

**RHEOLOGICAL CHARACTERIZATION OF  
LYOCELL SOLUTIONS**

**A THESIS**

*Submitted by*

**VIRALKUMAR J. PATEL**

**(R670215019)**

*in partial fulfillment for the award of the degree of*

**MASTER OF TECHNOLOGY IN**

**CHEMICAL ENGINEERING**

**(With Specialization in Process Design Engineering)**



**DEPARTMENT OF CHEMICAL ENGINEERING**

**COLLEGE OF ENGINEERING STUDIES**

**UNIVERSITY OF PETROLEUM AND ENERGY STUDIES**

**DEHRADUN**

**APRIL-2017**

## **DEDICATION**

This work is dedicated to my parents, J.N. Patel and C.J. Patel, sister, Shruti, wife, Dr. Mehal and the rest of family, for always encouraging and supporting me to achieve my goals.

**UNIVERSITY OF PETROLEUM AND ENERGY  
STUDIES  
DEHRADUN**

**BONAFIDE CERTIFICATE**

This is to certify that the thesis entitled “**RHEOLOGICAL CHARACTERIZATION OF LYOCELL SOLUTIONS**” submitted by **VIRALKUMAR J. PATEL (R670215019)**, to the University of Petroleum and Energy Studies, for the award of the degree of **MASTER OF TECHNOLOGY** in Chemical Engineering with specialization in Process Design Engineering is a bonafide record of project work carried out by him under our supervision. The results embodied in this project review report are based on literature and the research in PFIC-Aditya Birla Group R&D. This data is based on proprietary adsorbent of PFIC-Aditya Birla Group, hence only PFIC-Aditya Birla Group reserves all right to patent, publish and present the data.

Amit Gupta, PhD

Research Scientist

Pulp & Fiber Innovation Center

A Unit of Grasim Industries Limited

Maharashtra, India

Vijay Parthasarthy, PhD

Associate Professor and Head

Department of Chemical Engineering

University of Petroleum and Energy  
Studies, Dehradun, India

## ABSTRACT

The primary goals of the study were to prepare lyocell solutions from different wood pulps. An individual specific Protocol was developed for lyocell solution preparation from different cellulose sources. The cellulose sources included bleached hardwood and bleached softwood pulps.

Rheological measurements were used to characterize the behaviour of lyocell solutions, i.e. cellulose dissolved in *N*-methyl morpholine *N*-oxide (NMMO) monohydrate. Complex viscosities were measured and influence of parameters such as cellulose source, concentration, DP (function of molecular weight) and temperature were studied. The dominance of viscous behaviour,  $G'$  values, over elastic behaviour,  $G''$  values, is affected by pulp type, concentration, molecular weight and degrees of polymerization (DP). At lower concentrations and degrees of polymerization, dissolving pulp solutions show viscous, inelastic behaviour at low frequencies. At higher concentration and DP, dissolving pulp solutions are more elastic at higher frequencies.

## ACKNOWLEDGMENTS

I would like to thank all those who helping me to achieve the Master of Engineering degree in Chemical Engineering with specialization in Process Design.

I am very thankful to Dr. Amit Gupta, Dr. Vijay Parthasarthy, Dr Parag Patil and Dr. Niteen Deshmukh for his precious guidance and suggestion. Anwar Sayyed, Asmita Jadhav and Rahul Jagtap gave a great technical supports.

Especially, I am thankful to Dr. S.K Gupta, Dr. P.K Das and Aditya Birla Group for giving me an opportunity to work at Pulp and Fiber Innovation Center, counts among top research centers in India.

## TABLE OF CONTENTS

| Chapter   | Page<br>Number |
|---|----------------|
| <b>1. INTRODUCTION AND JUSTIFICATION</b>              | <b>1</b>       |
| 1.1 INTRODUCTION                                      | 1              |
| 1.2 JUSTIFICATION                                     | 2              |
| 1.3 RESEARCH OBJECTIVES                               | 3              |
| <b>2. LITERATURE REVIEW</b>                           | <b>4</b>       |
| 2.1 CELLULOSE   | 4              |
| 2.1.1 <i>Chemical Structure</i>                       | 4              |
| 2.1.2 <i>Crystalline Structure</i>                    | 5              |
| 2.1.3 <i>Chemical Reactions of Cellulose and NMMO</i> | 5              |
| 2.2 LYOCELL   | 9              |
| 2.2.1 <i>Cellulose Solvents</i>                       | 9              |
| 2.2.2 <i>Lyocell Process</i>                          | 10             |
| 2.3 RHEOLOGY  | 12             |
| 2.3.1 Rheology of Solutions and Melts                 | 13             |
| 2.3.1.1 <i>Shear Flow</i>                             | 13             |
| 2.3.1.2 <i>Elongational Flow</i>                      | 15             |
| 2.3.2 Measurement                                     | 16             |
| 2.3.2.1 <i>Measurement of Shear Viscosity</i>         | 16             |
| 2.3.2.1 <i>Measurement of Elongational Viscosity</i>  | 19             |
| 2.3.3 Rheological Tests on Polymers                   | 24             |
| 2.3.4 Applications                                    | 25             |
| 2.3.5 Molar Mass Distribution                         | 26             |
| 2.3.6 Branching                                       | 28             |
| 2.3.7 Fillers   | 28             |

| Chapter | Page |
|---------|------|
|---------|------|

|   | <b>Number</b> |
|---|---------------|
| <b>3. METHODS, INSTRUMENTS AND PROCEDURES</b>                           | <b>29</b>     |
| 3.1 PREPARATION OF LYOCELL SOLUTIONS                                    | 29            |
| 3.1.1 <i>Preparation of Cellulose Powder</i>                            | 29            |
| 3.1.2 <i>Preparation of Lyocell Solutions (Dope)</i>                    | 30            |
| 3.2 RHEOLOGICAL CHARACTERIZATION OF DOPE                                | 31            |
| <b>4. RESULTS AND DISCUSSION</b>  | <b>33</b>     |
| 4.1 DISSOLUTION STUDY FOR LYOCELL SOLUTIONS                             | 33            |
| 4.2 COMPLEX VISCOSITY OF LYOCELL SOLUTIONS<br>FROM DIFFERENT WOOD PULPS | 34            |
| 4.2.1 <i>Effect of pulp concentration on Dynamic Modulus</i>            | 35            |
| 4.2.2 <i>Effect of wood type on Dynamic Modulus</i>                     | 38            |
| 4.2.3 <i>Effect of pulping process on Dynamic Modulus</i>               | 39            |
| 4.2.4 <i>Effect of pulp concentration on Complex Viscosity</i>          | 40            |
| 4.2.5 <i>Effect of wood type on Complex Viscosity</i>                   | 42            |
| 4.2.6 <i>Effect of pulping process on Complex Viscosity</i>             | 42            |
| <b>5. CONCLUSION AND RECOMENDATIONS</b>                                 | <b>44</b>     |
| 5.1 CONCLUSIONS   | 44            |
| 5.2 FUTURE WORK   | 44            |
| <b>LIST OF REFERENCES</b>   | <b>45</b>     |

**LIST OF TABLES**

| <b>Table</b>  | <b>Page<br/>Number</b> |
|---|------------------------|
| <b>Table 2.1</b> Kinetic model calculations for lyocell solutions | 8                      |
| <b>Table 2.2</b> Cellulose Solvents                               | 10                     |
| <b>Table 2.3</b> Working Equation for Parallel Disks              | 18                     |
| <b>Table 2.4</b> Working Equations for Capillary Rheometer        | 23                     |
| <b>Table 3.1</b> Properties of pulps                              | 30                     |
| <b>Table 3.2</b> Composition of Lyocell solutions                 | 31                     |
| <b>Table 4.1</b> Specifications for undissolved particles         | 34                     |
| <b>Table 4.2</b> Crossover data for lyocell solutions             | 35                     |



## LIST OF FIGURES

| <b>Figure</b>   | <b>Page<br/>Number</b> |
|---|------------------------|
| <b>Figure 1.1</b> Chemical structure of <i>N</i> -methyl morpholine <i>N</i> -oxide (NMMO)  | 1                      |
| <b>Figure 2.1</b> Chemical structure of cellulose   | 4                      |
| <b>Figure 2.2</b> Phase diagram of ternary system NMMO-water-cellulose  | 6                      |
| <b>Figure 2.3</b> Side reactions and by-product formation in lyocell system   | 7                      |
| <b>Figure 2.4</b> Autocatalytic degradation of NMMO reported by Rosenau et al.  | 7                      |
| <b>Figure 2.5</b> Schematic of lyocell process  | 12                     |
| <b>Figure 2.6</b> Schematic of a parallel plate Rheometer   | 17                     |
| <b>Figure 2.7</b> Schematic of capillary Rheometer  | 22                     |
| <b>Figure 2.8</b> Conversion and analysis methods for rheological tests   | 25                     |
| <b>Figure 2.9</b> Mass distribution strategies for polymers   | 27                     |
| <b>Figure 4.1</b> Dynamic moduli of lyocell solutions prepared from pulp-1 (hardwood and sulphite process)  | 36                     |
| <b>Figure 4.2</b> Dynamic moduli of lyocell solutions prepared from pulp-2 (hardwood and sulphate process (Kraft process))  | 37                     |
| <b>Figure 4.3</b> Dynamic moduli of lyocell solutions prepared from pulp-3 (softwood and sulphate process (Kraft process))  | 37                     |
| <b>Figure 4.4</b> Dynamic moduli of lyocell solutions (cellulose concentration of 13% wt.) prepared from pulp-2 and pulp-3 (hardwood and softwood respectively)                               | 38                     |
| <b>Figure 4.5</b> Dynamic moduli of lyocell solutions (cellulose concentration of 13% wt.) prepared from pulp-1 and pulp-2 (hardwood with sulphite and sulphate pulping process respectively) | 39                     |
| <b>Figure 4.6</b> Complex viscosity of lyocell solutions prepared from pulp-1 (hardwood and sulphite process)   | 40                     |

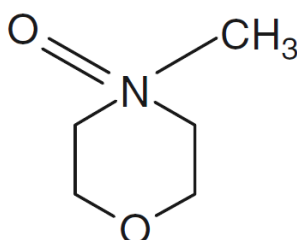
| <b>Figure</b>  | <b>Page<br/>Number</b> |
|--|------------------------|
| <b>Figure 4.7</b> Complex viscosity of lyocell solutions prepared from pulp-1(hardwood and sulphate (Kraft) process)   | 41                     |
| <b>Figure 4.8</b> Complex viscosity of lyocell solutions prepared from pulp-3 (softwood and sulphate process (Kraft process))  | 41                     |
| <b>Figure 4.9</b> Complex viscosity of lyocell solutions (cellulose concentration of 13%wt.) prepared from pulp-2 and pulp-3 (hardwood and softwood respectively)                        | 42                     |
| <b>Figure 4.10</b> Viscosity of lyocell solutions (cellulose concentration of 13%wt.) prepared from pulp-1 and pulp-2 (hardwood with sulphite and sulphate pulping process respectively) | 43                     |

## CHAPTER 1

### INTRODUCTION AND JUSTIFICATION

#### 1.1 INTRODUCTION

The primary goal of this project was to develop lyocell solutions (dope) from different wood pulps followed by rheological characterization. Cellulose, the most abundant raw material is a semi rigid chain polymer having high glass transition temperature ( $T_g$ ) in range of 100°C to 180°C (Ludwik et al 2008). Further high polarity of monomer is due to presence of hydroxyl groups in monomer leading to intra and inters hydrogen bonding. Because of the strong intermolecular bonds, cellulose does not dissolve readily in ordinary available solvents; chemists have resorted to derivatization of cellulose to render it soluble and processable. Among all solvents *N*-methyl morpholine *N*-oxide (NMMO) proved most versatile and commercially successful. Franks and Varga (1979), first came up with an important report shows dissolution of cellulose in NMMO. Other effective solvents or solvent systems are also discussed in consequent chapter.



**Figure 1.1** Chemical structure of *N*-methyl morpholine *N*-oxide (NMMO).

Lyocell solutions result in different phases mainly depending on hydration number ( $n$ ) of NMMO hydrate together with cellulose concentration and temperature (Dong et al 2002). Recently Kim et al (2002) reported a modified phase diagram of lyocell solutions focused on the critical concentration for producing mesophase is much lower than the value reported previously. Simultaneously, Chanzy et al (2002) also reported the physical properties of mesomorphic phase cellulose solutions in NMMO hydrates. Not only enthalpic but entropic effect must be aided to break hydrogen bonds in order to achieve salvation (Collier J. 2000).

Comprehension of steady rheological (or shear) properties of lyocell solutions is essential to determine the optimum spinning conditions of lyocell. It is important to analyze both, oscillatory and elongational shear rheology because of elongational rheological data would exhibit poor reproducibility due to long relaxation spectra. That is, accumulation of residual stress during dynamic rheological measurements might give incredible data. Also shearing rheology contributes to understand processing of solutions where else elongational behaviour influences fiber properties, especially orientation and fibrillation.

Fibers can be produced by heating the lyocell solutions to between 90°C and 100°C and spinning them through a spinneret into a water (may be other solution or system) bath below 90°C. The solvent can be recovered from the aqueous spinning bath by sorption onto a cation-exchange resin, filtration, and water removal for concentration. The fibers produced have a tendency to fibrillate, although this can be overcome by finishing treatment(s) and (or) alternate spinning conditions (Collier J. 2000).

