

Regenerated Cellulose by the Lyocell Process, a Brief Review of the Process and Properties

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Lyocell fiber has emerged as an important class of regenerated cellulose that is produced based on the N-methyl morpholine-N-oxide (NMMO) dissolution method, and it has unique properties compared to viscose fiber. The NMMO technology provides a simple, resource-conserving, and environmentally friendly method for producing regenerated cellulose fiber. In this paper, the manufacturing process, environmental impact, and product quality of lyocell fiber are reviewed and compared with those of the conventional viscose fiber.

Keywords: Lyocell fibers; NMMO; Manufacturing process; Environmental impact; Viscose fibers

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INTRODUCTION

The textile industry not only provides one of the necessities of life, but it also plays a very important role through its contribution to industrial output and employment opportunity, which is particularly true in Asia. In recent years, the demand for regenerated cellulose, which is characterized as sustainable material that is compatibility with the environment, in addition to having unique favorable properties, has experienced rapid growth (Quintana *et al.* 2013; Miao *et al.* 2014; Tian *et al.* 2014; Duan *et al.* 2015; Chen *et al.* 2015; Wang *et al.* 2006, 2015). The global production of textile fibers was predicted to increase from 72.5 million tons in 2010 to 133.5 million tons in 2030 (Haemmerle 2011). On the other hand, the cotton production will have a ceiling of 26 to 28 million tons per year (Sixta *et al.* 2013). For this reason, it is expected that the global dissolving pulp production will continue to grow (Chen *et al.* 2015; Li *et al.* 2015; Duan *et al.* 2016).

For many years, the viscose process has been the most dominant process for the production of regenerated cellulose fibers, while others such as the lyocell process, and the Cupro process, are rather limited (Hauru *et al.* 2014). In the conventional viscose process, the use of carbon disulfide, an environmentally sensitive chemical is one of the disadvantages. The development of carbon disulfide free- dissolving and regenerating cellulose, therefore, has been of practical interests.

N-methyl morpholine-N-oxide (NMMO), as a replacement for carbon disulfide, was developed as a solvent for cellulose by Eastman Kodak Inc. (Blackburn 2005; Sinclair,

2014). In 1982, the first pilot plant of regenerated cellulose using NMMO as a solvent was built in the United Kingdom (Sinclair 2014). It was later developed into a full-scale commercial process for producing staple cellulose, with “Tencel” as its brand name (Blackburn 2005). Another commercial production process of regenerated cellulose using NMMO as a solvent, known as “lyocell”, was established by Lenzing in Austria (Blackburn 2005; Sinclair 2014). In 2004, Lenzing completed the acquisition of Tencel Group and became the largest lyocell fiber producer (Sinclair 2014). In the lyocell process, NMMO with a small amount of water is used as the solvent to produce regenerated cellulose fibers (Chanzy *et al.* 1990; Bredereck and Hermanutz 2005; Perepelkin 2007).

Apart from the environmental advantage, the lyocell fibers are also of high quality; for example, they have been reported to have high strength and excellent tenacity in the wet state (Loubinoux and Chaunis 1987; Colom and Carrillo 2002; Gindl and Keckes 2006), good adaptability with other fibers, and excellent draping characteristics (Uddin *et al.* 2010). They also have good thermal resistance and shape stability, which can be used to produce home textile products, sleeping products, a variety of apparel, and industrial products, such as conveyor belts, medical dressings, *etc.* (Schurz and Lenz 1994; Macfarlane 1997; Burrow 1998).

The objective of this paper is to review the unique advantages of the lyocell process and the desirable properties of lyocell fibers over the closely related, but different, viscose process and viscose fibers. A comparative evaluation of the lyocell and viscose fibers will be given on the basic manufacturing processes, environmental impacts, and product qualities.

MANUFACTURE PROCESSES

The lyocell manufacturing process (Fig. 1) mainly consists of five steps (Fink *et al.* 2001; Rosenau *et al.* 2001; Biganska and Navard 2005; Bredereck and Hermanutz 2005; Hauru *et al.* 2014):

1) Dissolution: This step includes the disintegration of the pulp fibers and mixing with the solvent. Cellulose is dissolved in an aqueous system containing NMMO to form a dope of high viscosity. The pulp dissolution for the lyocell process is much simpler than that of the viscose process, where the dissolution of dissolving pulp consists of the mercerization stage (steeping with sodium hydroxide), aging, and xanthation using carbon disulfide.

2) Filtration: The formed dope is filtered to remove coarse components. In comparison, the purification of the viscose process includes ripening, filtering, and degassing.

3) Spinning regeneration: The dope is extruded through an orifice spinneret into an air gap, and then regenerated in a coagulation bath. In contrast to this, the production of viscose rayon requires a wet spinning process in an acid bath.

4) Washing: The resulting lyocell fibers are washed and the residual NMMO is recovered and recycled; while the viscose fibers are also washed for removal of the residual CS₂, the high volatility of CS₂ may lead to its loss *via* evaporation, causing a negative environmental impact for the viscose process.

5) Finishing: This step involves post-treatment of the fibers, including bleaching, finishing, and drying.

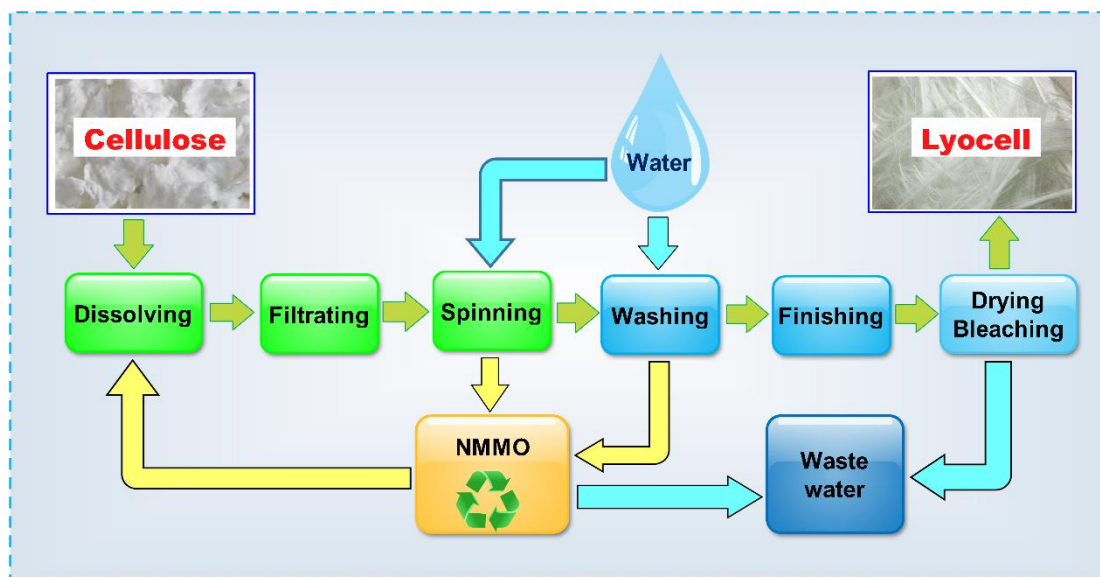


Fig. 1. Manufacture process for the lyocell fibers

The key differences between the lyocell process and the viscose process with respect to dissolution, spinning, and environment are listed in Table 1.

