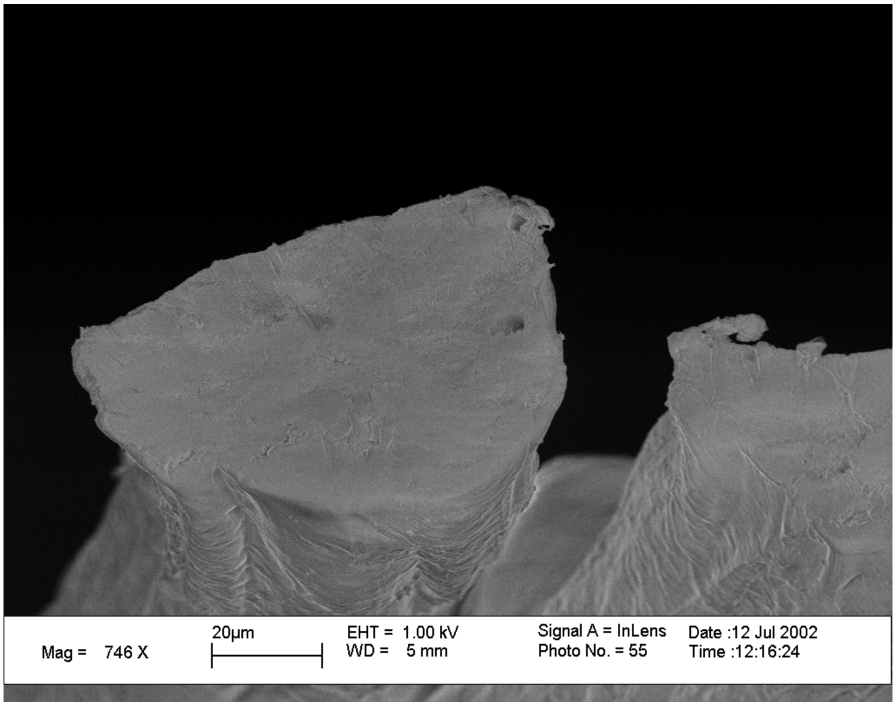

Figure 4.36. SEM of cross-section of lyocell fiber from 8% bagasse solution (90°C, air gap 10 cm, Hencky 7 die, elongation rate 5/s).

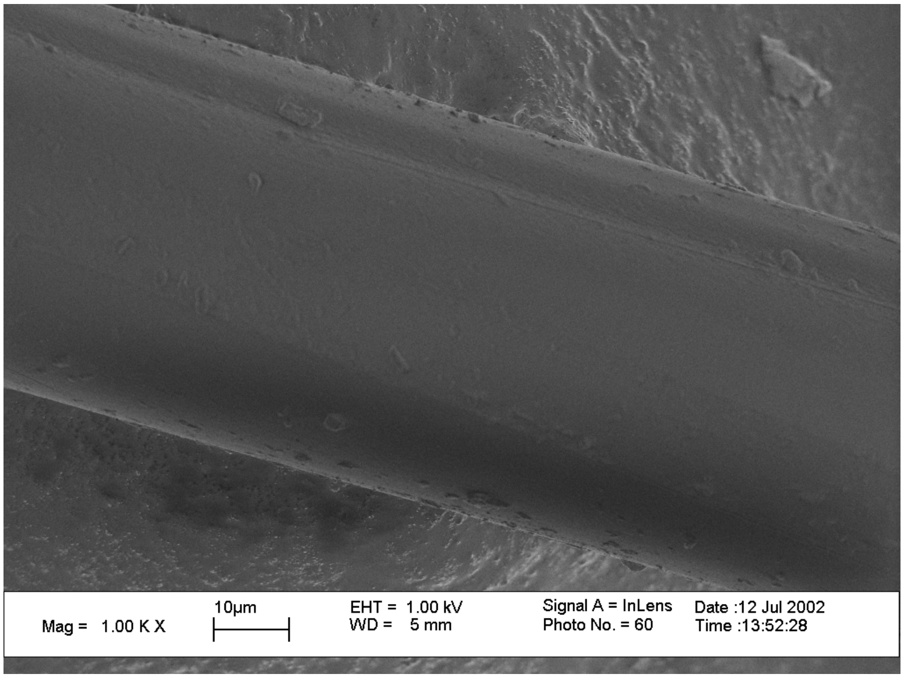

Figure 4.37. SEM of lyocell fiber from 14% DP 670 solution (90°C, air gap 10 cm, Hencky 7 die, elongation rate 1/s).