Lyocell fibers, a new type of rayon produced from an environment benign, nontoxic NMMO were commercialize in last few years. Typical composition of lyocell solutions content cellulose, 10-13% (by weight) and 11-12% (by weight) water to use it commercially. Lyocell fibers are biodegradable with excellent wrinkle resistant and abrasion resistance properties (better than in case of viscous rayon fabric) due to which they find use in composites, filters and battery separators. It can be blended (of course can be used separately) with other fibers, natural or manufactured and dyed or printed as market demands.

## **1.2 JUSTIFICATION**

It is very important to study various parameters associated with dope making process. Of course different wood pulps have specific range of major considerable impurities which gives individual or combined contribution to dope properties.

Also rheological properties can be influenced by properties of polymer (i.e. Degree of polymerization, Molecular mass distribution,  $\alpha$ -cellulose content), physicochemical behaviour of the solvent, dope concentration and dissolving state. All properties of pulp and cellulose dopes must be adapted for the shaping process, shaped product and intended application.

Lyocell solution characteristics are important criteria to adjust most secure air-gap spinning procedure and adjustment of intended fiber properties (i.e. fineness, tenacity and elongation).

### **1.3 RESEARCH OBJECTIVES**

Specific objectives were:

- i. To produce lyocell solutions to investigate influence of pulp type, cellulose concentration, and molecular weight on rheological behaviour especially complex viscosities.
- ii. To investigate the rheological behaviour of lyocell solutions prepared (i.e. Time-temperature superposition, flow and viscosity curve and transient tests (creep, stress relaxation and stress growth test)).

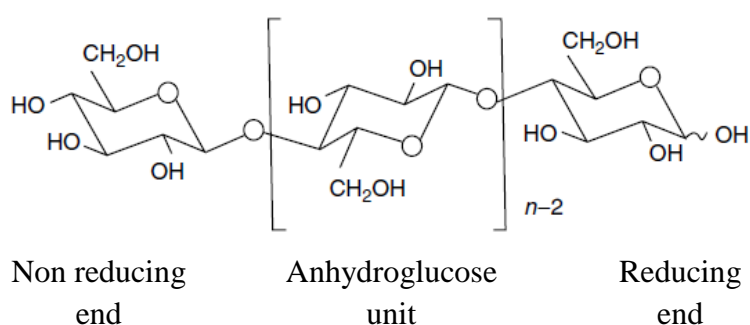
## CHAPTER 2

### LITERATURE REVIEW

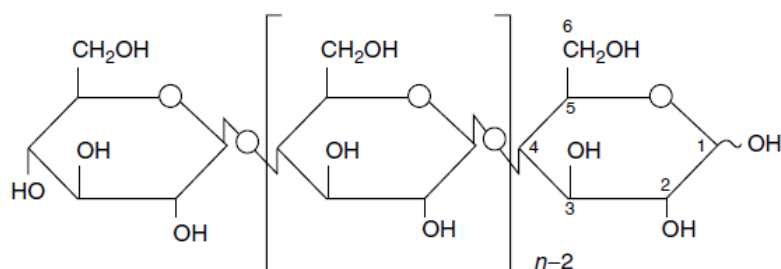
#### 2.1 CELLULOSE

##### 2.1.1 Chemical Structure

Cellulose, commonly found in walls of plants and other living systems, is plentiful thermoplastic polymer on the earth. Anselme Payen had discovered a chemical structure of cellulose (under continuous investigation) in 1839. Cellulose (Figure 2.1), a composed polymer structure of ring structured monomers, 1, 4- $\beta$ -D-linked polyanhydro glucopyranose (Nevell 1985a). The monomers aligned in chain with 180° rotation to each other. The degree of polymerization ( $n$ ) varies from 1000 to more than 15000 glucose units (Nevell 1985a).



Sometimes shown as



**Figure 2.1** Chemical structure of cellulose (Available on:

<http://www.fibersource.com/f-tutor/cellulose.html> (Accessed on: November 23, 2016)).

### **2.1.2 Crystalline Structure**

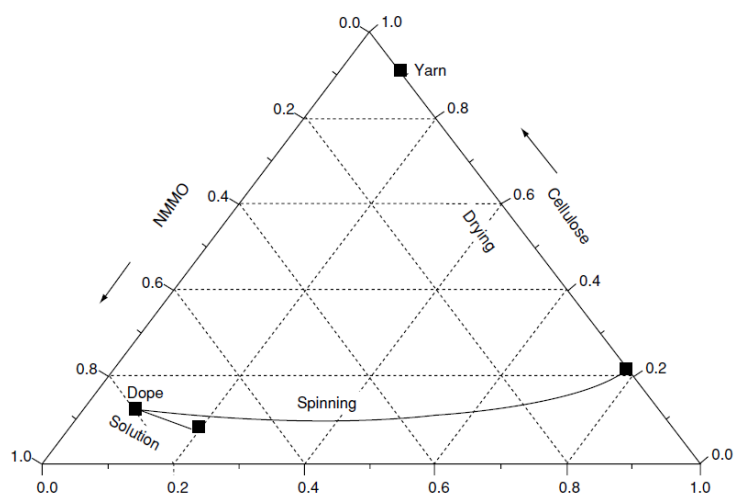
A key identification of cellulose is that its monomer bears three hydroxyl groups. Crystalline structures and other major physical properties of cellulose materials are due to presence and bonding of hydroxyl groups.

There are at list four cellulose crystalline structures: Cellulose I, II, III and IV (Nevell 1985a, Hermans 1949). Cellulose chains are packed parallel in Cellulose I, where else in cellulose II, Chains are packed in antiparallel fashion (Hermans 1949, Bayer et al 1998). Chemical treatment of cellulose I or cellulose II with liquid ammonia or amines or diamines results in cellulose III while cellulose IV can be obtained through thermal treatment of Cellulose I, II, and III in polar liquids (Roche 1981, Wada et al 2001, Buleon et al 1980, Happey 1979). Cellulose III and IV are seldom found in nature. Cellulose II is higher stable than cellulose I due to extensive hydrogen bonding. Cellulose I is natural cellulose and can be converted to cellulose II irreversibly after being treated with strong sodium hydroxide solution and regenerated from solution (Frank et al 2005).

### **2.1.3 Chemical Reactions of Cellulose and NMMO**

The ternary mixture of cellulose, NMMO and water represents the plastic mass for the lyocell process (dry and wet spinning). Phase diagram of cellulose-NMMO-water system is shown in Figure 2.2. Manufacture and plastic deformation of lyocell solutions occurs under the influence of temperature, mechanical energy, rate of condensation, and pressure (Frank et al 2005). Although the dissolution of cellulose in NMMO is entirely physical process, chemical kinetics appear under industrial conditions involving both discoloration and degradation reactions of cellulose and NMMO. These reactions may result in decreasing the recovery rate of NMMO and product performance. Handling dissolution process, between cellulose and NMMO at certain range of temperature gives coloured polymer, where else this exothermic reaction results in runaway reactions beyond certain value of process parameters and may be end up with deflagrations (Frank et al 2005).

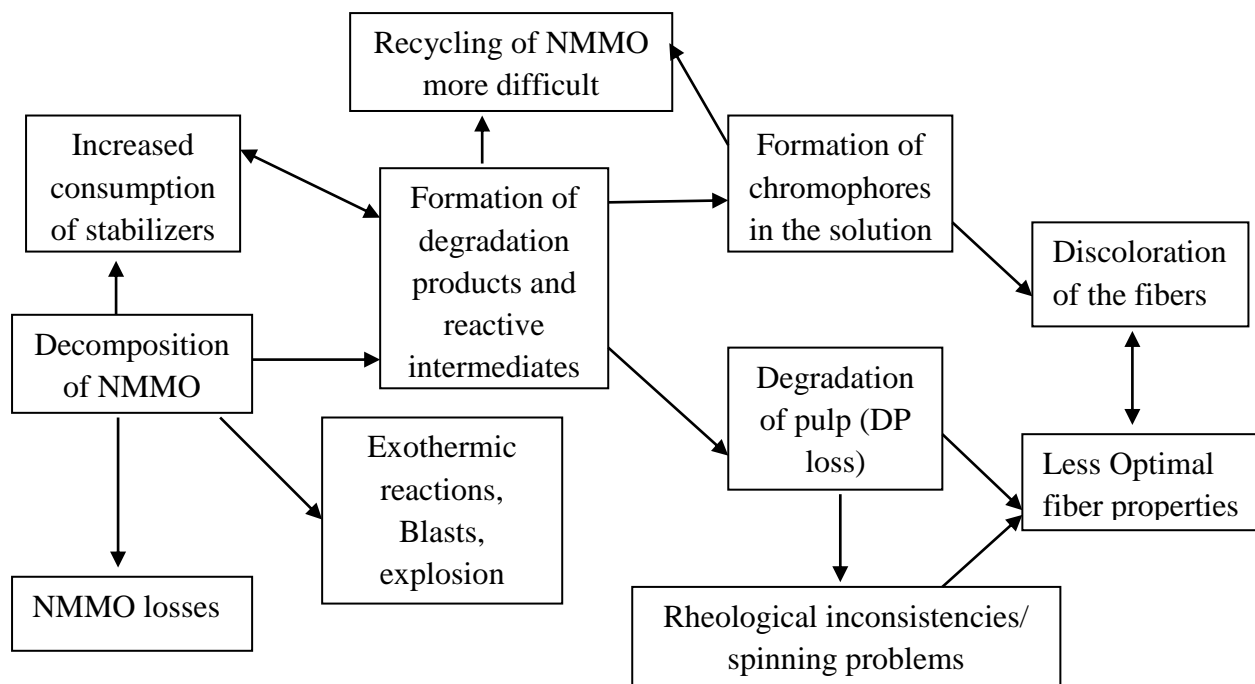
Chemistry of lyocell process is mainly depends on the amount of heavy metals (identification of thermal instability of NMMO) and reactive end groups of cellulose. Enrichment of energy due to N-O bond, certain numerous reactions result in degradation products mainly *N*-Methyl morpholine, morpholine, carbon dioxide and formaldehyde (Taeger et al 1991, Rosenau et al 2001). Figure 2.3 shows potential negative effects of side reactions. Furthermore highly reactive and unstable intermediates such as carboniuminium cation (Potthast et al 2000, Rosenau et al 2003) and aminiumyl radical (Rosenau et al 2002) have been found to occur, and commit autocatalytic degradation of NMMO (as shown in Figure 2.4).



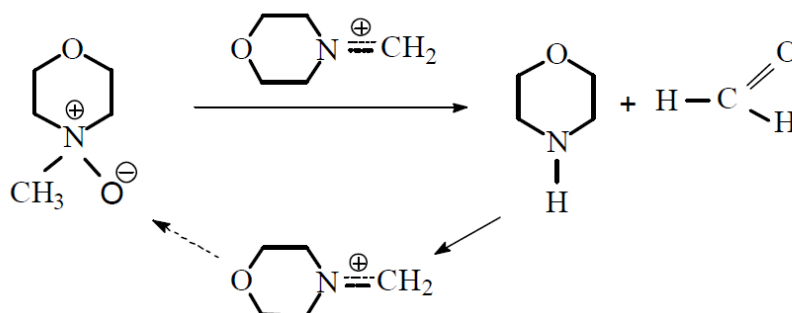
**Figure 2.2** Phase diagram of ternary system NMMO-water-cellulose (Rosemau et al 2001).

Stabilization of the system cellulose/NMMO is mandatory to control sporadic and uncontrollable reactions. The term autocatalysis refers to special term of homogeneous catalysis resulting in the formation of catalyst as reaction product during subsequent reactions which accelerates it additionally (Kerbre et al 1972, Wedler 1997). In fact, homogeneous distribution of cellulose (dissolved and undissolved) gives description of dissolution that can be accepted as a quasi-homogenous autocatalysis. Table 2.1 comprises the parameters for kinetic model calculations.





**Figure 2.3** Side reactions and by-product formation in lyocell system (Rosemau et al 2001).



**Figure 2.4** Autocatalytic degradation of NMMO reported by Rosenau et al (2001).

**Table 2.1** Kinetic model calculations for lyocell solutions (Frank et al 2005).

|                                 | Autocatalysis  | Thermal Degradation                            |
|---------------------------------|--|--|
| Reaction equation               | Start $A \xrightarrow{k_0} B$<br>$A + B \xrightarrow{k_1} 2B + P$            | $A \xrightarrow{k_2} C$                        |
| Reagents                        | A: NMMO<br>B: Catalyst<br>P: Chromophoric degradation product                | A: NMMO<br>C: Chromophoric degradation product |
| Concentration                   | $a_0, b_0$   | $a_0, c_0$                                     |
| Rate Constant                   | $k_1$  | $k_2$  |
| Accounting equation             | $x_1 = a_0 - a = b - b_0 = p$  | $x_2 = a_0 - a = c - c_0 = q$                  |
| Equation of the superimposition | $z = p + q$  |  |
| Rate law                        | $\frac{dx_1}{dt} = k_1 (a_0 - x_1) * (b_0 + x_1)$                            | $\frac{dx_2}{dt} = k_2 (c_0 - x_2)$            |
| Integration of rate law         | $k_1 t = \frac{1}{a_0 + b_0} \ln \frac{a_0 (b_0 + x_1)}{b_0 (a_0 - x_1)}$    | $k_2 t = \ln \frac{c_0}{c_0 - x_2}$            |
| Turning point                   | $\frac{d^2 x_1}{dt^2} = 0, t_{tp} = \frac{1}{a_0 + b_0} \ln \frac{a_0}{b_0}$ |  |

## 2.2 LYOCELL

Researchers have been seeking new environmentally friendly process that favours a fiber that is natural, non-toxic to environment and humans, biodegradable, comfortable, drapable, wrinkle resistance, soft, shrink resistance, and many more. Lyocell fiber became the first new generation cellulose fibers in last few decades and became famous commercially under a trade name Tencel in 1992.