Table 1. Key Differences between the Lyocell Process and the Viscose Processes

| Process | Lyocell process/ fibers | Viscose process/ fibers |
|--------------------|--|---|
| Dissolution | NMMO direct dissolution Physical dissolution Without chemical reactions | NaOH /CS₂ Mercerization/ xanthation Chemical reaction |
| Spinning | Dry-jet wet spinning Direct dissolution to form highly viscous dopes Fibers are formed via a) an orifice spinneret in a dry form into an air gap, b) then in a coagulation bath. Irregular molecules arrangement to form crystallites laminas (Wendler <i>et al.</i> 2011; Ramamoorthy <i>et al.</i> 2014;). | Wet spinning Dopes with relatively low viscosity Fibers are formed using spinneret immersed in an aqueous bath containing sulfuric acid and additives. Stretching is done after the regeneration. The formed fibers are relatively amorphous, with low-tenacity (Wendler <i>et al.</i> 2011; Ramamoorthy <i>et al.</i> 2014). |
| Environment | Environmentally friendly > 99% of the solvent recovered No harmful by-products formed High energy demand for solvent recycling | Heavy environmental loads CS ₂ (about 25-30%) not recovered (may also be converted to by-product) High demand for water |

Solvation and Dissolution

The mechanism of direct dissolution of cellulose in NMMO (with a small amount of water present), is shown in Fig. 2. Basically, the dissolution process of cellulose includes two stages, *i.e.*, swelling, gradual dissolution. The excellent dissolving capacity of NMMO on cellulose is due to its strong N-O dipoles and basicity, making NMMO an excellent hydrogen bond acceptor solvent. In the dissolution process, the N-O bond, which has a

stronger basicity than hydroxyl group, will interact with the hydrogen atom on the hydroxyl group of cellulose and form new hydrogen bonds between NMMO and cellulose, replacing the intermolecular and intramolecular hydrogen bonds in cellulose. The amount of bonded NMMO for each glucose unit is critical in dissolving cellulose, and it was found that on average, there were nine NMMO molecules for each glucose unit at the cellulose concentration of 7.5 to 10.5% (Fink *et al.* 2001).

A recent study based on all-atom molecular dynamic simulation showed that NMMO could contribute to 75% to 80% of the total amount of hydrogen bonds in the NMMO/ cellulose system (Rabideau and Ismail 2015). A thermodynamic simulation study on the crystalline and dissociated states showed that the effect of nonpolar (hydrophobic) effect of NMMO also plays an important role, in addition to the well-known polar (hydrogen bonding) effect (Rabideau and Ismail 2015).

There have been numerous papers documenting the good solubility of wood pulps in NMMO (Fink *et al.* 2001; Rosenau *et al.* 2001; Bocek 2003; Schild and Sixta 2011; Ingildeev *et al.* 2013), such as using the eucalyptus sulfite pulp with a DP of 592 and an α -cellulose content of 94.1% (Ingildeev *et al.* 2013), wood pulp having a DP of 750 and 96% cellulose (Schild and Sixta, 2011), and cotton linters with DP of 759 and α -cellulose content of 97.0% (Ingildeev *et al.* 2013).

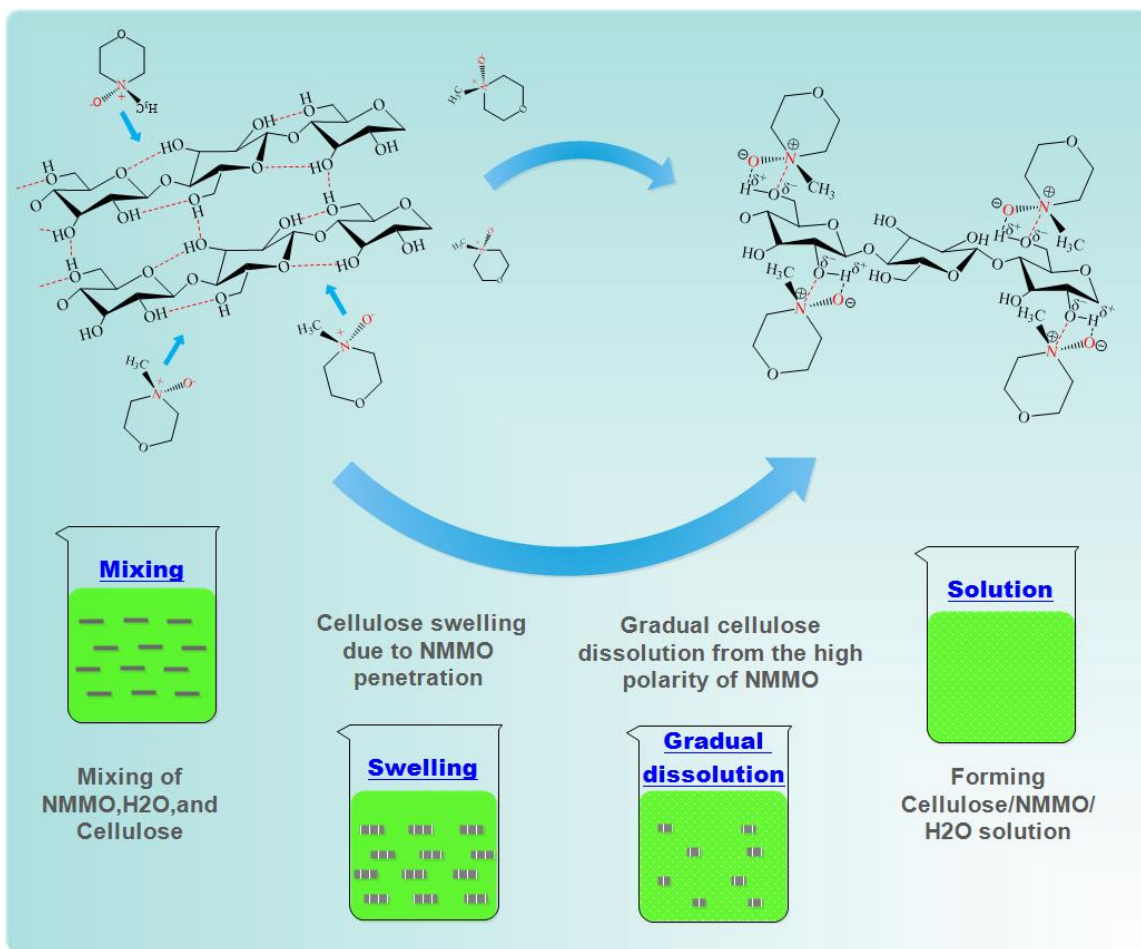


Fig. 2. The mechanism for NMMO dissolution of cellulose (Li *et al.* 2006; Singha 2012)