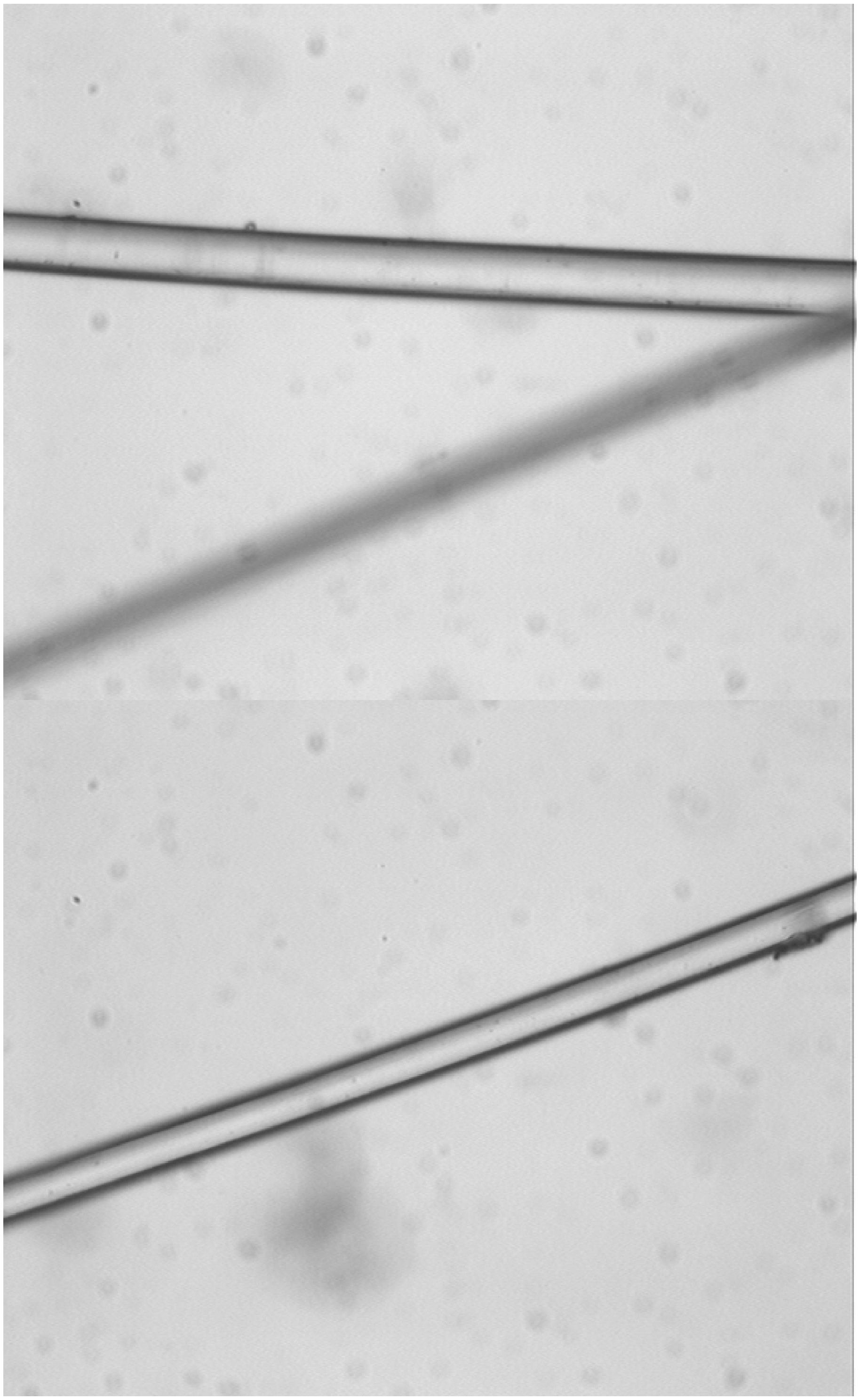

Figure 4.38. Lyocell fiber from 14% Bleached softwood solution (magnification 200, Spinning condition: 90°C, air gap 10 cm, Hencky 7 die, elongation rate 1/s).

typical bleached softwood lyocell fibers. The first fiber is of diameter 20.46 μm and the second one has a diameter of 14.12 μm.

FIBER TREATMENT TO PRODUCE LYOCELL MICROFIBERS

Lyocell fibers produced were subjected to different treatments to produce microfibers. Water, 2% H_2SO_4 and NaOH of 14% and 17.5% were used to treat the lyocell fibers.

Stirring-in-water Treatment

The fibers were cut into lengths of 30 mm. Twenty staple fibers were put into a flask of 150 mL tap water. The water was stirred with a magnetic stirring bar for 1.5 hrs. The fibers are then collected and observed under optical microscopy.

Figure 4.39 shows that some fibrils were obtained after the water-stirring treatment. The fibrillation degree depends on the treatment strength of the fiber during the process. During the treatment, fibers entangled with the magnetic stir bar and sometimes wrapped around it. The most severe wet abrasion should happen to the fiber segments that were held by the bottom of the stir bar against the flask bottom. For the fiber segments just stirred in the water, there was much less abrasion effect. The fibrillation is similar to that observed in commercial lyocell fabrics. The fibers demonstrated a collapsed structure after the treatment. This might be caused by the collapse of the inner voids in the fibers, but this needs to be further investigated.

Treatment with 14% NaOH at 25°C and with 2%w H_2SO_4 at 60°C

Fibers of length 30 mm were first treated with 14% NaOH for 1.5 hours at room temperature, then treated with 2%w H_2SO_4 solution for different time periods after rinsing with tap water.

The fibers in 14% NaOH solutions were stirred mildly at room temperature (25°C) with a magnetic stirring bar, and no fiber was abraded by the bottom of the bar against the flask bottom. With the continuing treatment with 2%w H_2SO_4 for 10 minutes at 60°C, the fiber fibrillated as demonstrated in Figure 4.40.