### 2.2.1 Cellulose Solvents

Cellulose dissolution may be divided into four major groups as specified in Table 2.2. Solvent recovery is an important factor hence; dissolution is not an ultimate objective. In addition to rendering the polymer soluble, the resulting solution must have certain desirable characteristics, such as thermal and chemical stability, proper viscoelastic properties, environmental friendliness, and general ease of manipulation, including ease of recovery.

NMMO is most commonly used for commercial lyocell process and belongs to the group of cyclic, tertiary amine oxides, aliphatic with a chemical structure as shown in Figure 1. Pure NMMO has crystalline appearance, melting point of 184°C , and a density of 1.25 g/cm<sup>3</sup>. It is thermally stable and completely miscible with water, normally available in stable hydrates, monohydrate (13.3% by weight H<sub>2</sub>O) and disesquihydrates (28% by weight H<sub>2</sub>O). A typical composition of aqueous NMMO solution is as follows,

|                               |         |
|-------------------------------|---------|
| NMMO content                  | 50.0%   |
| NMM content                   | 1 wt%   |
| H <sub>2</sub> O <sub>2</sub> | 100 ppm |

**Table 2.2** Cellulose Solvents (Laszkiewicz 1997).

| Cellulose as          | Solvents   |
|-----------------------|--|
| Base                  | Phosphoric, sulphuric, nitric acids<br>Zink chloride, thiocyanate, iodides,<br>bromides  |
| Acid                  | Organic amines, amino oxides, $\text{CH}_3\text{NH}_2$   |
| Complex               | Inorganic complexes of cadmium,<br>copper, iron<br>Organic complexes: $\text{CH}_3\text{NH}_2/\text{DMSO}$   |
| Cellulose derivatives | Stable compounds: esters, ethers<br>Unstable derivatives of<br>Sulphur: xanthates, $\text{SO}_2$ / amines-<br>sulphites<br>Nitrogen: $\text{N}_2\text{O}_4/\text{DMF}$<br>Carbon: $\text{DMSO}/ (\text{CH}_2\text{O})_x$ |

### 2.2.2 Lyocell Process

Graenacher and Sallmann first used tertiary amine oxide to dissolve cellulose (Laszkiewicz 1997); however, Johnson of Kodak has got credit with use of NMMO for cellulose dissolution. Lyocell solutions, cellulose in NMMO up to 23% can be prepared by a reaction of cellulose with aqueous NMMO (subsequently removing water) as reported by McCorsley and Varga (Laszkiewicz 1997). Franks and Varga demonstrated Coagulation of cellulose with excess water. Commercialization of cellulose fiber production pivoted on these fundamental researches (Wedler 1997, Laszkiewicz 1997).

The production of lyocell fibers is a modern, high efficient and non-polluting process involves following steps;

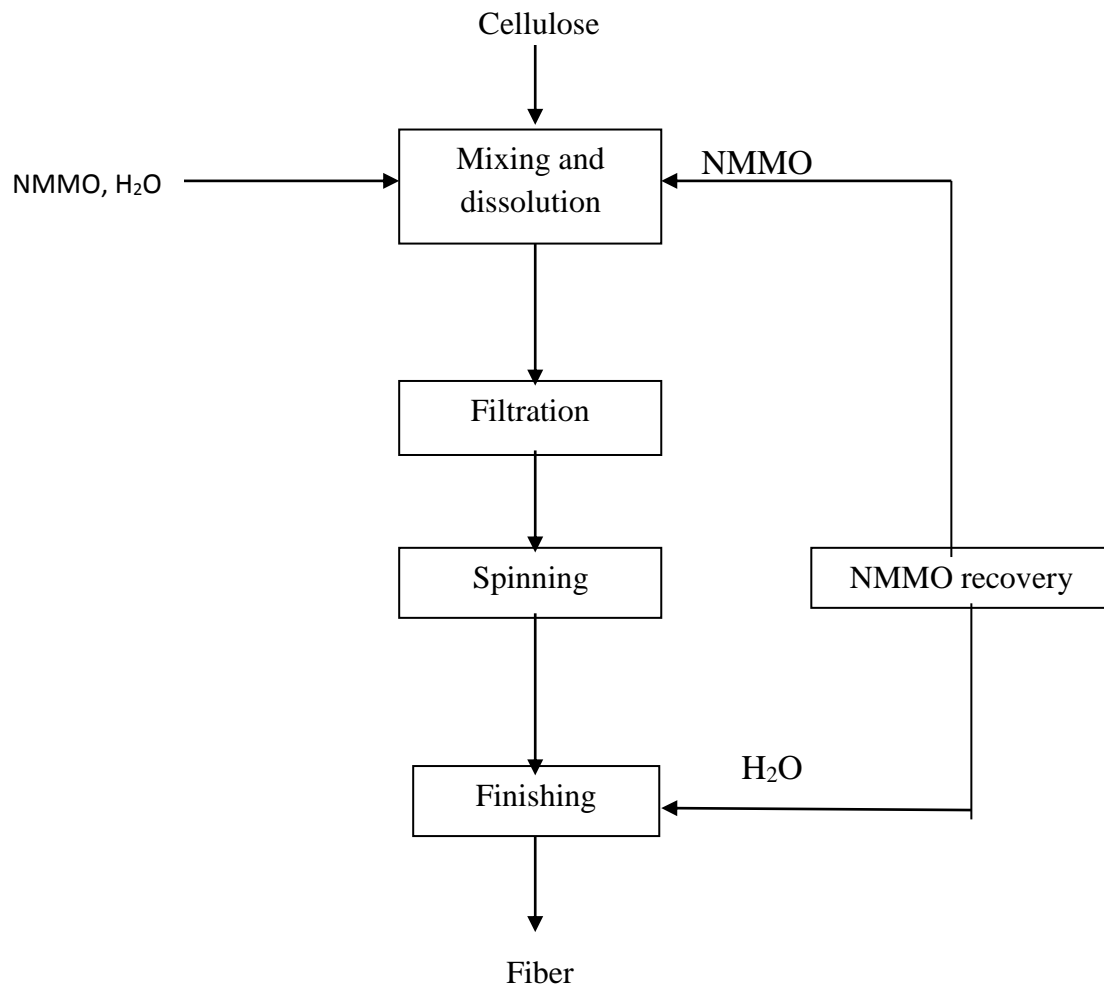
- i. Preparation of a homogeneous solution (dope) from wood pulp (cellulose) in NMMO hydrates (solvent)
- ii. Extrusion of highly viscous spinning dope at elevated temperature through air gap into a coagulation bath (dry-jet wet-spinning process)
- iii. Coagulation of lyocell fibers
- iv. Washing, drying and post-treatment of lyocell fibers
- v. Recovery of NMMO from coagulation baths

In commercial lyocell process, wood pulp is dissolved in aqueous amine oxide, and the excess water is removed to make homogeneous solution with minimum of undissolved particles (of course particle size is equally importance) and air bubbles. As shown in Figure 2.5, lyocell process is closed loop process in which solvent, NMMO is recycled. The solution is spun through an air gap to a water/ amine oxide bath (additives can be added) to generate fibers then washed and dried. NMMO in washing solution and coagulation bath can be recovered, purified, concentrated and recycled (Woodings 2001).

In fact, lyocell process resembles the dry-jet wet-spinning process but there is essentially no mass transfer in air gap and no chemical reaction in coagulation bath (Liu et al 2001). Lyocell fibers do not have apparent skin-core structure (Woodings 2001). Lyocell process is energy and water efficient process.

Industrial lyocell solutions (lyocell dope) initially contain nearly 50-60% NMMO, 20-30% water, 10-15% cellulose pulp and stabilizer. Excess water is evaporated and trapped as condensate under reduced pressure at predefined or set temperature until dissolution of pulp occurs to form spinning lyocell solution. The typical spinning dope composition is 13-14% cellulose, 11-13% water, 76% NMMO. Spinning temperature (normally 100°C to 120°C) can be set according to dope characteristics.

The production cycle is relatively short and does not exceed 8 h. On the other hand conventional viscous is time consuming, exceeding 40 h and requires handling of toxic gas by-product,  $\text{H}_2\text{S}$  and  $\text{CS}_2$ . Lyocell fibers are spun at higher spinning speed than that in rayon fibers. Lyocell fibers have excellent properties but increased susceptibility to fibrillation.



**Figure 2.5** Schematic of lyocell process (Laszkiewicz 1997).

### 2.3 RHEOLOGY

Rheology plays a significant role in polymer processing, food processing, coating and printing since it deals with a science of deformation and flow of matter. Today, polymers are among most important materials in existence as the properties of polymers can be adapted in a very wide range to fit the field of application. Some polymers are hard and brittle or tough and shock-resistant, while other polymers are

soft and flexible. The manufacturing and characterization of polymers is therefore the focus of activity for numerous industrial companies and research institutes.

Polymers are organic or semi-organic material with a high molecular weight. The length of the molecular chains and the entanglement between them are decisive parameters that influence the properties of the material. Many of the relevant properties can be characterized using rheological tests. Polymers have complex chemical and morphological structures and wide range of variation in the composition and possibility to modify the material. Therefore they show complex behaviours which need to be taken into consideration when using or manufacturing these materials, i.e. the viscoelasticity, non-Newtonian flow behaviour, anisotropy (dependent on orientation and modification), complex aging behaviour and much more. Describing the properties of polymers requires versatile procedures in order to obtain the needed information.

Many methods are used for processing and manufacturing polymers. The majority are forming and reforming procedures (compression molding, calendaring, film extrusion, blow and injection molding, etc.).

Characterization and significance of rheological properties are important to understand, predict, and control lyocell production and final lyocell fiber properties.

### **2.3.1 Rheology of Solutions and Melts**

Rheology deals with primary two flow modes, shear flow and elongational flow in polymer processing operations. Application oriented knowledge of both shear and elongational (or extensional) rheology is required in polymer processing because either alone cannot fully describe the flow characteristics.

#### **2.3.1.1 Shear Flow**

The viscosity is independent of shear rate and stress for a Newtonian fluids correlated by the equation (Barnes et al 1989).

$$\tau = \eta \dot{\gamma} \quad (2.1)$$

Where  $\tau$  is the shear stress,  $\eta$  is the viscosity of fluid and  $\dot{\gamma}$  is the shear rate. For non-Newtonian fluids, viscosity changes with variation of shear rate. It is essential to understand viscous behaviour for non-Newtonian fluids by an empirical power law (Barnes et al 1989).

$$\eta = k \dot{\gamma}^{n-1} \quad (2.2)$$

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 values of  $n$  is less than unity and for shear thickening fluids  $n$  is greater than one (Barnes et al 1989, Norrosian 2001).

Elastic deformation, return to zero as a function of time when force is removed and remaining deformation, viscous portion, not return to zero when force is removed are two distinguished properties for viscoelastic materials.

If applied force profile is sinusoidal then 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 (Norrosian 2001). The shear stress is a vector sum of elastic stress and viscous stress implies complex shear modulus  $G^*$  is defined as (Barnes et al 1989):

$$G^* = G' + iG'' \quad (2.3)$$

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

$$\tan(\delta) = \frac{G''}{G'} \quad (2.4)$$

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



$G'$  and  $G''$  can be calculated by measuring the in-phase and out-phase components of the response of strain to an imposed stress or vice versa at different frequencies. The modulus is a function of frequency scale of experiment. The complex viscosity ( $\eta^*$ ) measured is defined as

$$|\eta^*| = (\eta'^2 + \eta''^2)^{\frac{1}{2}} \quad (2.5)$$

$$= \frac{|G^*|}{\omega}$$

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

$$|G^*| = \sqrt{G''^2 + G'^2}$$

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

$$\omega = 2\pi f$$

Where  $\eta'$  is the dynamic viscosity,  $\eta''$  is the elastic part of complex viscosity,  $\omega$  is angular velocity and  $f$  is the frequency of oscillation.

### 2.3.1.2 Elongational Flow

Elongational flow is the dominant mode of fluid flow when rapid change of shape, stretching is involved in the operation. Extensional stretching flows are observed in many operations for polymer processing like extrusion through converging profiles, injection moulding, film stretching and fiber spinning.

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

$$v_x = \dot{\epsilon}x, v_y = -\dot{\epsilon}\frac{y}{2}, v_z = -\dot{\epsilon}\frac{z}{2} \quad (2.6)$$

Where  $\dot{\epsilon}$  is a constant elongational strain rate,  $v_x$ ,  $v_y$ , and  $v_z$  are the velocity component in  $x$ ,  $y$  and  $z$  directions respectively. The corresponding stress distribution is (Barnes et al 1989)

$$\sigma_{xx} - \sigma_{yy} = \sigma_{xx} - \sigma_{zz} = \dot{\epsilon} \eta_e(\dot{\epsilon}) \quad (2.7)$$

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

Where  $\eta_e$  is the elongational viscosity.

