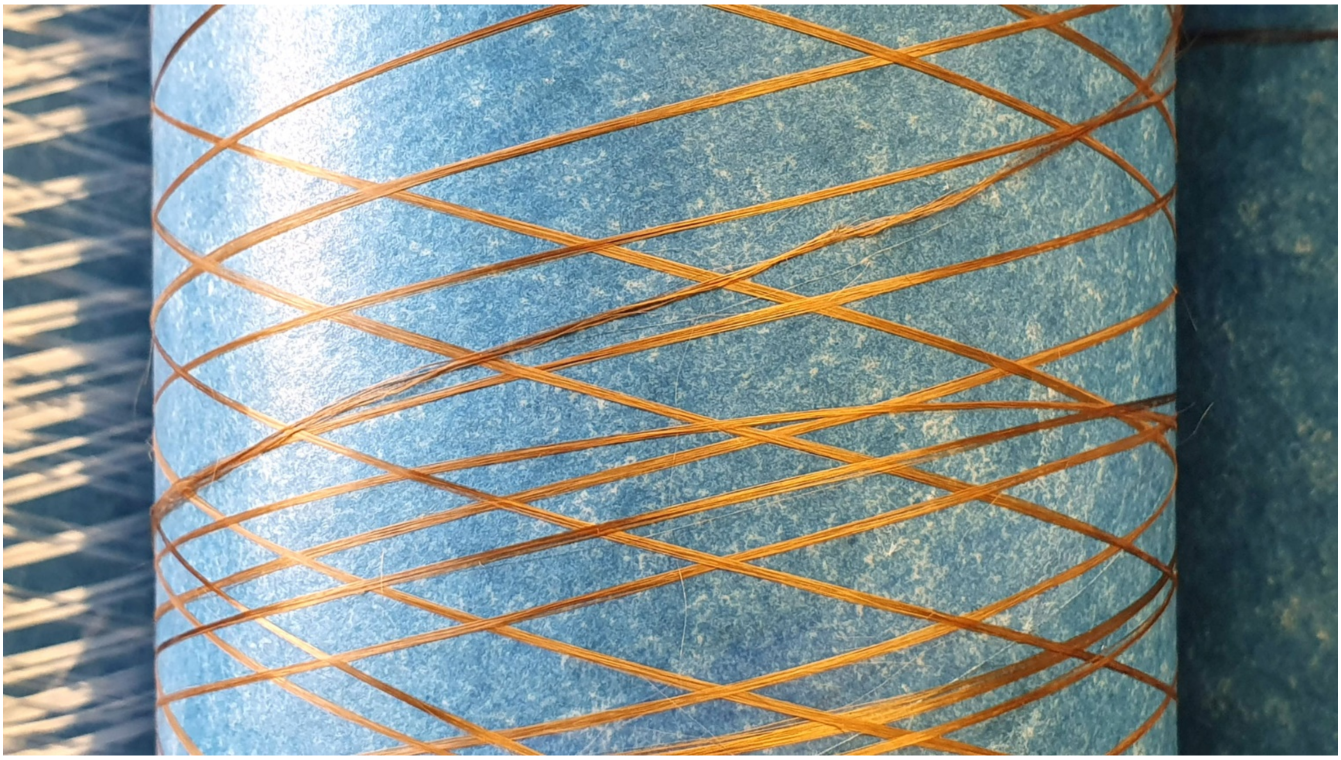
BIOECONOMY
White Paper



Towards bio-based reinforcing fibers: co-dissolution of cellulose and lignin for fiber spinning

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Bioeconomy Report No: 154

November 2020

Summary

Cellulose can be used for production of regenerated cellulose fibers such as viscose, modal and lyocell. Regenerated cellulose fibers are primarily used in textile applications, but they are also used in tire cord and can act as a bio-based precursor for production of stiff and strong carbon fiber. Recently, bi-component fibers spun from cellulose together with lignin have gained an increasing interest to act as a bio-based precursor for carbon fiber production, as it opens for the manufacture of carbon fibers with higher conversion yield and mechanical properties than when produced from cellulose or lignin only, respectively.