During the dissolution process of cellulose and the recovery / recycling of NMMO (by distillation of NMMO/water solution at high temperatures), a portion of NMMO will be thermally degraded to various compounds due to the homolytic and heterolytic cleavages, which include radical reactions, heterolytic deoxygenation, *Polonowski* type reaction, and autocatalytic decomposition (Rosenau *et al.* 2001). The main degradation products were N-methyl morpholine, morpholine, and formaldehyde. When transition metal ions are particularly present in dissolving pulp, the radical reaction of NMMO increases dramatically. To minimize the NMMO degradation, some stabilizers, for example, a combination of alkaline and antioxidant (NaOH, isopropyl gallate) can be added (Rosenau *et al.* 2001; Wendler *et al.* 2008; Ingildeev *et al.* 2013), and antioxidants also can be added to the dissolving tank.

During the cellulose pulp dissolution process, both swelling and dissolution occur (Rosenau *et al.* 2001; Zhang and Tong 2007; Ingildeev *et al.* 2013). Its first step is to rewet cellulose fibers in a dilute NMMO aqueous solution under the typical conditions of: 50 to 60% NMMO, 20 to 30% water, and 10 to 15% pulp (Rosenau *et al.* 2001), which will allow great cellulose swelling. Subsequently, an excess amount of water is removed by distilling, such that the desired ratio of cellulose/NMMO/water is obtained for cellulose dissolution. Typical compositions are 76% NMMO, 10 % water, and 14% cellulose (Rosenau *et al.* 2001). Under the above conditions, cellulose is dissolved, and a brown, transparent cellulose solution is obtained (Haule *et al.* 2014). Generally, the ternary solutions are prepared at elevated temperatures from 90 to 120 °C. It is desirable to for more water to be removed to reach the desired ratio of cellulose/NMMO/water to dissolve cellulose to form cellulose dope. However, a high temperature (*e.g.*, higher than 120 °C), will cause undesirable loss of NMMO due to degradation (Ingildeev *et al.* 2013). Therefore, a suitable temperature is desirable.

The direct cellulose dissolution in the NMMO/ water mixture of the lyocell process is fundamentally different from the reaction-dissolution process of the viscose process. Under the strong alkaline conditions of the viscose process,, the reactions of carbon disulfide and cellulose result in the formation of cellulose xanthate, which is responsible for the dissolution of cellulose (Bredereck and Hermanutz 2005; Hauru *et al.* 2014). In addition, the reaction-dissolution of the viscose process requires further steps such as steeping, pressing, shredding and aging, which are time-consuming.

Spinning

The lyocell process uses the so-called dry jet-wet spinning process, as shown in Fig. 3: 1) the dopes in the NMMO/ water system are extruded out from the spinning nozzle, then into an air gap; 2) the formed filament then immediately enters a coagulation bath to continue its formation (Rosenau *et al.* 2001; Biganska and Navard 2005; Perepelkin 2007). During the above spinning process, the spinning ray and the forming fibers undergo continuous changes. In the viscose process, only a wet spinning is conducted.

In the dry jet-wet spinning process, the spinning process ability depends highly on the process parameters, particularly the dope viscosity, air gap, spinning temperature, and spinning speed. The lyocell dope has a higher viscosity (DP of 500 to 600, based on the Staudinger method) than the viscose dope (DP of 250 to 350, based on the Staudinger method); such a difference is partially responsible for the superior strength properties of the lyocell fiber. Furthermore, the high viscosity of the spinning solution of the lyocell

process can allow it to maintain a very stable spinning of fibers through the air gap (Haule *et al.* 2014).

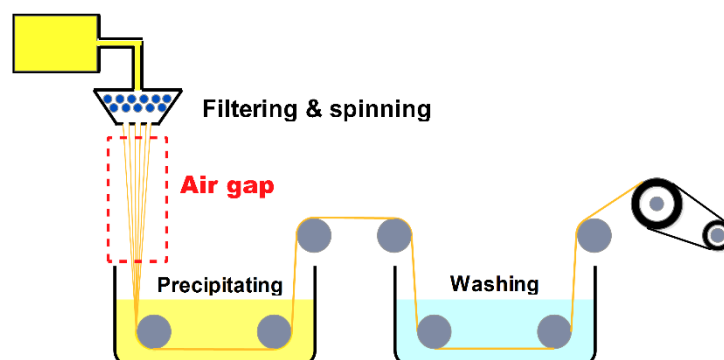


Fig. 3. Dry jet-wet spinning in the lyocell process (Kim *et al.* 2005)

In fact, the air gap is a critical element of the operation, with significant changes in the solution, and the spinning ray stretched and oriented (Mortimer and Peguy 1996a,b; Mortimer *et al.* 1996). A highly oriented structure is formed upon entering the aqueous precipitation bath. Air gap length influences the fiber strength (Mortimer and Peguy 1996a). Reducing the air gap length, *e.g.* from 250 to 20 mm, will reduce the fiber strength. A long air gap causes good orientation, increases in birefringence, and leads to high strength. However, if the air gap is too long, a reduction in orientation occurs, which is caused by relaxation effects before the fixation of the highly oriented solution in the bath. Therefore, an excessively long air gap should also be avoided.

The temperature of the coagulation and the wet spinning speed are also critical factors. When the temperature is fixed, the increase of speed (rise of draw ratio) leads to increases in fiber crystallinity, birefringence, and orientation, which contribute to the improvement in fiber strength (determined by orientation) and initial Young's modulus (determined by crystallinity). However, when the speed is fixed, with the increase of temperature, the fiber structure and properties show changes in the opposite direction (Maron *et al.* 1994). Good textile properties were reported for a draw ratio of less than 3 and for take-off speeds of 50 m/min (Fink *et al.* 2001).