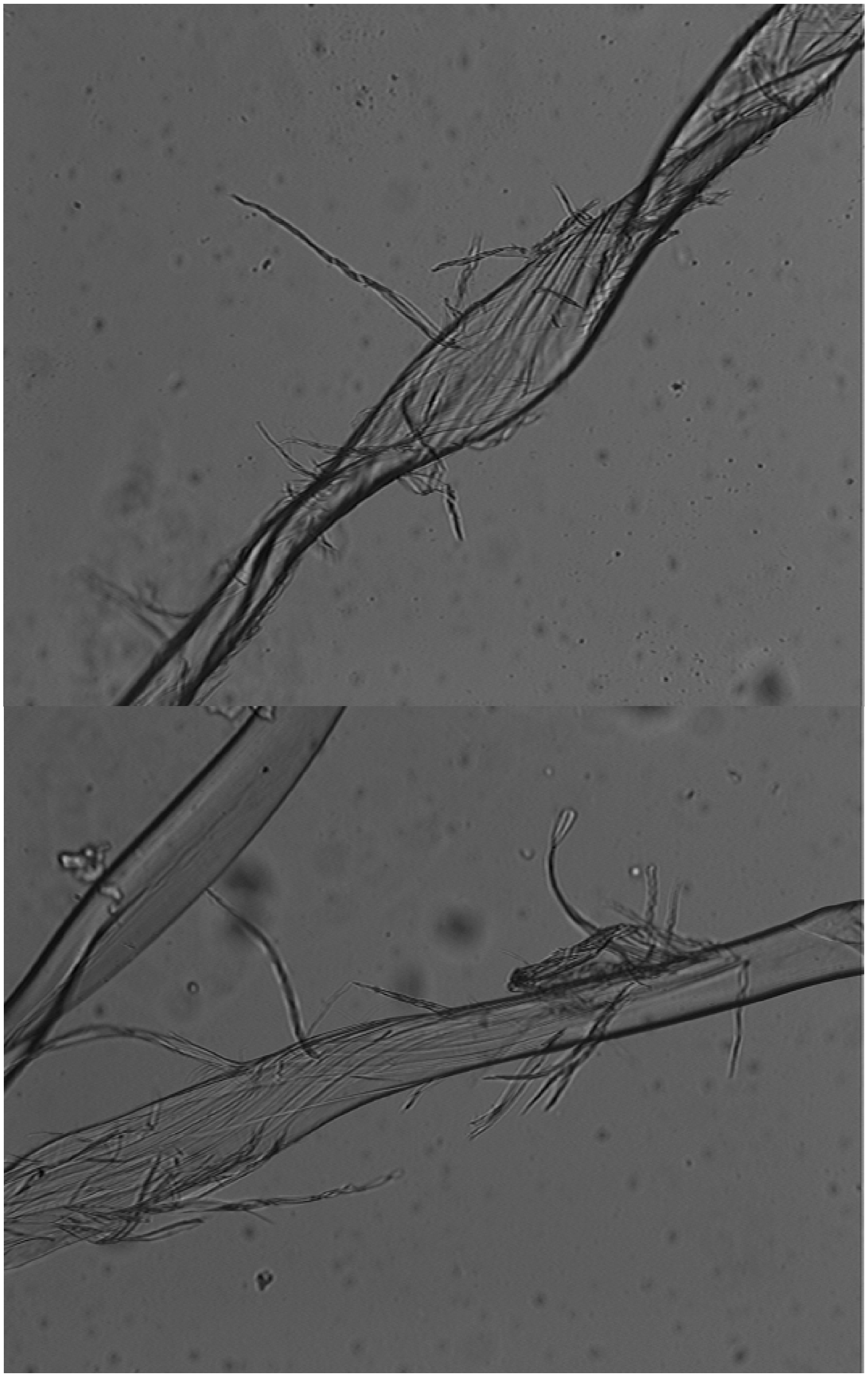

Figure 4.39. Stirring-in-water treated lyocell fiber from 14% DP 670 solution (magnification 200; spinning condition:90°C, air gap 10 cm, Hencky 7 die, elongation rate 1/s).