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

$$T_R = \frac{\eta_e(\dot{\epsilon})}{\eta(\dot{\gamma})} \quad (2.8)$$

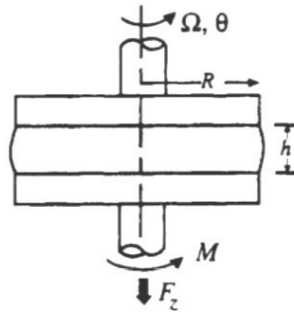
The elongational viscosity of Newtonian fluid is normally thrice the shear viscosity:  $\eta_e = 3\eta$  (Barnes et al 1989, Morrosian 2001).

## 2.3.2 Measurement

### 2.3.2.1 Measurement of Shear Viscosity

Most rheological characterization methods are pivoted on shear deformation since it is easier to measure. They are generally performed in one of four shear geometries: parallel-plate flow, cone-plate flow, capillary flow, and Couette flow. The property measured is quantity of force, pressure drop or torque that is directly related to the shear stress (Barnes et al 1989).

Capillary rheometry is used for polymers used to process for viscosities at high shear rates. Flow through a capillary is unidirectional and 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 (Barnes et al 1989). For small quantity of materials, that would be adversely affected by the severe contractions at the inlet of capillary parallel plate Rheometer and cone plate Rheometer are preferred. In a cone and plate geometry, a homogeneous flow can be produced in small angles since radial dependence of the shear rate and shear strain in parallel plate rheometry (Barnes et al 1989) where else highly viscous loading is a problem associated in case of cone plate Rheometer. Two types of method, static and dynamic are available to determine viscoelastic behaviour of polymers (Barnes et al 1989, Morrosian 2001). The parallel disks geometry is as shown in Figure 2.6.



**Figure 2.6** Schematic of a parallel plate Rheometer (Barnes et al 1989).

If we assume:

- i. Steady, laminar, isothermal flow
- ii.  $v_\theta(r, z)$  only,  $v_r = v_z = 0$
- iii. Negligible body forces
- iv. Cylindrical edge

Then the equation of motion reduce to

$$\theta: \frac{\partial \tau_{\theta z}}{\partial z} = 0 \quad (2.9)$$

$$z: \frac{\partial \tau_{zz}}{\partial z} = 0 \quad (2.10)$$

$$r: \frac{1}{r} \frac{\partial (r \tau_{rr})}{\partial z} - \frac{\tau_{\theta\theta}}{r} = -\rho \frac{v_\theta^2}{r} \quad (2.11)$$

Table 2.3 gives the working equations for this geometry.

**Table 2.3** Working Equations for Parallel Disks.

Shear strain

$$\gamma = \frac{\theta r}{h} \text{ (non homogeneous, depends on position)}$$

Shear rate at  $r = R$ 

$$\dot{\gamma}_R = \frac{R\Omega}{h}$$

Shear stress

$$\tau_{12} = \tau_{\theta z} = \frac{M}{2\pi R^3} \left[ 3 + \frac{d \ln M}{d \ln \dot{\gamma}_R} \right]$$

$$\tau_a = \frac{2M}{\pi R^3} \text{ apparent or Newtonian shear stress}$$

Representative shear stress

$$\eta(\tau) = \eta_a(\tau_a) \pm 2\%$$

$$\text{for } \tau = 0.76 \tau_a \text{ and } \frac{d \ln M}{d \ln \dot{\gamma}_R} < 1.4$$

Normal stress

$$N_1 - N_2 = \frac{F_z}{\pi R^2} \left[ 2 + \frac{d \ln F_z}{d \ln \dot{\gamma}_R} \right]$$

$$(F_z)_{inert} = 0.075\pi\rho\Omega^2 R^4$$

**Errors**

Inertia and secondary flow

Edge failure (same as cone and plate)

Shear heating

Non-homogeneous strain field (correctable)

Table 2.3 (Continued)

**Utility**

Sample preparation and loading is simpler for very viscous materials and soft solids

Can vary shear rate (and shear strain) independently by rotation rate  $\Omega$  and  $\theta$  or by changing the gap  $h$ ; permits increased range with a given experimental set up

Determine wall slip by taking measurements at two gaps

Delay edge failure to higher shear rate by decreasing gap during an experiment (requires change of cone angle in cone and plate)

Measure  $N_2$  when used with cone and plate thrust data

Preferred geometry for viscous melts for small strain material functions

**2.3.2.2 Measurement of Elongational Viscosity**

Measurement of elongational viscosity is more difficult than shear viscosity. The dominant problem is to maintain a uniaxial elongational flow as a function of time for the stress or strain rate to achieve steady state conditions, which enables the measurement of steady state elongational viscosity (Burkinshaw 1997a). The length of sample must be increased exponentially in order to attain a constant elongational strain rate (Barnes 1989).

Elongational viscosity can be measured by homogeneous stretching methods, constant stress devices, contraction flow devices, and spinning techniques. First two methods listed above are direct methods for measurement of elongational viscosity.

### *Homogeneous stretching method*

In 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 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 (Barner 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 1989, Cogwell 1969).

### *Constant Stress Devices*

The constant stress device was first introduced by Cogswell (Cogswell 1969) and was developed later by Münstedt (1975, 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.

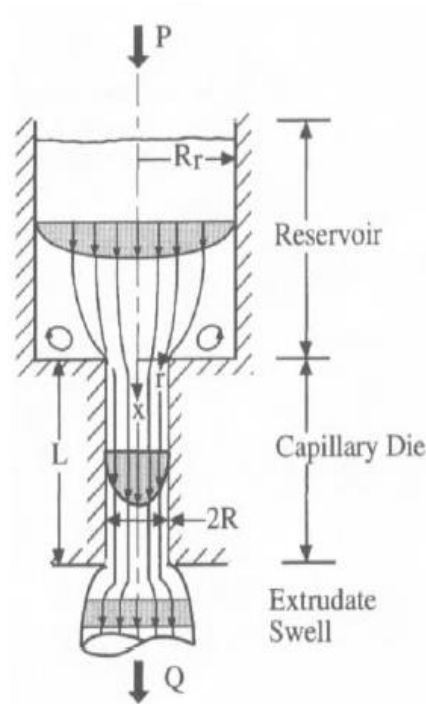
### *Contraction Flows*

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 (Munstedt 1975, Munstedt 1979) 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. Cogswell (Cogswell 1972a, Cogswell 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 (Burkinshaw 1997a).

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 (Cogswell 1969, Munstedt 1979). Collier 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 (Cogswell 1972b)). 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.

A capillary was the first Rheometer, and this device remains the most common method for measuring viscosity. The basic features of the instrument are shown in Figure 2.7. Gravity, compressed gas, or a piston is used to generate pressure on the

test fluid in a reservoir. A capillary tube of radius  $R$  and length  $L$  is connected to the bottom of the reservoir. Pressure drop and flow rate through this tube are used to determine viscosity.



**Figure 2.7** Schematic of capillary Rheometer.

In deriving the viscosity relation the important assumptions are as follow:

- i. Fully developed, steady, isothermal, laminar flow
- ii. No velocity in the  $r$  and  $\theta$  directions
- iii. No slip at the walls,  $v_x = 0$  at  $R$
- iv. The fluid is incompressible with viscosity independent of pressure

With these assumptions, the equation of motion in the  $x$  direction in cylindrical coordinates reduced to

$$0 = \frac{-\partial p}{\partial x} + \frac{1}{r} \frac{\partial(r\tau_{rx})}{\partial r} \quad (2.12)$$

Table 2.4 gives the working equations for this geometry.



**Table 2.4** Working Equations for Capillary Rheometer.

Wall shear stress

$$\tau_w = \frac{R}{2} \frac{P_c}{L}$$

Wall shear rate

$$\dot{\gamma}_{aw} = \frac{4Q}{\pi R^3}$$

$$\dot{\gamma}_w = \frac{1}{4} \dot{\gamma}_{aw} \left[ 3 + \frac{d \ln Q}{d \ln P_c} \right]$$

$$\dot{\gamma}_w = \frac{1}{4} \dot{\gamma}_{aw} \left[ 3 + \frac{1}{n} \right] \quad (\text{for power law model})$$

Representative shear rate

$$\eta(\dot{\gamma}) = \eta_a(\dot{\gamma}_a) \pm 2\%$$

$$\text{for } (\dot{\gamma}) = 0.83(\dot{\gamma}_a)$$

$$\text{and } 0.2 < \frac{d \ln Q}{d \ln P_c} < 1.3$$

For normal stress difference from Extrudate swell (not rigorous)

$$(T_{11} - T_{22})^2 = 8\tau_w^2 (B^6 - 1)$$

$$\text{Where } B = \frac{D_e}{2R} - 0.13$$

### Errors

Wall slip with concentrated dispersion

Melt fracture at  $\tau_c \approx 10^5 \text{ Pa}$

Reservoir pressure drop

Entrance pressure drop

Viscous heating- $Na \geq 1$

Material compressibility

Pressure dependence of viscosity

Shear history, degradation in reservoir

Table 2.4 (Continued)**Utility**

Simplest Rheometer, yet most accurate for steady viscosity

High  $\dot{\gamma}$

Sealed system: pressurize, prevent evaporation

Process simulator

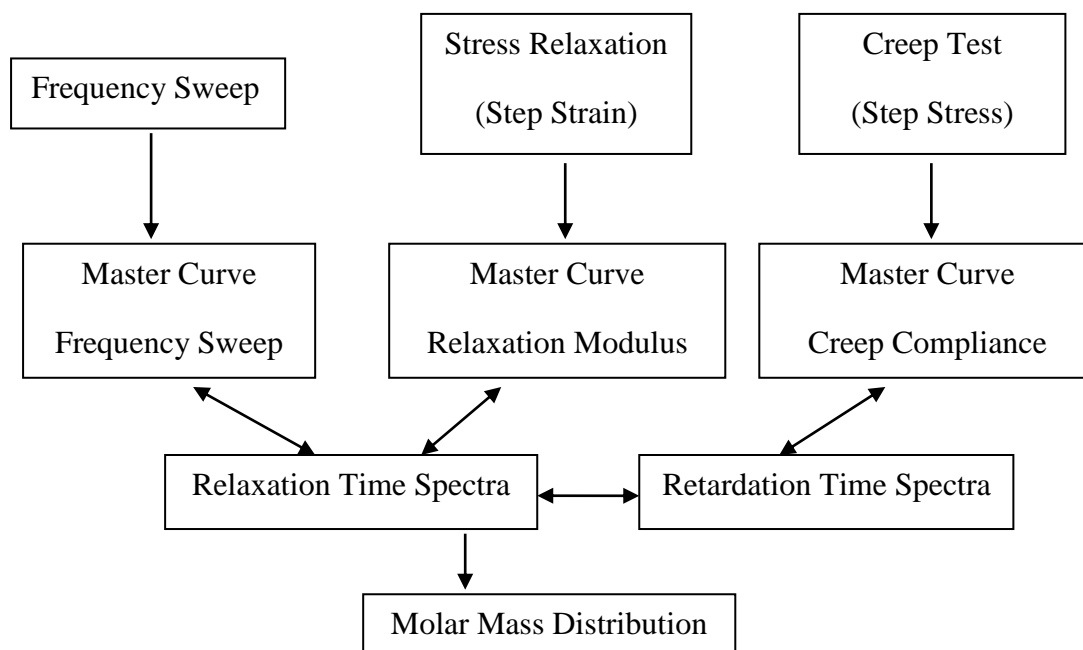
Quality control: melt index

Non-homogeneous flow, only steady shear material functions

Entrance corrections entail more data collection

**2.3.3 Rheological Tests on Polymers**

Measurements at low shear rates are mainly used for analysing manufacturing problems. Whereas manufacturing process such as extrusion or injection molding occur at high shear rates, difference between the materials are usually seen at low shear rates. Manufacturing problems often occurs at low shear rates, i.e. delayed die swell with extrusion or delay due to irregular relaxation during the cooling phase of injection molded parts. Polymer melts show pronounced shear thinning behaviour, e.g. the viscosity decreases with increasing shear rate. Flow curves are important to determine the energy required for the process. A inter relations between rheological tests are shown in Figure 2.8.



**Figure 2.8** Conversion and analysis methods for rheological tests.

#### 2.3.4 Applications (Polymer Analysis with MCR Rheometer 2016)

*Flow and Viscosity Curve (how to get information about the flow ability of polymer)*

Flow and viscosity curves reveal information about the flow ability of polymers under different shear and simulated process conditions. The zero shear viscosity at low shear rates is an important material property and is directly proportional to the average molar mass  $M_w$ . To determine a viscosity curve over a broad range of shear rates, a master curve can be calculated using the time-temperature superposition (TTS) in combination with the conversion method according to the Cox-Merz rule.

*Amplitude Sweep (how to determine the deformation stability and yield stress of a suspension or emulsion)*

Rotational tests, often used in the past, can deliver very different results when calculating the yield stress. Using  $G'$  and  $G''$  of an amplitude sweep with preset strain (Direct Strain Oscillation, DSO) plotted over the shear stress permits more reliable and practically relevant results for the yield stress value. Significant parameters for

evaluating the mechanical stability of a material can be calculated using automated analysis routines in the software.