With the air gap, in addition to the formation of lyocell fiber with highly oriented and crystalline structure, some weaker lateral links between the crystallites can lead to the so-called fibrillation, which is evident as some fibrous elements being exposed at the surface of the lyocell fiber under the condition of wet abrasion (Periyasamy and Khanum 2012). Fibrillation can be reduced via changing the various spinning parameters such as air gap conditions and draw ratio (Mortimer and Peguy 1996a; Periyasamy and Khanum 2012). Usually, a low spinning speed means a long spinning ray in the air gap, which will result in a low fibrillation. On the other hand, with a short air gap, a high draw ratio will increase the fibrillation degree significantly, while a low draw ratio will lead to the production of fibers with good strength but a low fibrillation degree. For long air gaps and draw ratios of up to 10, fibers with very good mechanical properties and low fibrillation can be obtained (Mortimer and Peguy 1996a).

Another key difference is found in the spinning technology: the dry jet-wet spinning (air gap spinning) for the lyocell process, versus the wet spinning (without air gap) for the viscose process. In the latter, there is not enough time for orientation of dope due to lack

of air gap (Periyasamy and Khanum 2012), which can result in a less orientated fiber structure having lower strength. It should be pointed out that the high orientation of lyocell fibers is unique and contributes significantly to the favorable strength of the material. In fact, this high orientation is only possible with the air gap spinning technology

Environmental Impact

The environmental advantage of the lyocell process is one of its key features. The direct dissolution technology avoids the use of toxic chemicals such as carbon disulfide; this makes it a more environment-friendly process. More than 99% of the NMMO solution can be recovered for the lyocell process (Rosenau *et al.* 2001; Gindl-Altmutter *et al.* 2014), and NMMO is biodegradable and has no harmful by-products (Woodings 1995; Chen *et al.* 2015). By contrast, in the viscose process, carbon disulfide is well known for its negative environmental impact, and cost-intensive investment in pollution-control systems must be made for the viscose process (Bredereck and Hermanutz 2005; Hauru *et al.* 2014). Only 70 to 75% of the highly volatile and toxic CS₂ is recoverable during the viscose fiber production process (Chen *et al.* 2015).

In addition to the carbon disulfide related issues, the viscose process also uses sodium and zinc salts in the coagulation bath, which also requires the corresponding post-treatments for pollution control (Ingildeev *et al.* 2013).

The traditional technology to remove water and to recover NMMO in the lyocell process is by distillation. Under the conditions that typically prevail in the industrial process, NMMO may be converted to N-Methyl morpholine and morpholine, *etc.*, which in the literature, is known as “fast exothermic processes” or “thermal runaway reactions” (Brandner and Zengel 1982). Therefore, the chemical stability is a crucial issue for the lyocell process at the commercial scale. Various stabilizers (*e.g.*, propyl gallate), have been studied and shown to be effective (Rosenau *et al.* 2002). The wash process is critical for an efficient recovery of NMMO. More wash water could potentially wash out more residual NMMO from the fibers (less NMMO loss); however, the energy demand would be too high for the subsequent evaporation. Therefore, it is needed to strike a balance between the amount of water used and the amount of NMMO recovered (Perepelkin 2007; Yau *et al.* 2013). New technologies such as membrane technologies, electro dialysis, may have potential to remove water from the NMMO/water solution (Perepelkin 2007).

PROPERTIES OF LYOCELL FIBER

Fiber Structure

The unique dry jet-wet spinning manufacturing process imparts special features to the structure of the resultant lyocell fibers. Comparison of the lyocell fibers *versus* viscose fibers is given in Fig. 4. The viscose fibers (Fig. 4a) have quite a rough surface, with oval shaped cross-sections and also more defects (Peng *et al.* 2003). In contrast, the lyocell fibers (Fig. 4b) show a rather smooth fiber surface, round cross-sections, and homogeneous appearance and dense fibrillar structure (Michud *et al.* 2015).

The average degree of polymerization and the crystallinity of the lyocell fibers are higher than those of the viscose fibers (Chavan and Patra 2004). The crystallinity index (CrI) of lyocell fibers (0.44) is much higher than that of viscose fibers (0.25) (Stana-Kleinschek *et al.* 2001). As a result, the lyocell fibers have higher mechanical properties,

higher dry and wet tenacity, and higher wet modulus, in comparison with viscose fibers (to be discussed in the next section).

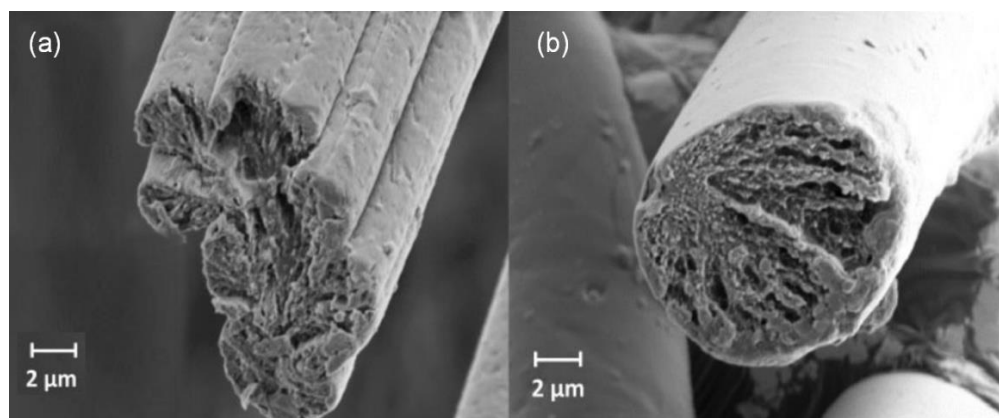


Fig. 4. SEM images of viscose (a); lyocell (b) from eucalyptus prehydrolysis kraft dissolving pulp (Michud *et al.* 2015)

During the air gap and coagulation stages of the lyocell spinning process, fibers are oriented and then crystallization occurs (Kampl and Leitner 1996; Burrow 2004), forming the unique fiber structure with high crystallinity (Fink *et al.* 2001), well-oriented amorphous regions, low surface roughness, and longitudinal arrangement (Chanzy *et al.* 1980). In the same process, some unexpected fibrillation can also occur on the regenerated fiber surface (Fig. 5) (Chavan and Patra 2004; Uddin *et al.* 2010). Therefore, some actions need to be taken to control the fibrillation. For example, treating lyocell fiber with various types of alkali, dyeing it with poly functional reactive dyes, and using cross-linking agents and enzymatic treatments (Lim *et al.* 2003; Periyasamy and Khanum 2012).