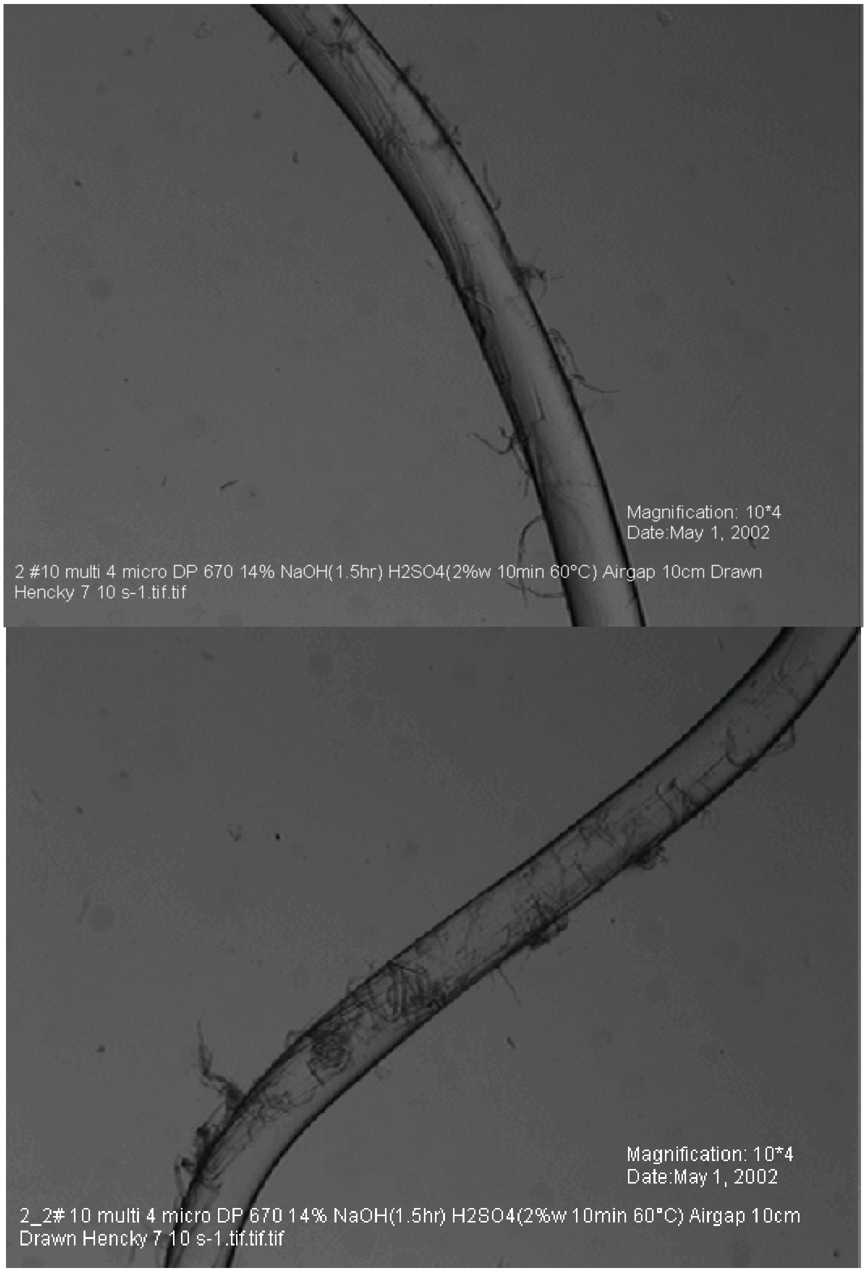

Figure 4.40. Fibrillation of 14% DP 670 lyocell fiber treated in 14% NaOH for 1.5 hrs at 25°C and in 2% H_2SO_4 for 10minutes at 60°C (Fiber was spun at 100°C, air gap 10 cm, Hencky 7 die, elongation rate 10/s).

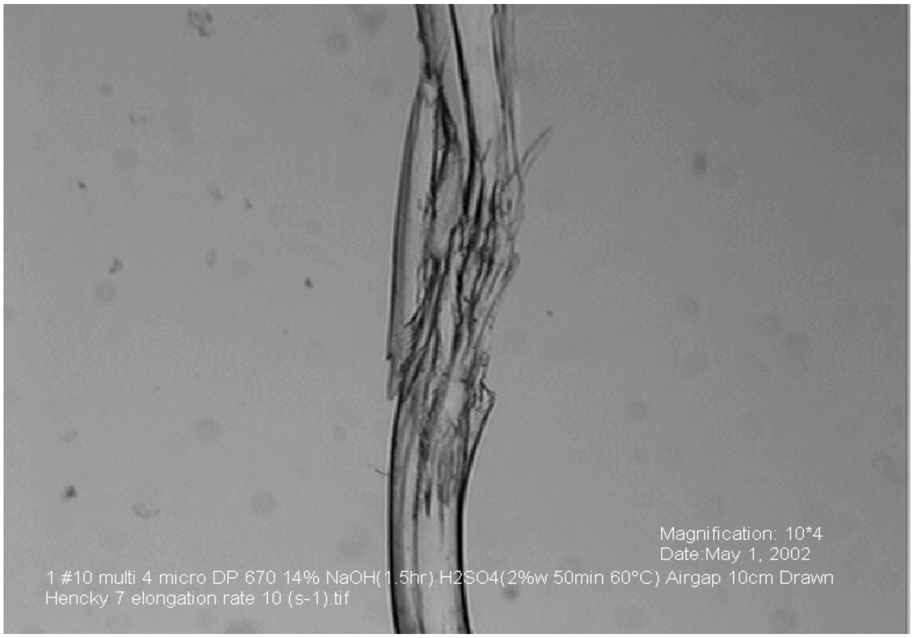

Figure 4.41. Fiber damage of 14% DP 670 lyocell fibers treated in 14% NaOH for 1.5 hrs at 25°C and in 2% H_2SO4 for 50 minutes at 60°C (Fiber was spun at 100°C, air gap 10 cm, Hencky 7 die, elongation rate 10/s).

This is still the type of fibrillation seen in commercial lyocell fibers, not the breaking up of the fiber into microfibrils that we are seeking. Longer H_2SO_4 treatments will cause significant fiber strength loss because too much damage is done to the fiber as shown in Figure 4.41.

Treatment with 17.5% NaOH at 25°C

Solutions of 17.5% NaOH were used to treat lyocell fibers to explore the possibility to produce cellulosic microfibers. The fibers were first treated for different times, and then pressed lightly with a cover glass on a microscope slide to break the fiber axially. The sample was observed under optical microscopy.

