RESEARCH ARTICLE | FEBRUARY 05 2019

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AIP Conf. Proc. 2065, 030062 (2019)
https://doi.org/10.1063/1.5088320

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Modified Lyocell Process for Producing Biopolymer Fiber

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Abstract. Cellulose is one of the most abundantly available biopolymer in nature. This semi crystalline cellulose cannot be melted directly to form fiber, as it degrades before melting. Hence processing of cellulosic fiber requires dissolution process. There are many solvents available for direct dissolution of cellulose to form polymer, N-Methyl Morpholine Oxide (NMMO) is one of the solvents, which has commercial feasibility to dissolve the cellulose to form spinnable polymer matrix. The process of direct dissolution of cellulose using NMMO is conventionally termed as Lyocell process. It is a multiple step process that involves swelling and dissolution of cellulose in N-Methyl Morpholine Oxide (NMMO) solvent and spinning of solvated cellulose solution to produce fiber by dry jet wet spinning. The conventional process of lyocell manufacturing consists of single stage of slurry (cellulose suspension in NMMO) preparation in which solvent gets penetrated in cellulose fibers (Swelling). It is necessary at slurry stage to have optimum pulp swelling and higher NMMO to cellulose ratio to achieve better uniformity of slurry for fast dissolution and homogeneous solvated cellulose polymer formation. To achieve this, pulp sheets are shredded to an optimum size before addition to aqueous solution of NMMO. The shredding of pulp sheet requires intensive energy and raises safety concerns due to the static charge generation which can lead to dust explosion. This makes conventional processes of dissolved cellulose preparation commercially and operationally unviable. In the present work a new method is developed to overcome the safety concern. In this new method, slurry preparation is carried out in two stages. In first stage dilute solvent is used to prepare slurry with low (4-6%) solid, slurry is later pressed to upto 45-50% solid percentage, the pressed solvent removes metal ion impurities and short chain hemicellulose by 10-20% from pulp. The pressed cake of cellulose is again mixed with high concentration of NMMO to form the slurry mixture for further processing. The dissolution of cellulose starts when monohydrate state of NMMO is reached by removing excess water from cellulose NMMO slurry to get Lyocell dope at 90-100 ^{0}C. This polymer solution is then spun through spinnerets by jet-wet spinning to get the Lyocell fiber. This method of cellulose-NMMO slurry preparation for the manufacturing lyocell fiber has shown reduction in undissolved particles of cellulose and metal ions impurities in polymer matrix of cellulose with no change in the fiber properties compared to the conventional process. The advantage of this process over conventional process is that high impurity pulp can be easily blended with good quality pulp in first stage of slurry-making, while the excess impurity is removed before second stage to get better quality of solvated cellulosic polymer network.

Keywords: Lyocell, NMMO, Slurry, dissolution, semi crystalline, bio polymer

INTRODUCTION

Cellulose is a linear polysaccharide available abundantly in nature. It has outstanding properties and many useful applications. Cellulose is converted into cellulose derivatives (ethers & esters) and regenerated cellulose (fiber, film, membrane etc.) by industrial processing techniques. This natural polymer cannot be liquefied by heating due to its semi crystalline structure and cannot be solubilized in many solvents because of its hydrogen bonded structure. There are two ways to get the cellulose in liquid form, it has to be chemically modified (derivatized way) or dissolved (by direct dissolution). The viscose technology utilizes derivatized way in which cellulose xanthogenate is formed using CS_2 as an intermediate derivative However this process accompanies environmentally hazardous byproducts such as CS_2, H_2S [1]. The direct dissolution process is purely physical process without any chemical changes [3]. Out of many solvents for direct dissolution, N-Methyl N-Morpholine Oxide (NMMO) is the well-known and commercialized solvent for cellulose dissolution process [5]. In lyocell process, pulp is converted to fiber in following way. Pulp is shredded and swelled in NMMO solvent by vigorous mixing and then the excess water is removed by vacuum application till it reaches required % cellulose. The dope formed out of this process then passed through spinnerets and stretched polymer is regenerated to form cellulosic fiber by diffusion driven precipitation of cellulose in precipitating dilute NMMO bath.