The bi-component fibers containing cellulose and lignin are spun by wet spinning techniques. Wet spinning requires complete dissolution of the cellulose and lignin that is to be spun into filaments. Of special interest is the direct dissolution strategy, without the need for chemical derivatization of cellulose and/or lignin. However, only a few solvent systems are capable of co-dissolving lignin and cellulose. This white paper aims at providing a summary of the solvent systems available for co-dissolution of cellulose and lignin and to give the reader a generic guide of important aspects to consider when working with this topic.

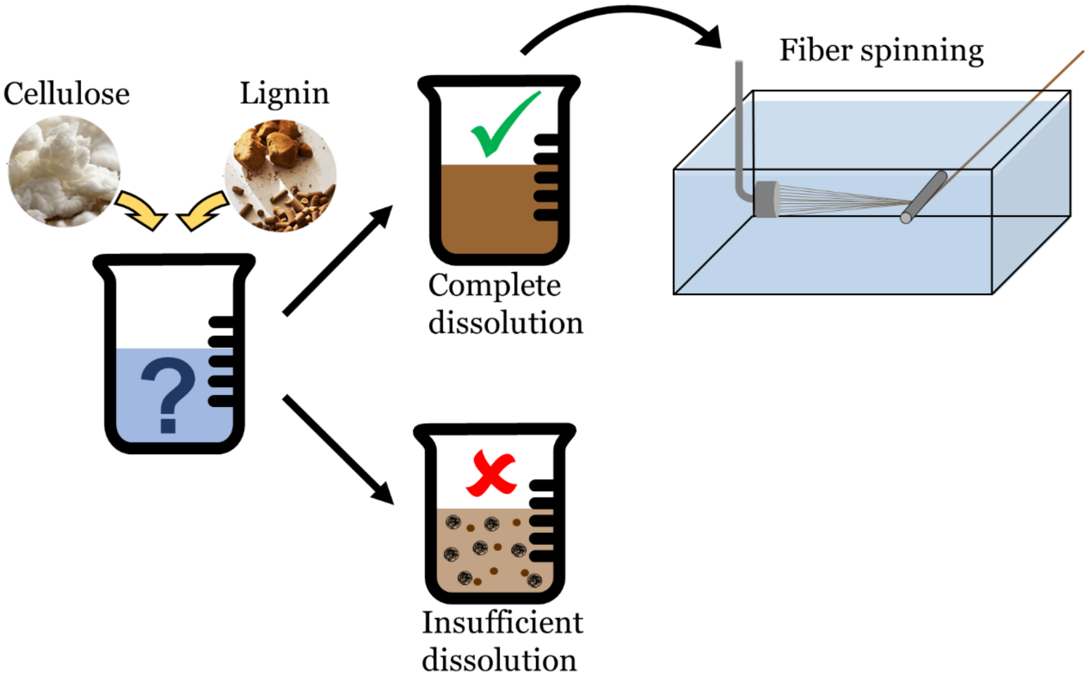

Illustration. What solvent systems are currently available that provides co-dissolution of cellulose and lignin for fiber spinning?

Background

Cellulose is a natural and linear polymer present in wood, cotton and other plants, and is the most abundant natural polymer on Earth. Wood-derived cellulose is generally considered as one of the most promising polymers to decrease our dependence on fossil-based sources for the manufacture of a wide range of materials. Besides being used for production of paper, tissue and packaging materials, wood-derived cellulose serves as a source for production of regenerated cellulose fibers such as viscose and lyocell fibers. The primary use of regenerated cellulose fibers are in textile applications where it is an alternative to cotton and synthetic fossil-based fibers. Regenerated cellulose fibers are also used in tire cord and can act as the precursor for production of carbon fibers.