Figure 4.42 shows treated lyocell fibers of 14% bleached softwood with 17.5% NaOH solution for 2 minutes. The fiber was spun in the ACER at an elongation rate of 10/s, using a Hencky 7 die and an air gap of 10 cm at 90°C. The fiber observed is of a

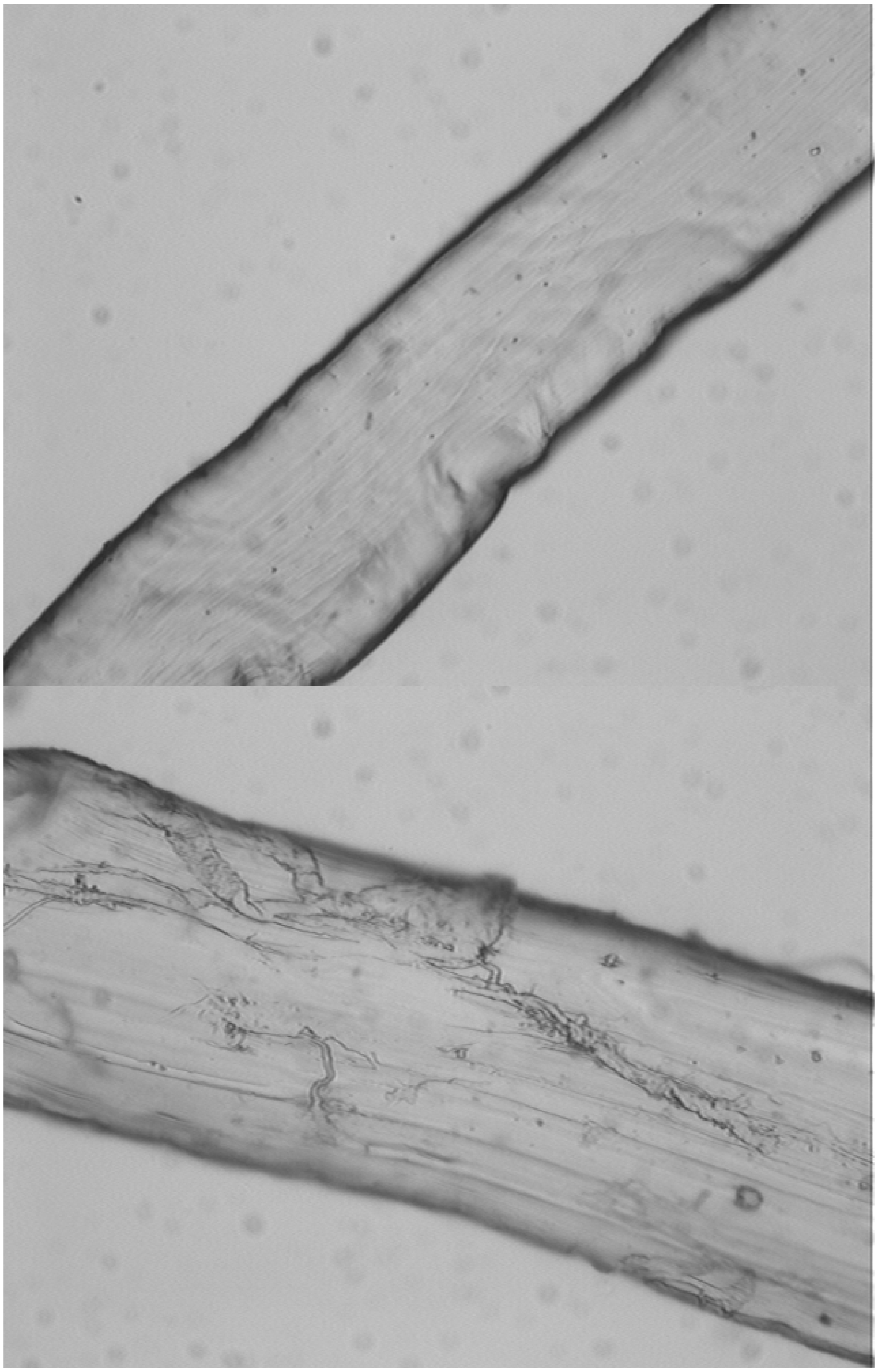

Figure 4.42. Treated Lyocell fibers of 14% bleached softwood with 17.5% NaOH for 2 minutes and pressed (Fiber was spun at 90°C, air gap 10 cm, Hencky 7 die, elongation rate 10/s).

flat form because of the pressure applied. There was no apparent fibrillation observed although part of the fiber surface peeled.

The treatment time was then increased to 5 minutes. The treatment effects of lyocell fibers of 14% bleached softwood with 17.5% NaOH for 5 minutes are shown in Figures 4.43 and 4.44. The longer treatment time in the 17.5% NaOH solutions increased the fibrillation. Five minutes' treatment fibrillated the lyocell fibers seriously. The fibers were broken into fibrils of a diameter of few microns along the fiber axis.