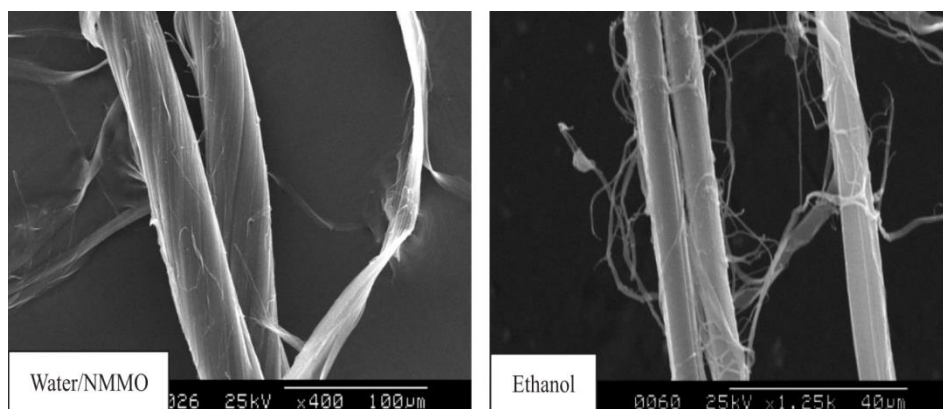


Fig. 5. SEM images of fibrillated bagasse regenerated fibers after coagulation from water/NMMO and ethanol respectively (Uddin *et al.* 2010).

In contrast, the viscose fibers have lower crystallinity and lower fibril orientation. Besides, compared to the lyocell fibers, the viscose fibers have a less homogeneous appearance (Fig. 4), and they also show a distinct “skin-core” structure (Fig. 6) (Abu-Rous *et al.* 2006). The orientation degree and density in the skin-region are higher than those in the fiber core (Biganska *et al.* 2002; Eichhorn *et al.* 2003; Abu-Rous *et al.* 2006). The

formation of “skin-core” structure in the viscose fiber is due to the heterogeneous precipitations taking place on the fiber cross-section during the wet spinning process: the viscose dope is extruded to the acid bath, and the a regenerated “skin” layer is formed first, then sulfuric acid gradually diffuses through the “skin” and solidifies the interior (Hauru *et al.* 2014).

Cross-linking is commonly practiced in the industry, which effectively reduces fibrils on the fiber surface (Bredereck *et al.* 1997). The lyocell fibers are more challenging in this regard in comparison to the viscose fibers in fabric and garment (Bates *et al.* 2004). Cross-linking agents, such as 2,4-diacryl- amido- benzene sulphonic acid have been known for many years to treat lyocell fibers, and they are typically small molecules containing multiple functional groups, (*e.g.*, they are capable of reacting with the hydroxy groups in cellulose to form crosslinks (Potter and Taylor 1998)).

There are big differences in the use of additives between the lyocell process and the viscose process. In the case of the lyocell process, the main objective is to increase the chemical stability of NMMO. Stabilizers (*e.g.*, propyl gallate,) have been demonstrated to be effective (Rosenau *et al.* 2005). Wendler *et al.* (2005) reported the use of a polymeric stabilizer system consisting of imino- diacetic acid sodium salt (ISDB) and benzyl amine (BSDB) covalently bound to a styrene/divinyl benzene copolymer in the cellulose/NMMO solutions. Such a system shows distinct improvements in the chemical stability of the Lyocell solution compared to the NaOH/propyl gallate stabilizer system (Wendler *et al.* 2006).

Additives are also applied in the viscose process, for example to control the rates of coagulation and regeneration and to reduce primary swelling of gel fibers (Levine and Burroughs 1959). These additives include aliphatic amines, dithio- carbamates and oxide derivatives of amine (Arthur 1948; Louis 1950; Maclaurin and Israel 1952). Recent development also includes the addition of antibacterial compounds to the spinning solution to impart antibacterial properties to the fibers (Bredereck and Hermanutz 2005a).

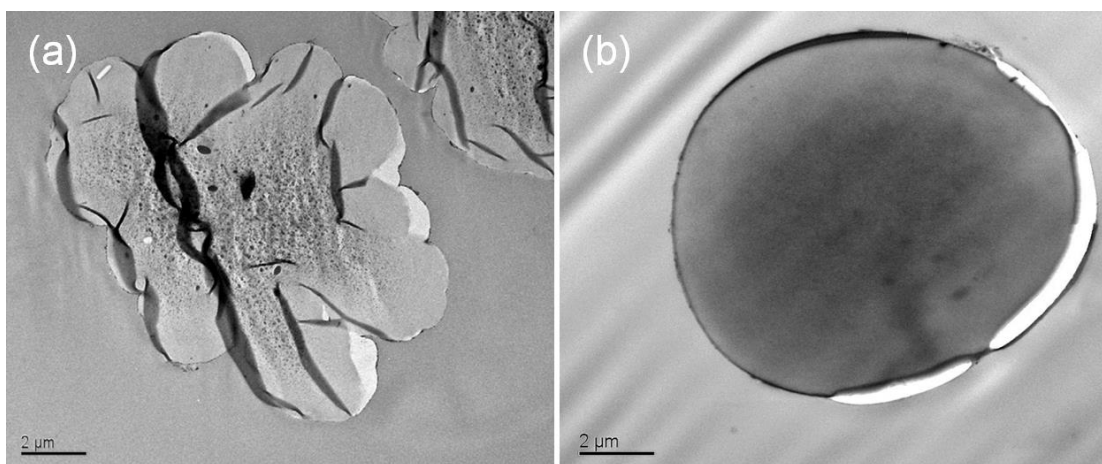


Fig. 6. TEM images of cross sections: Viscose fiber (a); lyocell fiber (b) (Abu-Rous *et al.* 2006).

Mechanical Properties

Typical mechanical properties of lyocell fibers, in comparison with viscose fibers, are shown in Table 2 (Perepelkin 2007).

Table 2. Typical Mechanical Properties of Lyocell Fibers Comparing with Viscose Fibers

| Properties | | Lyocell | Viscose |
|------------------------------|------|---------|---------|
| Tenacity (cN/dtex) | dry | 40-42 | 22-26 |
| | wet | 34-38 | 10-15 |
| Deformation modulus (GPa) | dry | 8-10 | 3-5 |
| | wet | 3-4.5 | 0.6-1 |
| Preservation of strength (%) | loop | 30-40 | 30-40 |
| | wet | 60-80 | 50-55 |
| Loop strength (cN/tex) | -- | 19 | 6 |
| Elongation (%) | Dry | 11-16 | 17-25 |
| | wet | 16-18 | 21-30 |

The lyocell fiber has excellent strength properties, in both dry and wet states. As shown in Table 2, the lyocell fiber has very high dry tenacity and modulus. The dry tensile strength is higher than the viscose fiber, and it retains much of its strength when wet, while the viscose fiber loses about half of its tensile strength when wet. The data in Table 2, also show that compared to viscose, the lyocell fiber is twice stronger when dry and three times when wet. The reasons include the higher orientation of the lyocell fiber (Chavan and Patra 2004). Also, compared to viscose fiber, the lyocell fiber is more than two times higher in modulus and almost five times when wet (Krüger 1994; Chavan and Patra 2004; Weigel *et al.* 1994). As noted in Table 2, the lyocell fiber has a lower elongation at break, which may be related to the higher crystalline zone and uniform structures in contrast to viscose fiber.