Regenerated cellulose fibers are produced by dissolving cellulose in a solvent prior to spinning of the solution into a fiber via wet spinning, dry-jet wet spinning or dry spinning techniques. The most suitable spinning technique is to a large extent dictated by the choice of solvent, cellulose properties and the targeted fiber properties for a specific application. Cellulose dissolution is a challenging task due to the strong intermolecular bonds in cellulose, making it difficult to dissolve in a wide range of solvents. Besides choosing a proper solvent, the most common strategy to overcome the poor solubility of cellulose is to decrease its degree of polymerization (DP) and/or to chemically modify its structure via derivatization. Unfortunately, lowering of the DP may yield unstable spinning and fibers with poor mechanical properties while derivatization usually requires the use of harmful chemicals (e.g. carbon disulfide in the viscose process). Due to its technical importance, cellulose dissolution is therefore an important research area, where more environmentally friendly and cost-efficient solvent systems and derivatization routes are sought for.

The challenge

A trending research area is the preparation of bi-component fibers spun from cellulose together with another polymer as this opens for cellulose-based fibers having altered properties compared to classical regenerated cellulose fibers. Of special interest is the bi-component fibers made from blends of cellulose and lignin.

Cellulose-lignin fibers are attractive as precursor for preparation of bio-based carbon fibers (Figure 1). High-performance carbon fibers from regenerated cellulose fibers (viscose) were commercialized in the 1960s but out-competed by the cheaper fossil-based polymer polyacrylonitrile. The main drawback with cellulose as a carbon fiber precursor is its relatively low carbon content (44%) which results in a low conversion yield (10-30%), making its use in carbon fiber production economically unfeasible. However, lignin is a renewable and heterogenous polymer with a relatively high carbon content (60-65%) which can be processed into carbon fibers at conversion yields of 40-45%. However, the lignin-based carbon fibers suffers from inferior mechanical properties. Furthermore, wet spinning of lignin without a fiber forming polymer such as cellulose is not possible. Therefore, co-dissolution of cellulose and lignin and spinning of the solution into a carbon fiber precursor has recently gained an increasing attention due to the possibility of taking advantage of the high carbon content of lignin and the beneficial molecular orientation of cellulose.

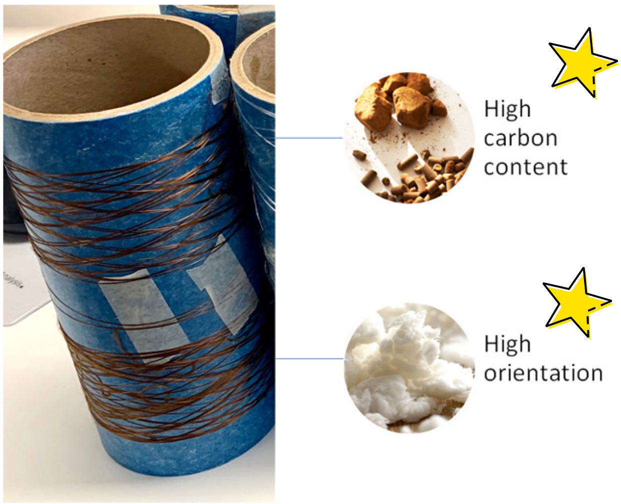

Figure 1. Wet spun cellulose-lignin yarn that can be used as a carbon fiber precursor. The lignin provides a high carbon content while cellulose provides high molecular mass and orientation.

As mentioned, dissolution of cellulose is an intriguing task, which is even more pronounced when it is to be co-dissolved with lignin. The challenge lies in finding a solvent that is capable of co-dissolving cellulose and lignin at technically relevant concentrations, ensuring that the solution is spinnable into fibers in a robust way (no spinneret clogging, filament breaks, etc.). In addition, the solvent shouldn't degrade the cellulose and/or the lignin in an unfeasible manner, be easy to handle and recycle, as well as being cost-efficient.