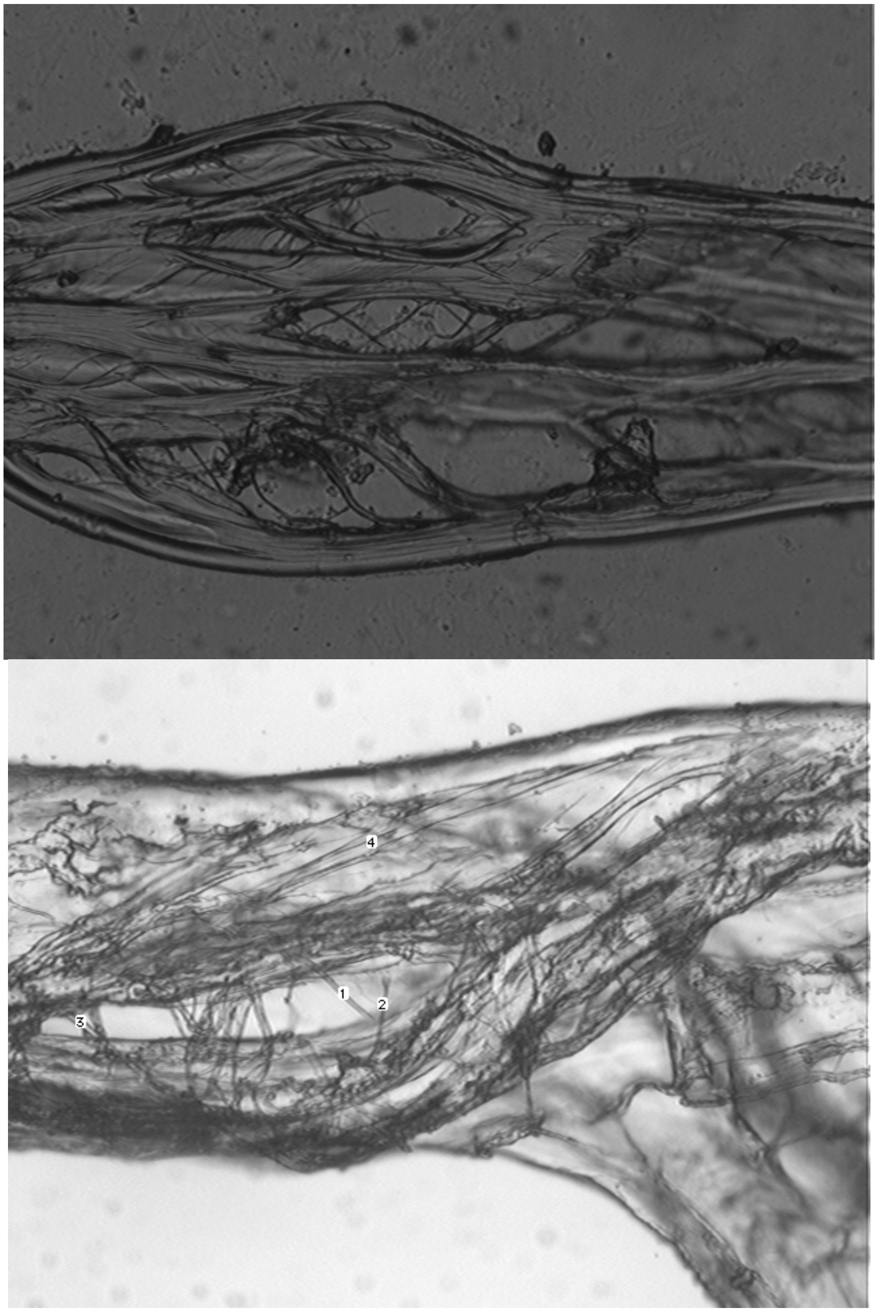

Figure 4.43. Treated Lyocell fibers of 14% bleached softwood with 17.5% NaOH for 5 minutes.