*Interval Thixotropy Test (how to measure the structural regeneration of a material after a short period of high shear)*

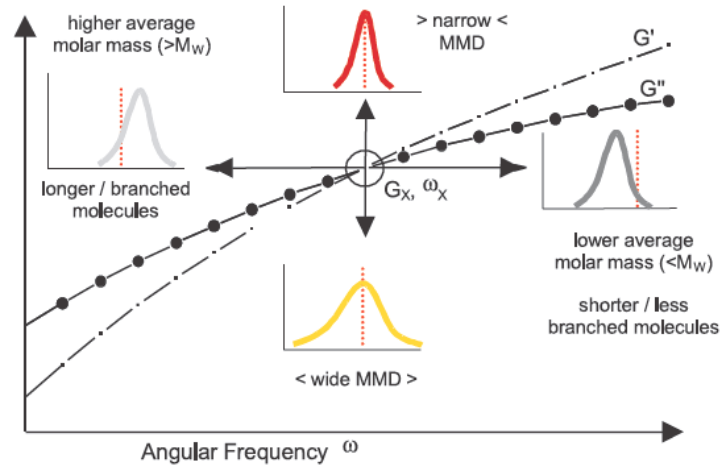
Almost every coating process consists of 3 phases (1 – at rest, 2 – structural decomposition, 3 – structural regeneration). The material's behaviour is described by  $G'$  and  $G''$  over time. Time-dependent effects such as levelling and sagging, dot sharpness, layer thickness and separation stability of emulsions and dispersions can be correlated directly to the curve progression.

*Transient Test Types (creep, stress relaxation tests) (what can we learn from the first normal stress difference?)*

Step stress (creep & recovery), step strain (stress relaxation) and step rate (stress growth / start-up flow) experiments are typically performed to measure the transient response of a material to a given constant shear stress, strain or rate. Besides the shear viscosity, the measurement of the first normal stress difference  $N_1$  and coefficient  $\psi_1$  also gives valuable information about the sample. MCR Rheometer include a patented normal force transducer which allows the evaluation of the first normal stress difference  $N_1$  and the coefficient  $\psi_1$  over a large range with virtually no thermal drift.

### **2.3.5 Molar Mass Distribution**

Recently, mathematical models have been developed which allow the determination of the molar mass distribution via rheological measurement. Correlations to molar mass distribution or material branching can be seen in the viscoelastic behaviour, which influence both, the manufacturing process and the properties of the end product. The molar mass is the most important structural parameter which affects the flow behaviour of polymers.



**Figure 2.9** Mass distribution strategies for polymers.

The viscosity curve becomes flatter with decreasing shear rate and the polymer melt shows Newtonian behaviour with a constant viscosity. This region at low shear rates is called the terminal relaxation zone or the 1<sup>st</sup> Newtonian plateau. The constant viscosity in this range is called the zero shear viscosity  $\eta_0$  and represents an important temperature dependent material parameter. For most technical polymers, the zero-shear viscosity is directly proportional to the average molar mass (Polymer Analysis with MCR Rheometer 2016). The rheological measurement therefore clearly shows small differences in the molar mass. At a constant average molar mass, the energy required for shear thinning in the manufacturing process can be correlated with the molar mass distribution. Polymers with a wide molar mass distribution have more of a tendency to shear thinning, even at low shear rates, than more narrowly distributed materials with the same average molar mass. Broadening the molar mass distribution aids extrusion and shaping (Polymer Analysis with MCR Rheometer 2016). This means, for example, that the surface quality of moulded plastic parts can be improved by varying the distribution width. The width of the molar mass distribution correlates with the cross-over point between the storage modulus  $G'$  and the loss modulus  $G''$  in a frequency sweep.

### **2.3.6 Branching**

The number, length and mobility of side chains influence the rheological properties (Polymer Analysis with MCR Rheometer 2016). If the side chains are not very long, this leads to increased viscosity at low shear rates and more pronounced shear thinning compared to the corresponding linear polymer (Polymer Analysis with MCR Rheometer 2016). If a polymer has long-chain branching, it will display low viscosity at low shear rates. The extent of branching can therefore be used to control manufacturing and product characteristics.

### **2.3.6 Fillers**

Fillers also influence the manufacturing process and the properties of the end product. Important factors are size, form and concentration of the fillers and the interactions between the particles. Fillers usually lead to an increase in the melting viscosity and a reduction of die swell (Polymer Analysis with MCR Rheometer 2016). From a rheological standpoint increasing filler content results in a smaller so-called linear viscoelastic (LVE) range, which can be determined in an amplitude or strain sweep (Polymer Analysis with MCR Rheometer 2016).

## CHAPTER 3

### METHODS, INSTRUMENTS AND PROCEDURE

Objectives of this research includes: a) preparation of lyocell solutions from different wood pulps; b) study of the rheological properties of the prepared lyocell solutions. To accomplish these objectives, lyocell solutions were made from different commercial bleached hardwood and softwood pulps of different swelling, average molecular weight and moisture content.

#### 3.1 PREPARATION OF LYOCELL SOLUTIONS

Preparation of lyocell solutions may be sub-divided in to three steps: a) grinding the wood pulp sheet in to fine powder; b) thermal treatment of NMMO; and c) mixing of wood pulp powder and anhydrous NMMO in sigma mixer head to result in lyocell solutions (dope).

##### 3.1.1 Preparation of cellulose powder

Wood pulps are normally available in form of sheets having sheet weight of 935 g/m<sup>2</sup> according to a standard test method ISO 356-1995. The pulp sheets were broken in to small pieces, and then put into a shredder followed by grinder to make the grounded powder (< 4mm diameter). They were allowed to dry at room temperature for 30 minutes and then put into plastic bags and sealed with vacuum sealer.

Pulp samples were analyzed to determine percentage of moisture, average molecular weight (Gel Permeation Chromatography) and swelling.

**Table 3.1** Properties of pulps.

| Pulp   | Wood type | Process          | Moisture content (%wt.) | Weight Average molecular weight (g/mol) | Number Average molecular weight (g/mol) | Polydispersity | Swelling study |               |
|--------|-----------|------------------|-------------------------|---|---|----------------|----------------|---------------|
|        |           |                  |                         |   |   |                | % weight gain  | % volume gain |
| Pulp 1 | Hardwood  | Sulphite         | 6.13                    | 291392                                  | 46253                                   | 6              | 710.8          | 438.8         |
| Pulp 2 | Hardwood  | Sulphate (Kraft) | 6.48                    | 275399                                  | 63612                                   | 4              | 797.7          | 477.5         |
| Pulp 3 | Softwood  | Sulphate (Kraft) | 7.68                    | 302066                                  | 70846                                   | 4              | 652.7          | 313.2         |

### 3.1.2 Preparation of lyocell solutions (dope)

Preparation of lyocell solutions (VP-01, VP-02, VP-03, VP-04, VP-05, VP-07) may be divided into two steps: a) preparation of slurry of cellulose-NMMO monohydrate; b) slurry prepared used to head to lyocell solutions in continuous batch operation. 76% concentrated NMMO mono hydrate is used to prepare all lyocell solutions.

Cellulosic wood pulp powder, NMMO·H<sub>2</sub>O, 0.18% (by weight on pulp) propyl gallate and 0.06% (by weight on pulp) hydroxyl amine as an anti-oxidants or stabilizers were mixed in sigma mixer to prepare slurry. Process parameters were fixed to make slurry as follow:

- i. Heating temperature: 80°C - 90°C
- ii. Pressure: 1 atm
- iii. Mixing Speed: 30-40 rpm



iv. Mixing time: 20-30 minutes

Slurry prepared is mixed until the solution was transparent with following process parameters. The solutions were stored in bags sealed with a vacuum sealer.

- i. Heating temperature: 90°C - 110°C
- ii. Pressure: 670 mmHg – 690 mmHg
- iii. Mixing speed: 40-50 rpm
- iv. Cooling temperature (to collect water as condensate): 2°C - 7°C

**Table 3.2** Composition of Lyocell solutions.

|                     | VP-01  | VP-02  | VP-03  | VP-04  | VP-05  | VP-07  |
|---------------------|--------|--------|--------|--------|--------|--------|
| Pulp                | Pulp-1 | Pulp-2 | Pulp-1 | Pulp-2 | Pulp-3 | Pulp-3 |
| Cellulose<br>(%wt.) | 13     | 13     | 11     | 11     | 13     | 11     |
| NMMO<br>(%wt.)      | 76     | 76     | 76     | 76     | 76     | 76     |
| Water<br>(%wt.)     | 11     | 11     | 13     | 13     | 11     | 13     |

### 3.2 RHEOLOGICAL CHARACTERIZATION OF LYOCELL SOLUTIONS

In the realm of lyocell processing, it is important to consider what affects viscosity. The major factor includes temperature, concentration, molecular weight distribution, and shear rate.

Like polymer melts, lyocell solutions exhibit time dependent viscoelastic behaviour, which is a combination of elasticity and viscosity. The combined viscoelastic behaviour can be examined by determining the effect of oscillating force on the response of the lyocell solution. Dynamic complex viscosities of all lyocell solutions were characterized with Anton paar Rheometer. A standard operating

process was developed and parallel plates (25 mm diameter) were used to determine complex viscosities. Nitrogen gas was used to provide inert environment in closed system with hood. Lyocell solutions in sufficient quantity were put between parallel plates to form 1 mm film. A thin layer of silicone oil was applied to prevent moisture uptake and coagulation of the sample after trimming of excess sample. Dynamic frequency sweep tests were conducted from 0.1 rad/s to 100 rad/s at a strain of 1% to analyze viscoelastic behaviour at different temperature, 125°C, 115°C, 95°C, 75°C, and 55°C.

## CHAPTER 4

### RESULTS AND DISCUSSION

Dissolution study was done to determine characteristics of undissolved particles in lyocell solutions. Frequency sweep test was performed for all lyocell solutions at different temperature to obtain temperature-time superposition (TTS), which provides shear and time dependent information about the viscoelastic properties of solutions.

Composition for all lyocell solutions was determined. Lyocell solutions were melted in closed container in oven at 100°C. A thin film of known quantity for all solutions was made by sliding solutions between two glass plates and cellulose was regenerated once film formed. Water wash was provided until solutions get free from NMMO or film become transparent or white in colour. Film was taken out from water and kept in oven at 100°C for 3 hours for drying and finally weighted to calculate % amount of cellulose in dope sample as shown in Table 3.2.

$$\% \text{ Cellulose} = \frac{\text{Weight of film after drying}}{\text{Initial weight of dope for analysis}} \times 100$$

Composition of solvent, NMMO·H<sub>2</sub>O was measured by refractometer. NMMO monohydrates have refractive index of 1.46917. All lyocell solution solutions have refractive index nearer to 1.47037 resulting solvent concentration ~76%. Remaining composition determined as for water. Table 3.2 gives detail information of composition of all lyocell solutions.

#### 4.1 DISSOLUTION STUDY FOR LYOCELL SOLUTION

Image analysis was also performed to determine number of undissolved particles present in lyocell solutions which lead us to judge the quality of dope for sequential operations. The lyocell solutions were melted in an oven and thin films were cast on

class slides. Images were then captured using an optical microscope at 5X magnification.

**Table 4.1** Specifications for undissolved particles.

|   | VP-01   | VP-02   | VP-03   | VP-04   | VP-05   | VP-07   |
|---|---------|---------|---------|---------|---------|---------|
| Average equivalent diameter (micron)          | 12.7349 | 15.8431 | 23.3085 | 19.4639 | 14.9902 | 18.1303 |
| Average number of particles per image analyze | 9       | 7       | 2       | 39      | 10      | 3       |
| Area per image (micron <sup>2</sup> )         | 0.0533  | 0.0533  | 0.0533  | 0.0533  | 0.0533  | 0.0533  |
| Total number of particles                     | 46      | 35      | 10      | 19      | 52      | 17      |
| Number of particles per unit area             | 86      | 66      | 19      | 37      | 98      | 32      |

## 4.2 COMPLEX VISCOSITY OF LYOCELL SOLUTIONS FROM DIFFERENT WOOD PULPS

Lyocell solutions were produced according to same protocol for all wood pulps as defined in Chapter 3. Lyocell solutions were prepared from different commercially dissolving pulps, bleached softwood and bleached hardwood produced from different processes like Sulphite or sulphate (Kraft) process. All pulps having different average molar mass as shown in Table 3.1.

Zero shear viscosities (ZSV) were determined by performing frequency sweeps at various temperatures followed by fitting the experimental data into master curve using time-temperature superposition. ZSV values at 115°C for the various lyocell solutions are given below in Table 4.2.

Effect of cellulose concentration in lyocell solutions, wood types and pulp making processes on complex viscosities and dynamic modulus at 115°C were compared. Values of storage or loss moduli and frequency at crossover for different solutions are given in Table 4.2.