Besides, other properties of the lyocell fiber, such as softness, absorbency, breathability, thermal resistance and shape stability, dyeability, and luxurious handle of lyocell fiber, are superior to those of the viscose fiber (Burrow 2004; Borbély 2008; Uddin *et al.* 2010).

It should be noted that in addition to regular rayon fibers, there are some major modifications of rayon fibers. The regular rayon has the largest market share, and its major application is for apparel and home furnishings, with the term “viscose” on their commercial labels. Regular rayon has a low wet strength. As a result, it becomes unstable and may stretch or shrink when wet. Special rayon fibers, such as Modal or polynosic fibers, can have much improved mechanical properties (Röder *et al.* 2009). For example, Modal is a trade name for special viscose fibers that have high wet modulus (HWM) (Lenz *et al.* 1988). In fact, Modal fibers have very similar properties to regular rayon, other than their high wet strength. Modal rayons can be machine washed and tumble dried and perform much like cotton in similar end uses. (Cook 1984).

APPLICATIONS OF LYOCELL FIBERS

Due to their inherent properties, lyocell fibers have been widely used in many applications, including textiles and various consumer and industrial products.

Lyocell fibers have the characteristics of high strength, soft and silky handling, luster and bulky touch, biodegradability, high absorbency, and easy processing (Borbély 2008), which could then be suitable for nonwovens. Lyocell fibers are good raw materials for house textile products, including mattresses, mattress pads, bed covers, linens (Macfarlane 1997; Burrow 1998); for different apparels, *e. g.*, denim, chino, underwear,

casual wear, and towels. Furthermore, filament lyocell fibers are excellent for both men's and women's clothing (Macfarlane 1997; Burrow 1998).



Fig. 7. Various applications of lyocell fibers

The non-textile products made from lyocell fibers include wipes, medical swabs, gauzes, filters, biocomposites, and battery separators (Chavan Patra 2004; Wang *et al.*, 2011). In addition, lyocell fibers were used to produce conveyor belts due to the high modulus and shape stability. Specialty paper can be produced from lyocell fibers, which can have excellent strength, opacity, and low air resistance (Borbély 2008).

However, the lyocell process is still in its early stage of commercial development in comparison with the well-established viscose process, and one of the most important factors in hindering the rapid and wide adoption is its high cost (Wang *et al.* 2012). Therefore, it is desirable to decrease the overall production cost of lyocell fibers; for example, by using more cost-effective sources of pulps as the raw materials. It was reported that using high hemicellulose content pulp can be a good way to decrease the production cost for lyocell fibers (Zhang and Tong 2007; Zhang *et al.* 2008).

CONCLUSIONS

The NMMO-based lyocell process and its unique production processes, such as dry jet-wet spinning, have received many commercial interests. In contrast to the commercial viscose fiber manufacturing process, the NMMO-based lyocell process is much more environmentally friendly and efficient. The overall manufacturing process for lyocell fiber includes dissolution, spinning (deformation, cooling, relaxation, coagulation), washing and

finishing. Lyocell fibers have unique fiber structure and properties, and they have rather a uniform fibril orientation between the central and the periphery region of the fibers, high crystallinity, long crystallites, thus possessing very high strength and modulus in comparison with viscose fibers. These favorable properties render lyocell fibers suitable for many applications. With the continuing effort in decreasing the overall production cost, the lyocell process/ fibers can be expected to have increased importance in the production of regenerated cellulose products in the future.

REFERENCES CITED

- Abu-Rous, M., Ingolic, E., and Schuster, K. (2006). "Visualisation of the nano-structure of Tencel® (lyocell) and other cellulose as an approach to explaining functional and wellness properties in textiles," *Lenzinger Berichte* 85, 31-37.
- Biganska, O., and Navard, P. (2005). "Kinetics of precipitation of cellulose from cellulose-NMMO-water solutions," *Biomacromolecules* 6(4), 1948-1953. DOI: 10.1021/bm040079q
- Biganska, O., Navard, P., and Bédué, O. (2002). "Crystallisation of cellulose/N-methylmorpholine-N-oxide hydrate solutions," *Polymer* 43(23), 6139-6145. DOI: 10.1016/S0032-3861(02)00552-9
- Blackburn, R. S. (2005). *Biodegradable and Sustainable Fibres (Vol. 47)*., Taylor & Francis US.
- Bochek, A. (2003). "Effect of hydrogen bonding on cellulose solubility in aqueous and nonaqueous solvents," *Russian Journal of Applied Chemistry* 76(11), 1711-1719. DOI: 10.1023/B:RJAC.0000018669.88546.56
- Borbély, É. (2008). "Lyocell, the new generation of regenerated cellulose," *Acta Polytechnica Hungarica* 5(3), 11-18.
- Brandner, A., and Zengel, H. (1982). "Molding and spinning compositions based on cellulose with a low content of low-molecular-weight degradation products," *Paper presented at the Chem Abstr.*
- Bredereck, K., and Hermanutz, F. (2005). "Man-made cellulose," *Review of Progress in Coloration and Related Topics* 35(1), 59-75. DOI: 10.1111/j.1478-4408.2005.tb00160.x
- Burrow, T. (1998). "Recent results with lyocell fibers in textiles," *Lenz Ber* 78, 37-40.
- Burrow, T. (2004). "Recent advances in chemically treated lyocell fibers," *Chemical Fibers International* 54, 304-305.
- Chanzy, H., Paillet, M., and Hagege, R. (1990). "Spinning of cellulose from N-methylmorpholine N-oxide in the presence of additives," *Polymer* 31(3), 400-405. DOI: 10.1016/0032-3861(90)90376-A
- Chanzy, H., Peguy, A., Chaunis, S., and Monzie, P. (1980). "Oriented cellulose films and fibers from a mesophase system," *Journal of Polymer Science: Polymer Physics Edition* 18(5), 1137-1144. DOI: 10.1002/pol.1980.180180517
- Chavan, R., and Patra, A. (2004). "Development and processing of lyocell," *Indian Journal of Fibre and Textile Research* 29(4), 483.
- Chen, C., Duan, C., Li, J., Liu, Y., Ma, X., Zheng, L., Stavik, J., and Ni, Y. (2016). "Cellulose (dissolving pulp) manufacturing processes and properties: A mini review," *BioResources* 11(2), 5553-5564.