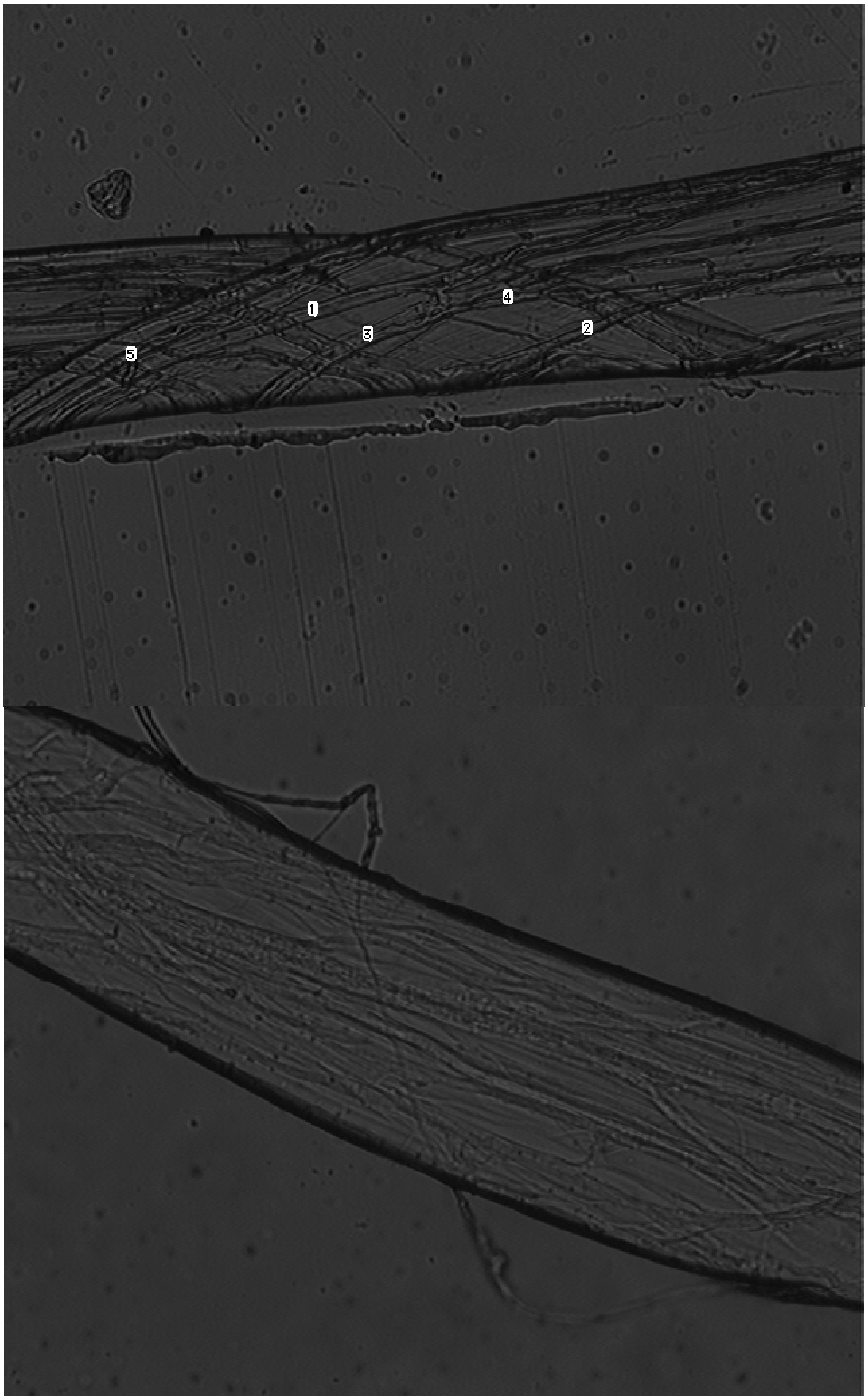

Figure 4.44. Treated Lyocell fibers of 14% bleached softwood with 17.5% NaOH for 5 minutes and pressed (Diameter of microfiber 1 to 5: 5.21 μm, 4.30μm, 5.56 μm, 2.82 μm and 2.53 μm).

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

Lyocell solutions were successfully prepared from different cellulose sources including agricultural by-products and recycled paper pulps. The cellulose sources included commercial dissolving pulps, commercial bleached hardwood, unbleached hardwood, bleached softwood, unbleached softwood, bleached TM pulp, unbleached TM pulp, bleached recycled newsprint, unbleached recycled newsprint, bagasse and kudzu. The protocol developed produced lyocell solutions of four concentrations (4%, 6%, 8% and 14%) from the sources. According to the protocol, the cellulose was first ground into small particles if applicable, then mixed with NMMO monohydrate and 1% antioxidant in a Brabender mixer at 90°C. The mixing time of lyocell solutions depended on the target concentration.

The complex viscosities of all the solutions were measured with the ARES using parallel plates geometry with a diameter of 25 mm. The measurements were taken at a constant strain of 2%. The effective elongational viscosities of lyocell solutions were measured with the ACER capillary rheometer using a Hencky 7 hyperbolic die.

It was shown that cellulose source affected the rheology of the resulting lyocell solutions. Concentration is also a significant factor for complex viscosity and effective elongational viscosity. By increasing the concentration, both viscosities increased. The crossover point of the *G'* and *G"* curves shifted from higher angular velocities and lower moduli to lower angular velocities and higher moduli when the lyocell concentration was increased although there were exceptions for hardwood and softwood solutions. The higher the concentration, the more elastic the lyocell solution is.

The differences between bleached and unbleached sources are more apparent for hardwood and softwood at lower concentrations, yet more apparent for TM and recycled newsprint pulps at higher concentrations. Bleaching does not show a consistent pattern for source and concentration. According to the statistical analysis, bleaching has significant effects on 4% and 6% lyocell solutions from hardwood and softwood and 6% TMP lyocell solutions. But there is no significant effect on 4% TMP solutions and 4% and 6% lyocell solutions from recycled newsprint. For the lyocell solutions of 8% and 14%, significant bleaching effects were demonstrated on the complex viscosities of most solutions except 8% TMP and 14% hardwood.

Bleaching has the effect of decreasing the molecular weight; it also purifies the cellulose. The decrease of molecular weight may result in lower complex viscosities, but the purification may result in fewer impurities and relatively high percentage of cellulose in the solution, which might result in a higher complex viscosity. Cellulose degradation can be a factor in the lyocell preparation process, decreasing the complex viscosity. The lyocell solutions from unbleached pulps may suffer more severe degradation because of the higher percentage of impurities and subsequently longer solution preparation times.