**Table 4.2** Crossover data for lyocell solutions.

|       | Wood Type | Pulp Making Process | Cellulose Concentration (%wt.) | ZSV at 115°C (Pa·s) | Crossover frequency $\omega$ (rad/s) | Crossover Modulus $G' = G''$ (Pa) |
|-------|-----------|---------------------|--------------------------------|---------------------|--------------------------------------|-----------------------------------|
| VP-01 | Hardwood  | Sulphite            | 13                             | 881                 | 23.4                                 | 2945                              |
| VP-02 | Hardwood  | Sulphate (Kraft)    | 13                             | 960                 | 33.6                                 | 5201                              |
| VP-03 | Hardwood  | Sulphite            | 11                             | 401                 | 37.1                                 | 2266                              |
| VP-04 | Hardwood  | Sulphate (Kraft)    | 11                             | 434                 | 54.8                                 | 4017                              |
| VP-05 | Softwood  | Sulphate (Kraft)    | 13                             | 2031                | 14.7                                 | 5584                              |
| VP-07 | Softwood  | Sulphate (Kraft)    | 11                             | 836                 | 27.7                                 | 4167                              |

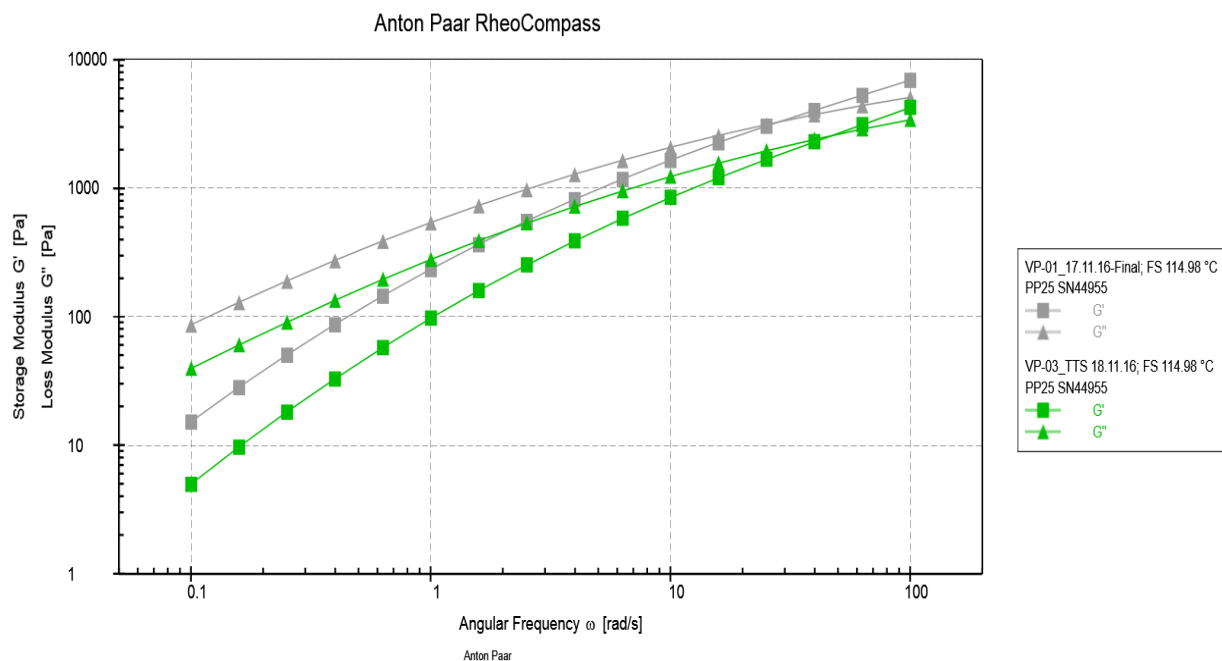
Storage modulus ( $G'$ ) and loss modulus ( $G''$ ) of different lyocell solutions were analyzed as a function of concentration, wood type and pulping process. The storage modulus gives information about elastic character of the fluid or the energy storage takes place during the deformation whereas the loss modulus reveals information about the viscous character of fluid or energy dissipation that occurs in flow.

#### 4.2.1 *Effect of pulp concentration on dynamic modulus*

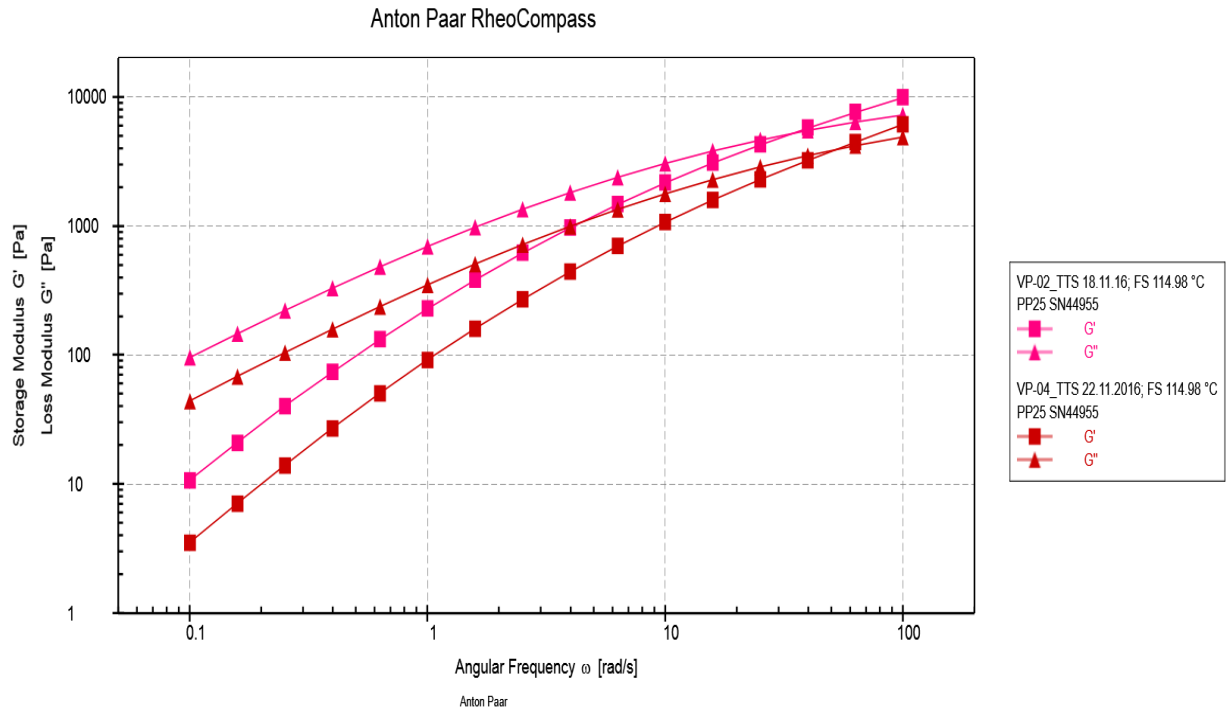
Dynamic moduli of lyocell solutions of different concentrations from all pulps (pulp-1, pulp-2 and pulp-3) are shown in figure 4.1 – 4.3.

The dynamic moduli increased with concentration for all wood types and pulping processes. The values of dynamic moduli increase with frequencies for individual solution. This is because the low frequencies allow enough time for the molecules to untangle and significant relaxation occurs resulting in more viscous behaviour than elastic ( $G'' > G'$ ). When the lyocell solution deformed at high frequencies the entangled chains do not have sufficient time to relax and moduli rise up resulting in  $G'$  higher than  $G''$ .

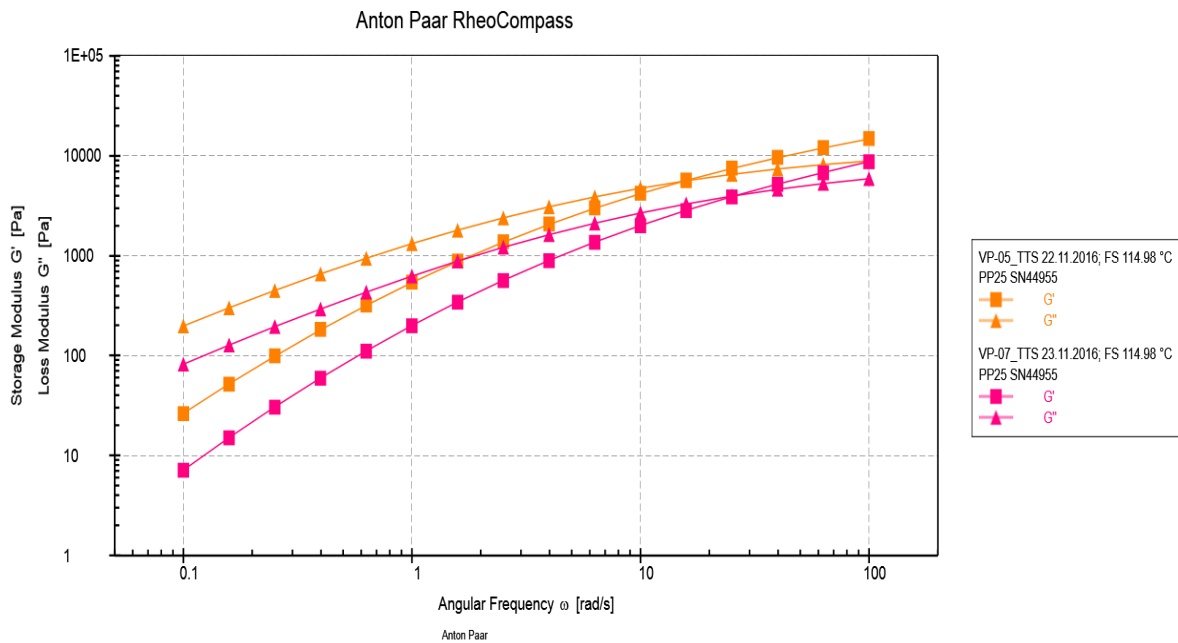
From all figures, we realize that the cross over points of  $G'$  and  $G''$  curves of all lyocell solutions shift from higher angular velocity and lower modulus to lower angular frequency and higher modulus as concentration increases. At lower strain rate than the cross over strain rate values of  $G'$  are lower than  $G''$  values, indicating the dominance of viscous response where more vice versa at higher strain rate than cross over strain rate indicating elastic response dominates for all lyocell solutions.



**Figure 4.1** Dynamic moduli of lyocell solutions prepared from pulp-1 (hardwood and sulphite process).



**Figure 4.2** Dynamic moduli of lyocell solutions prepared from pulp-2 (hardwood and sulphate process (Kraft process)).



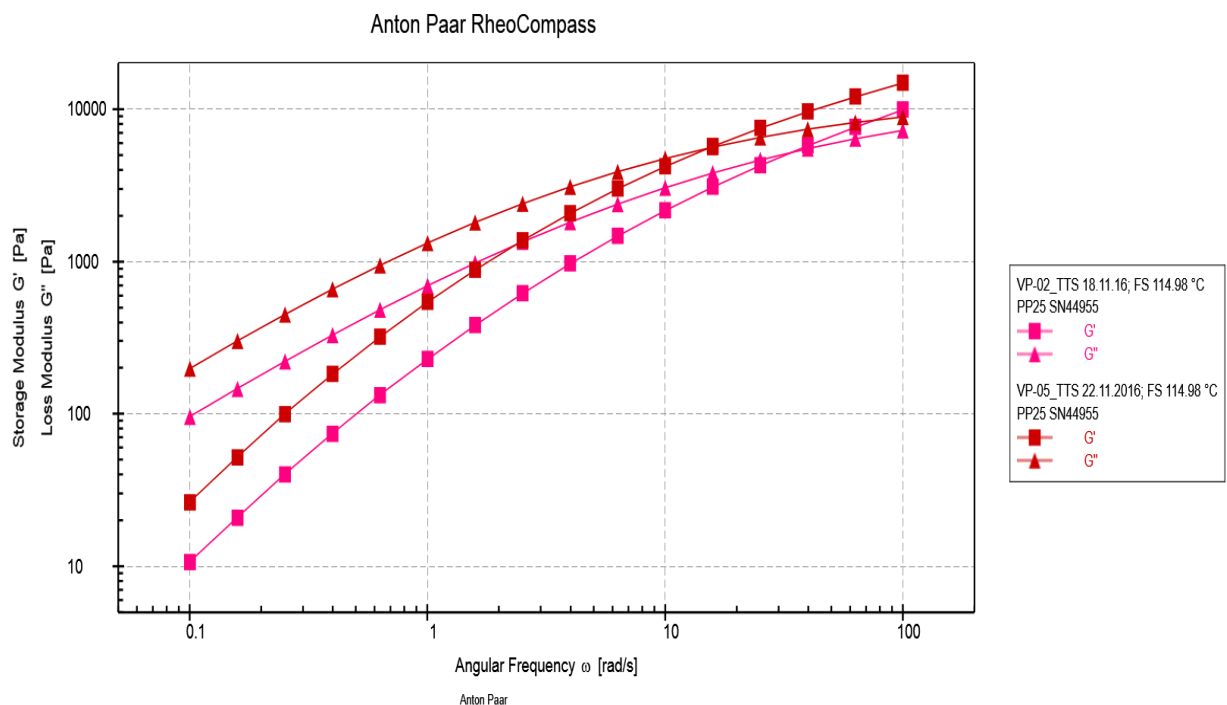
**Figure 4.3** Dynamic moduli of lyocell solutions prepared from pulp-3 (softwood and sulphate process (Kraft process)).

The viscoelastic response of lyocell solutions is a combination of the contributions from the polymer and from the solvent. Therefore, since the solvents are typically much less elastic, a lower concentration, and hence higher solvent content, causes the viscous response to dominate up to higher crossover strains.