Solvents for lignin and cellulose co-dissolution

Few solvents are known to have the capability of co-dissolving cellulose and lignin without the need for chemical derivatization. The prime motivation of using solvents that can directly co-dissolve cellulose and lignin is the possibility of lowering production costs and having a more environmentally friendly process. In this section, the solvents capable of providing direct co-dissolution of cellulose and lignin are presented.

N-Methylmorpholine-N-oxide (NMMO)

N-Methylmorpholine-N-oxide, NMMO, is used commercially as a solvent for cellulose in the production of textile fibers by the Lyocell process (Chanzy et al. 1982). The solubility depends on the degree of polymerisation, DP, of the cellulose as well as dissolution conditions such as the ratio of NMMO and water, temperature etc. Up to 15% cellulose can be dissolved in NMMO and as much as 35% lignin. A solution with a solids content of 15% of both dissolved lignin and cellulose can be obtained. NMMO is non-toxic and biodegradable. However, NMMO is an oxidant and relatively unstable. It has been reported to degrade cellulose, and therefore an antioxidant such as n-propyl gallate is usually added to the solution in order to prevent degradation of cellulose and the solvent. In the commercial Lyocell process, NMMO is recycled to a high degree by evaporation of water making the process economically feasible.

Ionic liquids (ILs)

Ionic liquids, ILs, are salts in liquid state. For the purpose as solvent for wood components, the ILs of interest are restricted to salts with a melting temperature below 100°C. Low vapor pressure, non-flammability, and low reaction temperatures renders ILs attractive for green chemistry approaches in biorefinery processes. ILs that are highly viscous and hygroscopic are difficult to handle and therefore not suitable. ILs offers the opportunity to directly co-dissolve cellulose and lignin at relatively high concentrations (10-20 wt%) without the need for derivatization. These high concentrations lead to spinning solutions of high viscosity which therefore are possible to spin into fibers by dry-jet wet spinning. This spinning technique is slightly different from the classical wet spinning process used for viscose production. Dry-jet wet spinning makes it possible to apply higher amounts of fiber stretching which generally results in cellulose fibers with higher tensile properties superior to viscose fibers. Below, ILs of interest for wood components are presented.

Imidazolium-based ILs

Several ionic liquids are based on the cation imidazolium with different alkyl substituents. For efficient cellulose dissolution, the counter anion needs to be either chloride, acetate or phosphate. A higher the water content reduces the solubility.

EmimAc and EmimCl, 1-ethyl-3-methyl imidazolium acetate and chloride respectively, can dissolve both cellulose and lignin, EmimAc being the most efficient. The chloride containing EmimCl is corrosive, which limits large scale use. It requires relatively high temperature, which may lead to cellulose degradation.

EmimAc has been used to prepare carbon fiber precursors via dry-jet wet spinning of cellulose and kraft lignin. Spinning solutions with concentrations up to 18 wt% could be spun into precursor fibers comprised of 70 wt% lignin and 30 wt% cellulose, demonstrating the high dissolution capacity of EmimAc.

Non-Imidazolium based IL

One type of IL which is reported to successfully co-dissolve cellulose and lignin is 1,5-diazabicyclo[4.3.0]non-5-enium acetate, [DBNH][OAc]. The solvent has been developed by researchers at Helsinki University and Aalto university where the main objective was to find a solvent for direct dissolution of cellulose for the dry-jet wet spinning of cellulose fibers for textile applications. This process is, although not commercialized, called Ioncell-F. In parity with EmimAc, [DBNH][OAc] has been reported to be able to co-dissolve lignin and cellulose at concentrations up to 17 wt%. However, the questions regarding solvent recyclability is still a question that needs to be ruled out.