Water plays an important role in cellulosic dissolution. According to the phase diagram of NMMO-water-cellulose mixture, dissolution of cellulose starts at monohydrate form of NMMO (87.5%) [5]. Hence to obtain good quality dope, balance of NMMO/water needs to be maintained using vacuum and temperature application. It has

Proceedings of PPS-34
AIP Conf. Proc. 2065, 030062-1–030062-6; https://doi.org/10.1063/1.5088320
Published by AIP Publishing. 978-0-7354-1793-9/$30.00

also been reported in literature that at elevated temperatures, there are chances to form degraded products of solvent which can lead to runaway reaction. To control this degradation, propyl gallate is used as anti-oxidant. Higher concentration of metal ions in the mixture can induce haemolytic reactions, particularly copper and iron [3]. These metal impurities are bound to come through cellulose pulp. Hence, the quality of pulp affects significantly in the safety of this process on industrial scale.

To achieve better swelling and homogeneity of polymer solution, NMMO/Cellulose ratio in slurry needs to be maintained. In conventional lyocell process, pulp sheets are shredded. Shredding of pulp consumes extensive amount of energy and raises safety concern due to static charge. To deal with this safety and energy concern, in the modified lyocell process, proposed by us, the pulp shredding is replaced by slurry preparation in two stages in such a way that it requires less energy and reduces total metal impurities in the dope to process it in safer way. In first stage 5% cellulose slurry in 20-60% NMMO is made in pulper and then pressed in slurry press (hydraulically operated system) to get 45-60% cellulose cake. This cake is further shredded and mixed with 76-82% NMMO to get slurry composition of 11-12% cellulose, 68-70% NMMO and rest water. The distinct advantages of two stage slurry process are pulp pre-treatment, less power requirement for mixing pulp in solvent, better swelling of pulp, ease of blending of different pulps, pulp impurities removal, faster dissolution, and good dope quality. In this paper the advantages of Modified lyocell process over conventional are discussed and presented in detail.

EXPERIMENTAL

Materials:

Cellulosic pulp was provided by Sappi. (11.2 cP). NMMO was provided by "Amines & plasticizers, Mumbai" and had initial water content of 35% (w/w) and propyl gallate was purchased from "Sigma Aldrich".

Methods for Analysis:

Analysis of all the samples is performed at Analytical lab of Aditya Birla science & technology company, Mumbai (India).

Elemental Analysis:
Inductive coupled plasma (ICP) method is used for element analysis in the pulp using Spectro acros instrument. The test has been performed using standard characterization method which is developed in-house with reference of TAPPI T266 om-02 method. The samples are analysed by software, smart analyzer vision.

Yield Stress Analysis for Slurry:
The mixture of cellulose pulp and NMMO solvent behaves like pseudo plastic material hence yield stress would be an important parameter to analyze it. Yield stress would give the maximum force required for a material to initiate the flow and it will help characterizing the nature of slurry [4]. Yield stress values are measured by using Brookfield viscometer DV2T HBTJ0. In this viscometer, yield stress is measured by static vane spindle based test method. The particular vane (V-74) is selected according to the viscosity of the sample, this selected vane is then lowered into the undisturbed sample and given a torque slowly. This sample deforms elastically to the maximum point of stress where yield stress is attained.

Rheological Characterization:
The rheological behavior of dope was monitored with Anton Paar Rheometer PHYSICA MCR 301. Time-temperature-superposition (TTS) plots are obtained for conventionally prepared lyocell dope and for modified lyocell processed dope at 115 ^{0}C, corresponding to the three temperatures (95 ^{0}C, 115 ^{0}C and 125 ^{0}C). TTS is a master curve that gives detailed information about the viscoelastic behavior and homogeneity of the cellulosic polymeric solution.