- Chen, J.-H., Guan, Y., Wang, K., Xu, F., and Sun, R.-C. (2015). "Regulating effect of hemicelluloses on the preparation and properties of composite lyocell fibers," *Cellulose* 22(3), 1505-1516. DOI: 10.1007/s10570-015-0608-0
- Colom, X., and Carrillo, F. (2002). "Crystallinity changes in lyocell and viscose-type fibres by caustic treatment," *European Polymer Journal* 38(11), 2225-2230. DOI: 10.1016/S0014-3057(02)00132-5
- Duan, C., Li, J., Ma, X., Chen, C., Liu, Y., Stavik, J., and Ni, Y. (2015). "Comparison of acid sulfite (AS)-and prehydrolysis kraft (PHK)-based dissolving pulps," *Cellulose* 22(6), 4017-4026. DOI: 10.1007/s10570-015-0781-1
- Duan, C., Verma, S. K., Li, J., Ma, X., and Ni, Y. (2016). "Combination of mechanical, alkaline and enzymatic treatments to upgrade paper-grade pulp to dissolving pulp with high reactivity," *Bioresource Technology* 200, 458-463. DOI: 10.1016/j.biortech.2015.10.067
- Eichhorn, S., Young, R., Davies, R., and Riekkel, C. (2003). "Characterisation of the microstructure and deformation of high modulus cellulose fibres," *Polymer* 44(19), 5901-5908. DOI: 10.1016/S0032-3861(03)00540-8
- Fink, H.-P., Weigel, P., Purz, H., and Ganster, J. (2001). "Structure formation of regenerated cellulose materials from NMMO-solutions," *Progress in Polymer Science* 26(9), 1473-1524. DOI: 10.1016/S0079-6700(01)00025-9
- Gindl-Altmutter, W., Eichhorn, S. J., Burghammer, M., and Keckes, J. (2014). "Radial crystalline texture in a lyocell fibre revealed by synchrotron nanofocus wide-angle X-ray scattering," *Cellulose* 21(1), 845-851. DOI: 10.1007/s10570-013-0140-z
- Gindl, W., and Keckes, J. (2006). "Strain hardening in regenerated cellulose fibres," *Composites Science and Technology* 66(13), 2049-2053. DOI: 10.1016/j.compscitech.2005.12.019
- Haemmerle, F. M. (2011). "The cellulose gap," *Lenzing Ber* 89, 12-21.
- Haule, L., Carr, C., and Rigout, M. (2014). "Investigation into the removal of an easy-care crosslinking agent from cotton and the subsequent regeneration of lyocell-type fibres," *Cellulose* 21(3), 2147-2156. DOI: 10.1007/s10570-014-0225-3
- Hauru, L. K., Hummel, M., Michud, A., and Sixta, H. (2014). "Dry jet-wet spinning of strong cellulose filaments from ionic liquid solution," *Cellulose* 21(6), 4471-4481. DOI: 10.1007/s10570-014-0414-0
- Ingildeev, D., Effenberger, F., Bredereck, K., and Hermanutz, F. (2013). "Comparison of direct solvents for regenerated cellulosic fibers via the lyocell process and by means of ionic liquids," *Journal of Applied Polymer Science* 128(6), 4141-4150. DOI: 10.1002/app.38470
- Kampl, R., and Leitner, H. (1996). "Processing behavior and applications of lyocell," *Lenzinger Berichte* (75), 97.
- Kim, D. B., Pak, J. J., Jo, S. M., and Lee, W. S. (2005). "Dry jet-wet spinning of cellulose/N-methylmorpholine N-oxide hydrate solutions and physical properties of lyocell fibers," *Textile Research Journal* 75(4), 331-341. DOI: 10.1177/0040517505054852
- Krüger, R. (1994). "Cellulosic filament yarn from the NMMO process," *Lenz Ver* 74, 49.
- Li, H.-J., Cao, Y.-M., Qin, J.-J., Jie, X.-M., Wang, T.-H., Liu, J.-H., and Yuan, Q. (2006). "Development and characterization of anti-fouling cellulose hollow fiber UF membranes for oil-water separation," *Journal of Membrane Science* 279(1), 328-335. DOI: 10.1016/j.memsci.2005.12.025

- Li, J., Zhang, H., Duan, C., Liu, Y., and Ni, Y. (2015). "Enhancing hemicelluloses removal from a softwood sulfite pulp," *Bioresource Technology* 192, 11-16. DOI: 10.1016/j.biortech.2015.04.107
- Lim, K. Y., Seong, Y. J., and Kim, B. C. (2003). "Reduction of fibrillation of lyocell fiber with cellulose-g-poly (vinyl alcohol) copolymer," *Polymer Journal* 35(9), 691-696. DOI: 10.1295/polymj.35.691
- Loubinoux, D., and Chaunis, S. (1987). "An experimental approach to spinning new cellulose fibers with N-methylmorpholine-oxide as a solvent," *Textile Research Journal* 57(2), 61-65. DOI: 10.1177/004051758705700201
- Macfarlane, K. (1997). "Nonwovens applications of lyocell fibers," *Chemical Fibers International* 47(4), 328-332.
- Maron, R., Michels, C., and Taeger, E. (1994). "Investigations for preparation of cellulose solutions in NMMO and the following forming," *Lenzinger Berichte* 74(9), 27-29.
- Miao, Q., Chen, L., Huang, L., Tian, C., Zheng, L., and Ni, Y. (2014). "A process for enhancing the accessibility and reactivity of hardwood kraft-based dissolving pulp for viscose rayon production by cellulase treatment," *Bioresource Technology* 154, 109-113. DOI: 10.1016/j.biortech.2013.12.040
- Michud, A., Tantt, M., Asaadi, S., Ma, Y., Netti, E., Kääriäinen, P., Persson, A., Berntsson, A., Hummel, M. and Sixta, H. (2015). "Ioncell-F: ionic liquid-based cellulosic textile fibers as an alternative to viscose and lyocell," *Textile Research Journal* 86(5), 543-552. DOI: 10.1177/0040517515591774
- Mortimer, S., and Peguy, A. (1996a). "The formation of structure in the spinning and coagulation of lyocell fibres," *Cellulose Chemistry and Technology* 30(1-2), 117-132.
- Mortimer, S., and Peguy, A. (1996b). "The influence of air-gap conditions on the structure formation of lyocell fibers," *Journal of Applied Polymer Science* 60(10), 1747-1756. DOI: 10.1002/(SICI)1097-4628(19960606)60:10<1747::AID-APP28>3.0.CO;2-#
- Mortimer, S., Peguy, A., and Ball, R. (1996). "Influence of the physical process parameters on the structure formation of lyocell fibres," *Cellulose Chemistry and Technology* 30(3-4), 251-266.
- Perepelkin, K. (2007). "Lyocell fibres based on direct dissolution of cellulose in N-methylmorpholine N-oxide: Development and prospects," *Fibre Chemistry* 39(2), 163-172. DOI: 10.1007/s10692-007-0032-9
- Periyasamy, A. P., and Khanum, M. R. (2012). "Effect of fibrillation on pilling tendency of lyocell fiber," *Bangladesh Textile Today* 4, 31-39.
- Quintana, E., Valls, C., Vidal, T., and Roncero, M. B. (2013). "An enzyme-catalysed bleaching treatment to meet dissolving pulp characteristics for cellulose derivatives applications," *Bioresource Technology* 148, 1-8. DOI: 10.1016/j.biortech.2013.08.104
- Rabideau, B. D., and Ismail, A. E. (2015). "Effect of water content in N-methylmorpholine N-oxide/cellulose solutions on thermodynamics, structure, and hydrogen bonding," *The Journal of Physical Chemistry B* 119(48), 15014-15022. DOI: 10.1021/acs.jpcc.5b07500