#### 4.2.2 Effect of wood type on dynamic modulus

Lyocell solutions of cellulose concentration of 13% (wt.) produced from pulp-2 and pulp-3 are hardwood pulp and softwood pulp respectively having same pulping process (sulphate (Kraft) process). They were compared to analyze effect of wood type on dynamic moduli at 115°C as shown in Figure 4.4.

The crossover point or the change over from viscous to elastic behaviour happen earlier (higher frequencies) for hardwood pulp (lower molecular weight) compared to softwood pulp (higher molecular weight). This correlates well with the fact that at similar concentration the crossover frequency is inversely proportional to the molecular weight.



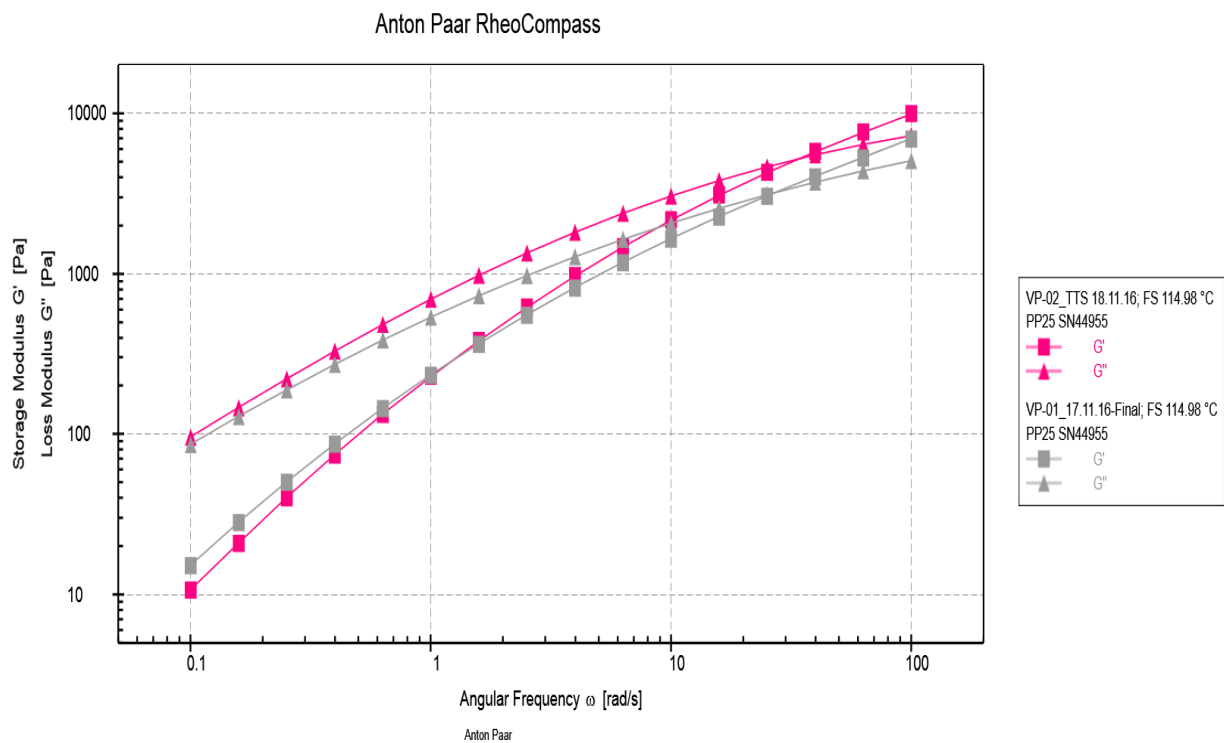
**Figure 4.4** Dynamic moduli of lyocell solutions (cellulose concentration of 13%wt.) prepared from pulp-2 and pulp-3 (hardwood and softwood respectively).



### 4.2.3 Effect of pulping process on dynamic modulus

Pulp-1 and pulp-2 which are hardwood pulps with different pulping process were used to make lyocell solutions having 13% (wt.) cellulose concentration. Angular frequencies vs. dynamic moduli data are as shown in Figure 4.5. Measurements were done at 115°C.

$G''$  for sulphate process pulp is always higher at all frequency. However,  $G'$  is higher for the sulphite process at low frequencies while at higher frequencies sulphate (Kraft) process pulp shows higher  $G'$ .

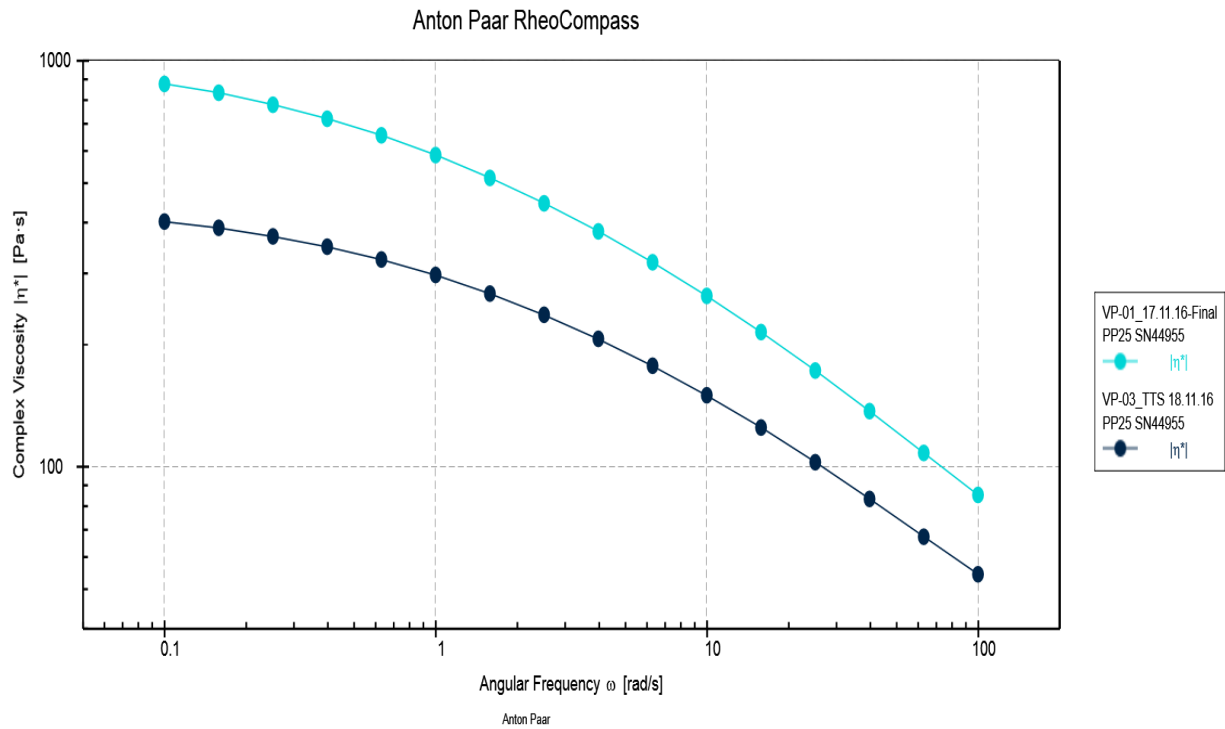


**Figure 4.5** Dynamic moduli of lyocell solutions (cellulose concentration of 13%wt.) prepared from pulp-1 and pulp-2 (hardwood with sulphite and sulphate pulping process respectively).

Value of crossover modulus increases at nearly same angular frequency from lyocell solutions from hardwood pulp by sulphite pulping to sulphate pulping. This could be due to difference in level of  $\alpha$ -cellulose generated by different pulping process.

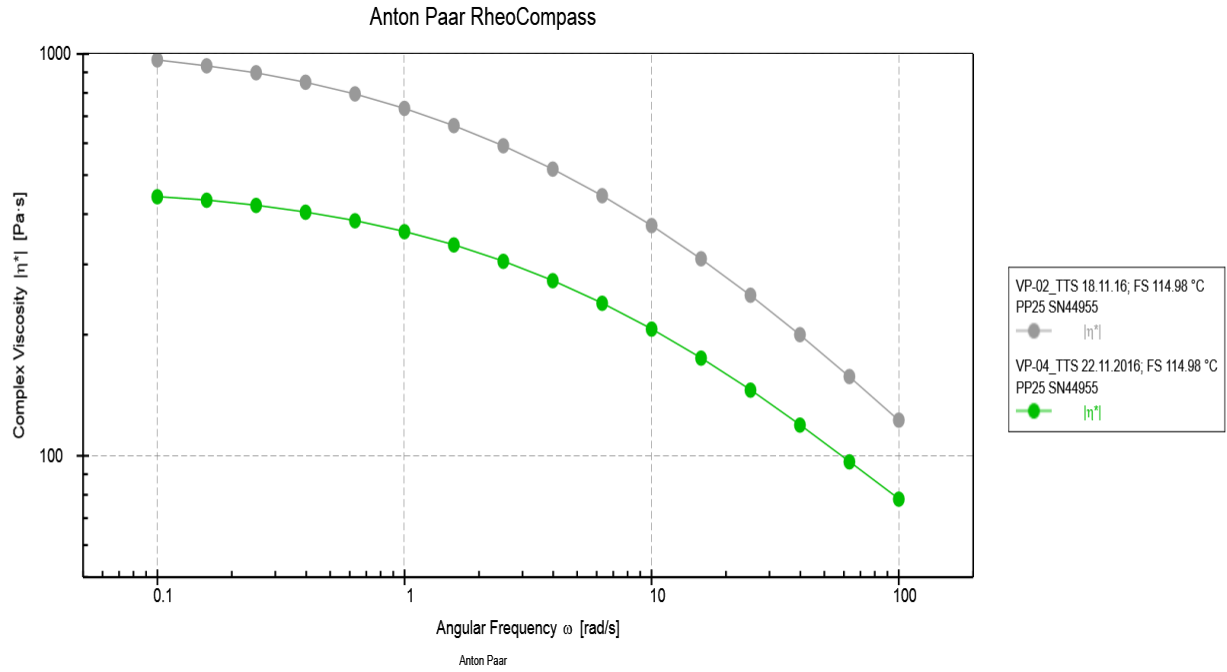
#### 4.2.4 Effect of pulp concentration on complex viscosity

Complex viscosities were measured at 115°C for lyocell solutions. All lyocell solutions exhibited shear-thinning behaviour. The complex viscosity decreased with the increase of angular velocity.

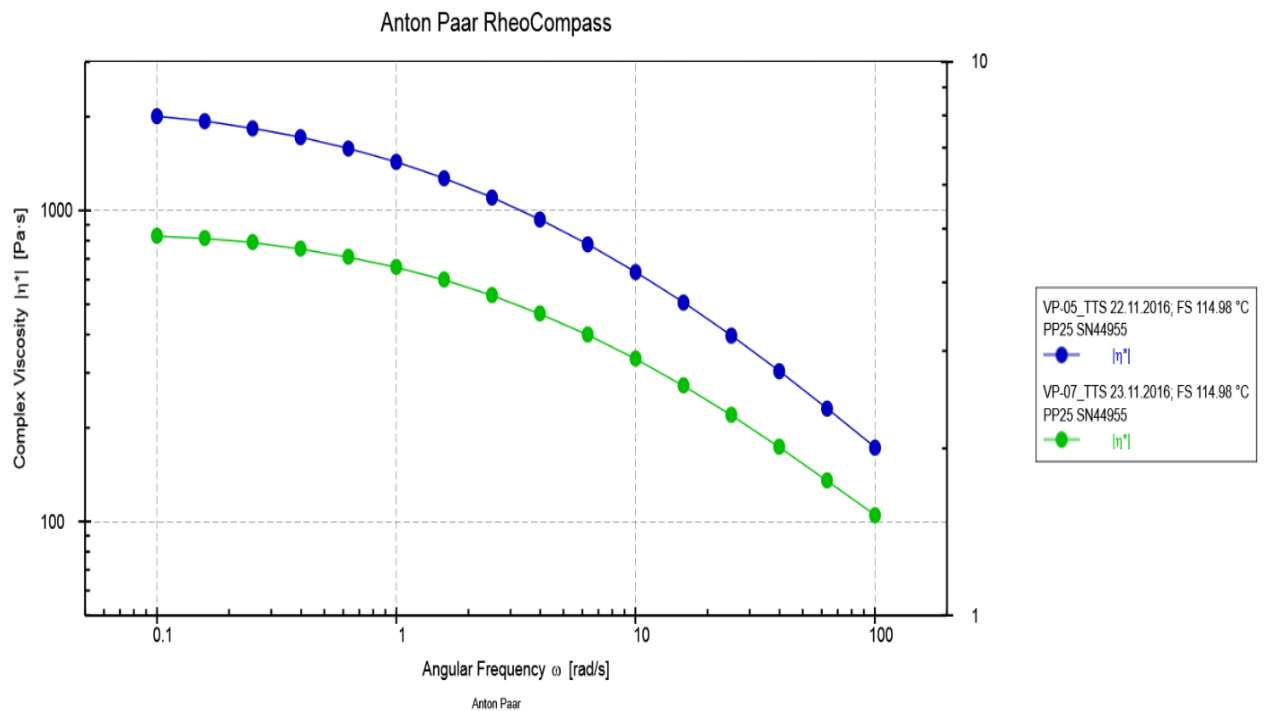


**Figure 4.6** Complex viscosity of lyocell solutions prepared from pulp-1 (hardwood and sulphite process).

Complex viscosities increased with increase of concentration at all frequencies which corroborates well with the fact that viscosity of a polymer solution is a function of concentration, molecular weight and temperature. At fixed temperature and molecular weight, any increase in concentration should lead to increase in viscosity because of presence of more material between the shearing plates. Difference in viscosity gradually decreases from lower to higher angular frequencies.