Deep eutectic solvents

Deep eutectic solvents, DES, represent liquid solvent systems that are based on a hydrogen donor, such as amines, amides, carboxylic acids, or polyols, and a hydrogen acceptor, for example quaternary ammonium salts. DES has the advantages of ILs, such as low vapor pressure and low melting point, and additionally they are less costly to manufacture, less toxic and often biodegradable. However, the disadvantage in the present context is that it selectively dissolves lignin and only little or no cellulose is dissolved.

Sodium hydroxide (water-based solvent system)

Phenolic and carboxyl groups on lignin are deprotonated, making it soluble in sodium hydroxide (alkali). This is the only solvent system that is water-based, which suggests an environmentally friendly solvent system. Lignins are generally soluble in alkali. Factors improving lignin solubility are lower molecular weight (DP), higher amount of phenolic hydroxyl and carboxylic groups, higher pH and lower ionic strength. Carboxyl groups are more efficient for lignin solubility than phenolic hydroxyl groups. Divalent cations are more detrimental for lignin solubility than monovalent cations.

Cellulose is also directly soluble in alkali, but within very narrow conditions; the concentration of sodium hydroxide needs to be in the range 6-10wt% and the temperature must be low, around 2°C to -10°C. Because of the low temperature, the process is referred to as the cold alkali process. The amount of cellulose possible to dissolve depends highly on DP of cellulose. Additives, such as ZnO or urea improve the solubility and stability of the spinning solution by delaying the time for gelation.

Alkali is also used for cellulose dissolution in the viscose process. However, in this process cellulose is not directly solubilized, it is derivatized by xanthation prior to dissolution. This makes it possible to dissolve cellulose in alkali in a broader temperature range with improved stability of the solution. However, the use of neurotoxic carbon disulfide for the xanthation is a clear disadvantage and requires extensive safety precautions.

Solubility

The length of polymers determines to a large extent the solubility of the polymer. The correlation between DP and amount of cellulose dissolved in different solvents is seen in Figure 2. It is well known that the strength of the fiber spun correlates both with cellulose DP and cellulose concentration as both higher DP and higher concentration gives higher strength. However, since a higher cellulose concentration is achieved mainly by decreasing the DP, it is necessary to find a compromise between cellulose concentration and DP.