- Ramamoorthy, S. K., Skrifvars, M., and Rissanen, M. (2014). "Effect of alkali and silane surface treatments on regenerated cellulose fibre type (lyocell) intended for composites," *Cellulose* 22(1), 637-654. DOI: 10.1007/s10570-014-0526-6
- Rosenau, T., Potthast, A., Sixta, H., and Kosma, P. (2001). "The chemistry of side reactions and byproduct formation in the system NMMO/cellulose (lyocell process)," *Progress in Polymer Science* 26(9), 1763-1837. DOI: 10.1016/S0079-6700(01)00023-5
- Schild, G., and Sixta, H. (2011). "Sulfur-free dissolving pulps and their application for viscose and lyocell," *Cellulose* 18(4), 1113-1128. DOI: 10.1007/s10570-011-9532-0
- Schurz, J., and Lenz, J. (1994). "Investigations on the structure of regenerated cellulose fibers; Herrn Professor Janeschitz-Kriegl zum 70. Geburtstag mit den besten Wünschen gewidmet," in *Macromolecular symposia* (Vol. 83, No. 1, pp. 273-289). Hüthig & Wepf Verlag.
- Sinclair, R. (2014). *Textiles and Fashion: Materials, Design and Technology*, Elsevier.
- Singha, K. (2012). "Importance of the phase diagram in lyocell fiber spinning," *Int. J. Mater. Eng.* 2(3), 10-16.
- Sixta, H., Iakovlev, M., Testova, L., Roselli, A., Hummel, M., Borrega, M., van Heiningen, A., Froschauer, C. and Schottenberger, H. (2013). "Novel concepts of dissolving pulp production," *Cellulose* 20(4), 1547-1561. DOI: 10.1007/s10570-013-9943-1
- Tian, C., Zheng, L., Miao, Q., Cao, C., and Ni, Y. (2014). "Improving the reactivity of kraft-based dissolving pulp for viscose rayon production by mechanical treatments," *Cellulose* 21(5), 3647-3654. DOI: 10.1007/s10570-014-0332-1
- Uddin, A. J., Yamamoto, A., Gotoh, Y., Nagura, M., and Iwata, M. (2010). "Preparation and physical properties of regenerated cellulose fibres from sugarcane bagasse," *Textile Research Journal* 80(17), 1846-1858. DOI: 10.1177/0040517510369408
- Wang, H., Gurau, G., and Rogers, R. D. (2012). "Ionic liquid processing of cellulose," *Chemical Society Reviews* 41(4), 1519-1537. DOI: 10.1039/C2CS15311D
- Wang, L., Zhang, Y., Gao, P., Shi, D., Liu, H., and Gao, H. (2006). "Changes in the structural properties and rate of hydrolysis of cotton fibers during extended enzymatic hydrolysis," *Biotechnology and Bioengineering* 93(3), 443-456. DOI: 10.1002/bit.20730
- Wang, Q., Liu, S., Yang, G., Chen, J., and Ni, Y. (2015). "Cationic polyacrylamide enhancing cellulase treatment efficiency of hardwood kraft-based dissolving pulp," *Bioresource Technology* 183, 42-46. DOI: 10.1016/j.biortech.2015.02.011
- Wang X., Jian, H., and Jin, L. (2011). "Preparation ultra-fine fibrillated lyocell fiber and its application in battery separator," *Int. J. Electrochem. Sci* 6, 4999-5004.
- Weigel, P., Gensrich, J., and Fink, H. (1994). "The structural format of cellulose fibers from amine oxide solutions," *Lenz Ber* 74, 31-37.
- Wendler, F., Konkin, A., and Heinze, T. (2008). "Studies on the stabilization of modified lyocell solutions," in: *Macromolecular Symposia* (Vol. 262, No. 1, pp. 72-84). Wiley-VCH Verlag. DOI: 10.1002/masy.200850208
- Wendler, F., Persin, Z., Stana-Kleinschek, K., Reischl, M., Ribitsch, V., Bohn, A., Fink, H.P. and Meister, F. (2011). "Morphology of polysaccharide blend fibers shaped from NaOH, N-methylmorpholine-N-oxide and 1-ethyl-3-methylimidazolium acetate," *Cellulose* 18(5), 1165-1178. DOI: 10.1007/s10570-011-9559-2

- Woodings, C. (1995). "The development of advanced cellulosic fibres," *International Journal of Biological Macromolecules* 17(6), 305-309. DOI: 10.1016/0141-8130(96)81836-8
- Yau, E., Badal, K., Brodeur, G., Collier, J., Telotte, J., and Ramakrishnan, S. (2013). "Enzymatic hydrolysis of N-methyl morpholine n-oxide and ionic liquid-treated cellulose: A comparative study," *Indian Chemical Engineer* 55(4), 235-246. DOI: 10.1080/00194506.2013.851993
- Zhang, H., and Tong, M. (2007). "Influence of hemicelluloses on the structure and properties of lyocell fibers," *Polymer Engineering & Science* 47(5), 702-706. DOI: 10.1002/pen.20743
- Zhang, H., Zhang, H., Tong, M., Shao, H., and Hu, X. (2008). "Comparison of the structures and properties of lyocell fibers from high hemicellulose pulp and high α -cellulose pulp," *Journal of Applied Polymer Science* 107(1), 636-641. DOI: 10.1002/app.27129

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