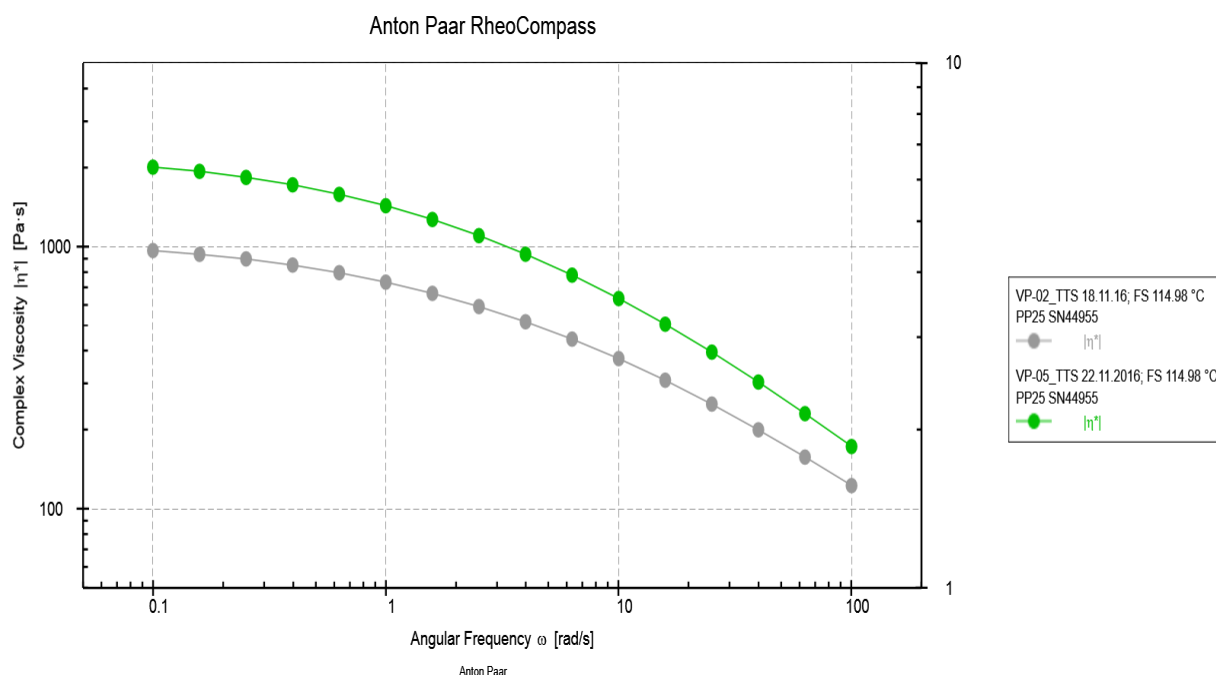
**Figure 4.7** Complex viscosity of lyocell solutions prepared from pulp-2 (hardwood and sulphate (Kraft) process).



**Figure 4.8** Complex viscosity of lyocell solutions prepared from pulp-3 (softwood and sulphate process (Kraft process)).

#### 4.2.5 Effect of wood type on complex viscosity

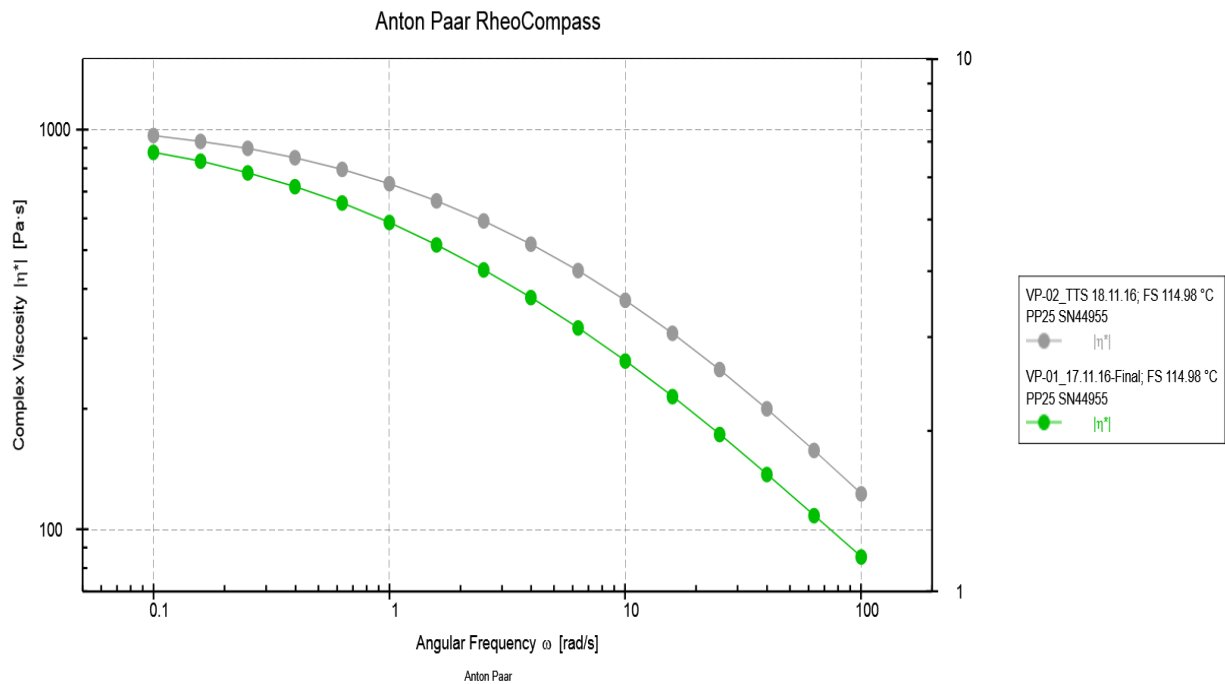
Lyocell solutions (13% wt. cellulose concentration) prepared from pulp-2 and pulp-3 was analyzed to study effect of wood type on complex viscosity at 115°C. Characteristics of both pulps are given in Table 3.1. Pulp-3 (softwood) has a higher molecular weight than pulp-2 (hardwood) as a result the complex viscosity for softwood pulp is higher than that of hardwood pulp at all frequencies.



**Figure 4.9** Complex viscosity of lyocell solutions (cellulose concentration of 13% wt.) prepared from pulp-2 and pulp-3 (hardwood and softwood respectively).

#### 4.2.6 Effect of pulping process on viscosity

Complex viscosities were studied for lyocell solutions of 13% wt. cellulose concentration prepared from pulp-1 and pulp-2. Complex viscosities as a function of frequencies at 115°C were observed as shown in Figure 4.10.



**Figure 4.10** Viscosity of lyocell solutions (cellulose concentration of 13% wt.) prepared from pulp-1 and pulp-2 (hardwood with sulphite and sulphate pulping process respectively).

Complex viscosities gradually decreased with increase of angular velocities with the sulphate process resulting in pulp that gives higher complex viscosity at all frequencies.

## CHAPTER 5

### CONCLUSIONS AND RECOMMENDATIONS

#### 5.1 CONCLUSIONS

Standard operating procedures were followed to make lyocell solutions of different concentrations from variety of pulps and rheological measurements. The mixing time of lyocell solutions depended on the target concentration and type of wood pulp used.

It was shown that cellulose concentration, wood types and pulping processes affected the rheological characteristics of resulting lyocell solutions. The higher the concentration, the more elastic the lyocell solution is. Wood type makes a most significant effect on complex viscosities.

#### 5.2 FUTURE WORK

Future efforts could focus on to determine elongational viscosities, a depth study on complex viscosity for lyocell solutions from softwood pulps and combined both hardwood and softwood pulps. Temperature test and transient test types can be performed to give a depth to rheological characterization.

## LIST OF REFERENCES

- Barnes, H. A., Hutton, J.F., Walters, K., *An introduction to rheology*, Elsevier Science Publishers, 1989.
- Bayer et al., Cellulose, cellulases and cellulosomes. *Current Opinion In Structural Biology* 8[5], 548-557. 1998.
- B.J.Collier, M. Dever, S. Petrovan, J.R.Collier, Z. Li, X. Wei, Rheology of Lyocell Solutions from Different Cellulose Sources. *Journal of Polymers and the Environment* 8[3], 151-154.2000.
- Buleon, A., Chanzy, H., Single crystals of cellulose IV: preparation and properties. *Journal of polymer Science, Polymer Physics Edition* 18[6]. 1209-1217. 1980.
- Burkinshaw, S.M., Gandhi, K., The wash-off of reactive dyes on fibrillation of lyocell fabric. *AATCC Book of Papers. AATCC*, 476-482. 1997a.
- Cogwell, F.N., Rheology of polymer melts under tension. *Plastic and Polymers* 36[122]. 109-111. 1968.
- Cogswell, F.N., Converging flow of polymer melts in extrusion dies. *PolymerEngineering and Science* 12[1], 64-73. 1972a.
- Cogswell, F.N., Measuring the extensional rheology of polymer melts. *Transactions of the Society of Rheology* 16[3], 383-403. 1972b.
- Dong Wook Chae, Byoung Chul Kim, Wha Seop Lee, Rheological Characterization of Cellulose Solutions in *N*-methyl morpholine *N*-oxide Monohydrate. *Journal of Applied Polymer Science* 86, 216-222.2002.
- Franks, N. E., Vargs, J. K. U.S. Pat. 4145532, 1979.
- Franks, N. E., Vargs, J. K. U.S. Pat. 4196282, 1980.
- Frank Wendler et al., Evidence of autocatalytic reactions in cellulose/NMMO solutions with thermal and spectroscopic methods. *Lenzinger Bericht* 84. 92-102. 2005.

- Happey, F., *Applied fiber science*, New York, Academic Press. 1979.
- Hermans, P.H., *Physics and chemistry of cellulose fiber*, Netherland, Elsevier publishing company. 1949
- Kerber, R et al. Ullmanns Encyklopadie der technischem Chemie Bd. 1. VCH, Weinheim 1972.
- Laszkiewicz, B., Manufacture of cellulose fibers without use of carbon disulphide. *ACGM LODART, AS. Lodz, Poland*. 1997.
- Liu, R. et al. An analysis of lyocell fiber formation as a melt-spinning process. *Cellulose* 8[1], 13-21. 2001.
- Ludwik szczesniak, Adam Rachoki, Jadwiga Tritt-Goc, Glass transition temperature and thermal decomposition of cellulose powder. *Cellulose* 15[3], 445-451.2008.
- Morrosian, F.A., *Understanding Rheology*, Oxford University Press. 2001.
- Münstedt, H., Viscoelasticity of polystyrene melts in tensile creep experiments. *Rheologica Acta* 14[12], 1077-1088. 1975.
- Münstedt, H., New universal extensional rheometer for polymer melts. Measurements on a polystyrene sample. *Journal of Rheology (New York, NY, United States)* 23[4], 421-436. 1979.
- Nevell, T. P., Zeronian, S. H., *Cellulose and derivatives: chemistry, biochemistry and applications*, New York, Ellis Horwood Ltd.. 1985a.
- Polymer Analysis with MCR Rheometers (Available on: <http://www.anton-paar.com/?eID=documentsDownload&document=2718&L=0>, Accessed on: 25.11.2016)
- Potthast A., Rosenau, T. Kosma, P., Chen, C.L., Gratzl, J.S.: *Journal of Organic Chemistry* 54. 101-103. 2000.



Roche, M., Chanzy, H., Electron microscopy study of the transformation of cellulose I in to cellulose IV in Valonia. *International Journal of Biological Macromolecules* 3[3], 201-206. 1981.

Rosenau, Y., Potthast, A., Sixta, H., Kosma, P. :*Prog. Polym. Sci.* 26. 1763-1837. 2001.

Rosemau, T. et al. Phase diagram of ternary system NMMO-water- cellulose. *Prog. Sci.* 26. 1763. 2001

Rosenau, T., Pottast A., Sixta, H., Kosma, P., *Tetrahedron* 58. 3073-3078. 2002.

Rosenau, T. Potthast A., Kosma, P., Chen, C.L., Gratzl, J.S.: *Journal of Organic Chemistry* 60, 301-306. 2003.

Taeger, E., Michels, C., Nechwatal, A.: Papier 12. 784-788. 1991.\

Wada, M. et al., Improved structural data of cellulose III prepared in supercritical ammonia. *Macromolecules* 34[5]. 1237-1243. 2001.

Wedler, G.: Lehrbuch der physikalischen Chemie. VCH, Weinheim 1997.

Woodings, C.R., *Regenerated Cellulose Fibers*, woodhead publishing Ltd. Cambridge, England. 2001.

Young, R.A., Rowell, R.M., *Cellulose structure, modification and hydrolysis*, New York, John Wiley & Sons. 1986.