In order to find out which cellulose sources have the potential to produce lyocell solutions having similar complex viscosities to those from commercial dissolving pulps, one-way ANOVA post hoc tests were carried out to identify homogeneous subsets. Lyocell solutions of DP 670 and bagasse were grouped together. Commercial lyocell solutions are made of blends of dissolving pulps and DP 670 is among the most frequently used ones. This study demonstrated the potential of bagasse as a substitute or a partial substitute for DP 670 in industrial lyocell production. Lyocell solutions from both bleached and unbleached softwood and hardwood were classified as one homogenous subset. The solutions demonstrated lower complex viscosities than did DP 670.

All lyocell solutions measured with the ACER demonstrated strain rate thinning of effective elongational viscosity in the measured strain rate range. Shear thinning was also demonstrated in the complex viscosity results. Both effective elongational viscosity and complex viscosity increased with the decrease in temperature. The viscosities of low concentration lyocell solutions are comparable to those of polymers used for meltblowing; and they could be used for meltblowing.

Although bagasse lyocell solutions have similar complex viscosity to DP 670, the solutions demonstrated poor spinnability in our studies. Eight percent, 10%, 12% and 14% bagasse solutions produced lyocell extrudates. However these extrudates broke so easily whenever drawing was applied that it was not possible to produce drawn bagasse lyocell fibers. SEM images of longitudinal and cross-sectional directions of bagasse lyocell fibers showed minimal fibrillar structure.

Eight percent and 14% lyocell fibers of DP 670 and bleached softwood were spun from the ACER with a Hencky 7 die and an air-gap of 10 cm. The fibers were successfully drawn into small diameter fibers and observed under SEM and optical microscopy. The fiber diameter of the drawn fibers was in the range of 10 μm to 30 μm. There was no fibrillation on the fiber surface. In comparison with bagasse lyocell extrudates, the DP 670 lyocell fibers had very smooth fiber surfaces. This may be due to the good dissolvability of these cellulose sources. It was difficult to get well-dissolved homogeneous bagasse lyocell solutions.

Lyocell fibers were treated to produce microfibers. The first treatment method used tap water. Mechanical action produced some fibril hairs on the surface of the fibers treated, but it was not the kind of fibrillation that could result in microfibers.

The second method treated lyocell fibers with 14% NaOH at room temperature followed by treatment with 2%w H_2SO_4 solution after rinsing with tap water. The fibers had fibrillated hairs on the surface, but the acid also caused damage to the fibers. This kind of fibrillation is still similar to that occurring in commercial lyocell fibers with wet abrasion.

The third method, which was the most effective, used 17.5% NaOH solutions to treat the fibers for different time periods. Transverse pressure was then applied on the fiber to induce axial fibrillation. After five minutes' treatment the fiber broke into discrete fibrils along the fiber axis. The diameters of the fibrils were in the range of 2 to 6 μm, and there were also finer fibrils with diameters less than 1 μm.

FUTURE WORK

In this study, there was only limited success in reproducing the microfiber structure in the lyocell extrudates.

Future efforts could focus on finding the phase separation conditions for the lyocell solutions. Phase separation is induced in elongational flow in which the cellulose-rich fibers are rejected from the solvent rich phases (Romanoschi, 1998). The lack of a fibrillar structure in our lyocell extrudates may have been due to some spinning conditions used in this study such as the low elongation rates of 1/s and 10/s and spinning temperatures from 90 to 120ºC. Higher elongation rates help the molecular orientation and hence the formation of fibrillar structure. Anisotropy may be critical for fibrillar structure formation in the lyocell fibers. In order to make anisotropic lyocell solutions, further studies should focus on the effects of the NMMO/water solvent system, cellulose characteristics, lyocell concentration and temperature (Chanzy et al., 1980). The cellulose mesophases can be obtained, in general, at temperatures lower than 90°C, when the solution is at least 20% cellulose (Chanzy et al., 1980). At the same time, the NMMO-water system should have a mole ratio water/anhydrous NMMO of less than unity (Chanzy et al., 1980). Higher molecular weight also contributes to the achievements of cellulose mesophase (Chanzy et al., 1980). In this study, the NMMO monohydrate obtained by boiling the 50%w NMMO solution was used. Further studies should perhaps use NMMO monohydrate mixed with anhydrous NMMO to produce solvents of a mole ratio less than unity. Undissolved particles were found in the solutions especially in those of bagasse and kudzu.

The effects of lignin and other chemicals on the phase separation process in lyocell solutions are not certain yet. In future work, lignin or other components can be intentionally added in order to achieve phase separation for fibrillar structure. In addition to the solution and temperature parameters, the processing conditions play an important role in the structure of fibers. Further work should perhaps focus on high Hencky strain dies, a short, dry and cold air-gap, high line speeds, and a coagulation bath of pure water, which were reported to help fibrillation structure formation of the final fibers (Mortimer and Peguy, 1996b, Mortimer and Peguy, 1996a). Construction of a comprehensive model to describe the lyocell spinning process may result in better understanding and control of the fiber structure formation, especially during the period when the lyocell solution passes through the die and the air-gap to the coagulation bath. Studies on the internal pores in the fibers could also help understand and control the development of microfibers. Dye penetration studies might be helpful to the investigation on the internal pores in lyocell fibers. The microfiber treatments demonstrated the potential to produce lyocell microfibers, but the process is far from industrial application. Further efforts are required to find new methods or to modify current methods to produce lyocell microfibers more efficiently and with higher productivity.

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