Optical Microscopy:
The measurement of undissolved number of cellulose particles in dope solution is analyzed by optical microscopy using microscope with polarized light and 5X magnification lens. Microscope used for this analysis is from Zeiss

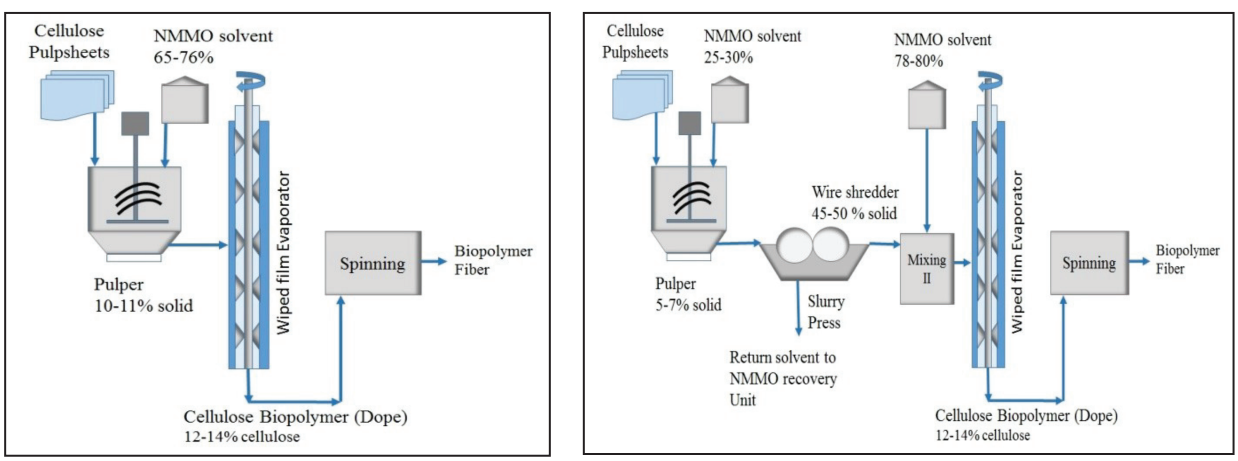
scope A1. Biovis Image plus V4.59 –Serial 7536 software is used to capture images and to get detailed statistical information on undissolved particles of cellulose.

Fiber Properties Measurement:
The strength and elongation of fiber is analysed using Vibrodyne equipment from Lenzing model no. 400. The fiber properties are measured using constant rate of extension method.

Procedure:

Conventional lyocell process: Aqueous NMMO solution (65-76% w/w), cellulose pulp, n-propyl gallate (antioxidants) are mixed together in sigma mixer. This mixture was heated upto 100 ^{0}C and mixed vigorously. Simultaneously excess water in the mixture is distilled off using vacuum till the mixture reaches 6.33 ratio of NMMO/cellulose (w/w) converting pulp into the brown transparent viscoelastic cellulose solution (dope) is formed [FIGURE 1(a)]. This viscoelastic solution is then passed through spinneret with a number of holes and later stretched through dilute NMMO solution (precipitation bath), to regenerate the bio polymeric fiber.

Modified lyocell process: Modified process of fiber preparation consists of two stages of slurry preparation as explained earlier. The slurry prepared in first stage of mixing of cellulose, NMMO and water contains cellulose in low concentration (4-7% cellulose) with dilute NMMO (25-60% w/w) and propyl gallate as stabilizer. This mixture is mixed vigorously. This thin slurry is then pressed through slurry press (hydraulically operated device) to get solid cake of 45-50% cellulose and the squeezed out NMMO solvent is recovered to study metal impurity removal from pulp. In second stage, this solid cake is shredded and mixed vigorously with high NMMO conc (78-80% w/w) in sigma mixer to form slurry of same concentration as that of the slurry in conventional process (10-11% cellulose). Then similar to conventional process, this mixture is heated upto 100^{0}C (M.P.of monohydrate NMMO) and mixed vigorously. Simultaneously excess water in the mixture is distilled off using vacuum till the mixture reaches 6.33 ratio of NMMO/cellulose (w/w) till the brown transparent cellulose solution was prepared [FIGURE 1(b)]. This viscous solution is then passed through spinnerets and stretched later through dilute NMMO solution, to regenerate the biopolymer fiber. To study the difference in quality for two process, slurry, dope and fiber prepared by two processes are analysed. The slurry is analysed for yield stress, dope is analysed for number of undissolved particles by Optical Image analysis and metal impurities by elemental analysis and fiber is analysed for tenacity and elongation by using Vibrodyne instrument by constant rate elongation method.



(a) (b)

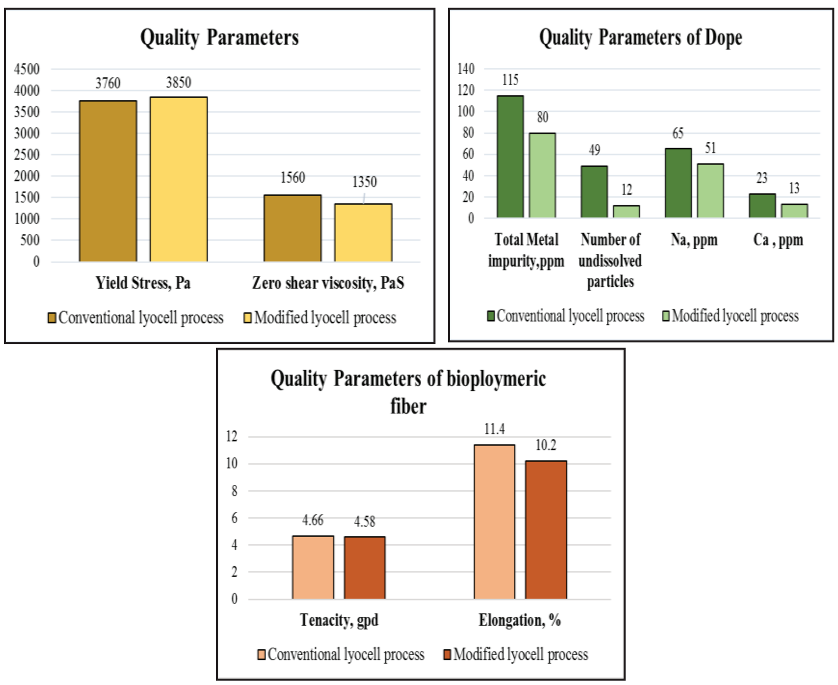
FIGURE 1. Process Flow Diagram of Lyocell Process from Pulp to Fiber (a) Conventional (b) Modified

RESULTS AND DISCUSSION

Effect of Process Changes on Slurry Quality/Flow ability: The slurry flow ability is a strong factor of % solid in the mixture. As the solid concentration in the slurry prepared by two processes is similar (10-11% cellulose), yield stress of slurry made using both the processes are similar with 10% CV as shown in FIGURE 2 (a).

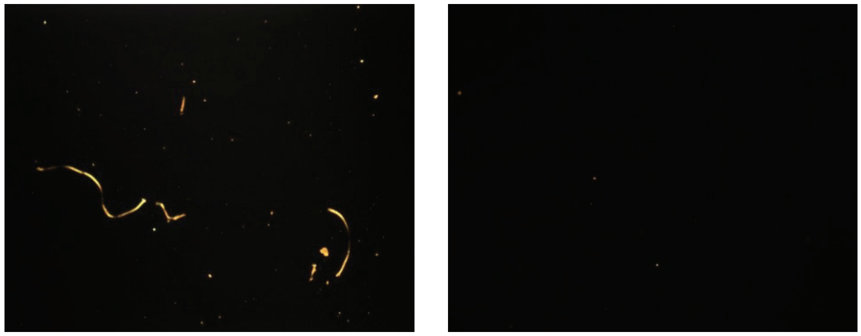
Effect of Process Changes on Solvated Cellulosic Solution (dope): As discussed in introduction section, metal impurities can induce homolytic reactions. Hence it is necessary to keep check on metal impurity concentration. From FIGURE 2(b), it can be clearly seen that concentration of metal impurity in the dope has reduced in case of modified process. This is because at low solid concentration and low solvent concentration, swelling of pulp helped solvent penetrate the pulp effectively and when slurry is pressed, impurities from the pulp are extracted out along with solvent. Hence stage I slurry and slurry pressing facilitates removal of impurities from pulp. Due to effective swelling in stage I slurry, dissolution is made effective as can be seen from reduction in number of undissolved fibers in dope prepared by modified process [Refer FIGURE 2 (b) and FIGURE 3]. As the % solid targeted at the end of the dope making process is same, zero shear viscosity and rheological characteristics [FIGURE 4 and FIGURE 2(a)] of both the dopes are similar. Removal of impurities and hemicellulose from the pulp, lessens the zero shear viscosity of polymer solution prepared by modified process than conventional Lyocell Process.

Effect of Process Changes on biopolymer fiber: The fiber properties such as tenacity and elongation remained same with 10 % CV [FIGURE 2(c)].



(a) (b) (c)

FIGURE 2. Quality Parameters of Viscous Biopolymer (a,b) and Quality Parameters of Biopolymer Fiber (c)



(a) (b)

FIGURE 3. Optical Image Analysis of (a) Conventionally Processed Polymer (b) Modified Processed Polymer

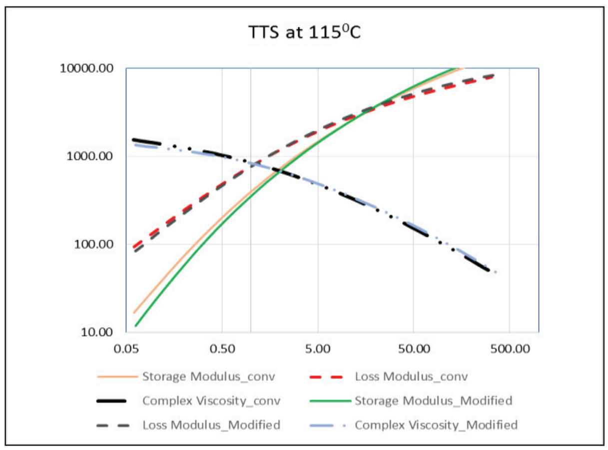


FIGURE 4. Time-Temperature-Superposition Curve for Rheological Analysis of Polymer solution (*conv: conventional process)

SUMMARY

Modified lyocell process is dealing with safety aspect of pulp shredding by squeezing out metal impurities from pulp before processing it to dope. This feature gives scope for manufacturers to have flexibility in choosing different grades of pulps as raw material. This method is demonstrated to be a better process to dissolve the cellulose effectively as can be seen from significant reduction in undissolved cellulose particles. Using modified lyocell process, 30% reduction of total metal impurity, 75% reduction in undissolved fiber is achieved for final polymer solution (dope). The process also helps to save energy by reduction in slurry mixing time from 15 min to 7 min. However with all these advantages, dope with less metal impurity did not show any adverse effect on fiber mechanical properties. Hence, Modified lyocell process helps to meet similar flow behavior of the slurry and dope, keeps fiber properties same as that of conventional lyocell process, improves dissolution and builds a safer process to process the cellulose biopolymer for fiber preparation.

ACKNOWLEDGMENTS

The authors would like to acknowledge Grasim Industries and Aditya Birla Science & Technology Company pvt ltd. (ABSTC) for taking up this activity as a part of project and for financial support. We are sincerely grateful to Dr. Madan Singh, Dr. Lalaso Mohite, Dr.Gurudatt Krishnamurthy and Dr. Biswajit Basu for their support and co-operation. We are also grateful to Dr. Shailesh Nagarkar and his team for their support from analytical department of Aditya Birla Science & Technology Company Pvt Ltd, Navi Mumbai, India

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