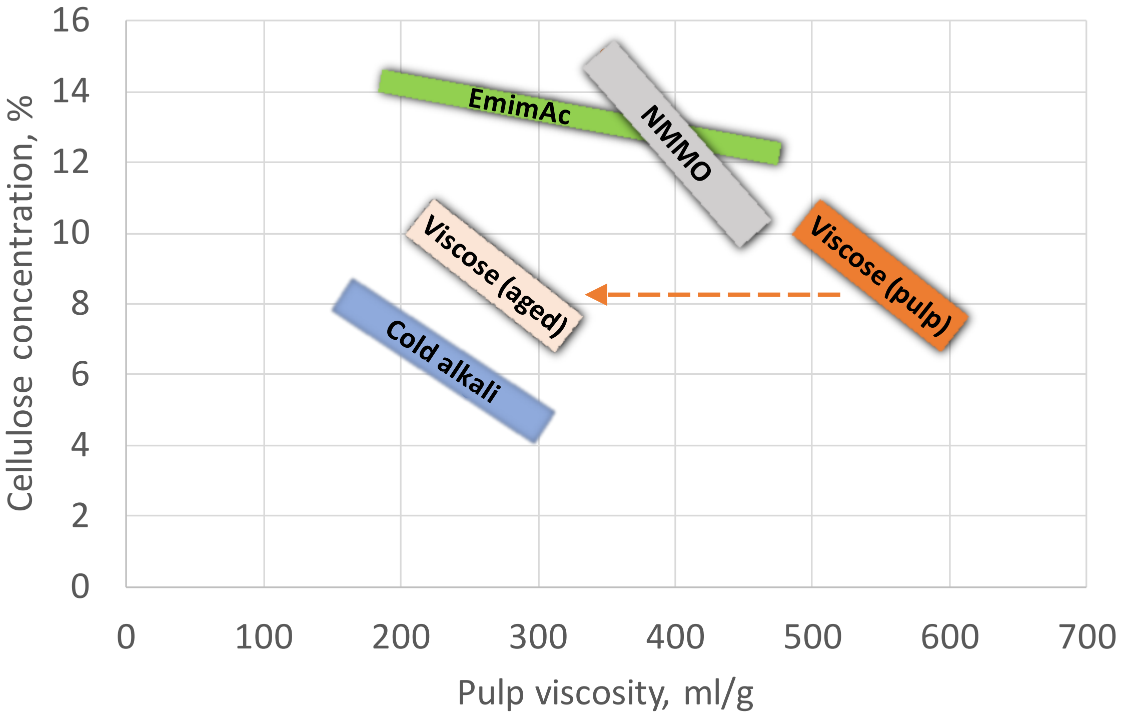

Figure 2. Amount of cellulose dissolved in depending on degree of polymerization (DP) given as pulp viscosity, ml/g, for direct dissolution and derivatized cellulose (viscose) in alkali and direct dissolution in alkali, NMMO and EmimAc.

In Figure 3, a comparison is made on solubility of lignin and cellulose in different solvents. As seen, cellulose solubility is the limiting factor. The solvent systems presented here all work well for lignin dissolution. However, the highest cellulose solubility is in NMMO and EmimAc while cold alkali and DES have limited capability of dissolving cellulose.

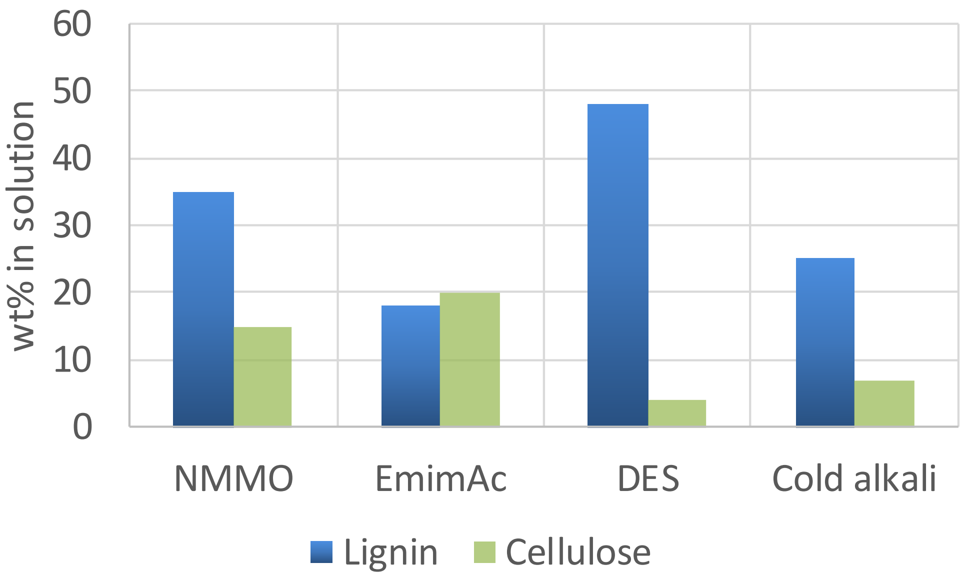

Figure 3. Estimated maximum concentration possible by direct dissolution of cellulose and lignin in different solvents.

Processability

In an ideal world it would have been easy to state that the amount of dissolved cellulose and lignin should be as high as possible. If more material can be dissolved, there will be less consumption of expensive solvent per mass unit of fiber produced. In theory, that is true. However, in a wet spinning process (Figure 4) there is an operating window where robust spinning can be carried out. Robust spinning means that fibers can be produced without spinneret clogging, breakage of individual filaments along the spinning line, with the possibility to stretch, wash, dry and wind the fibers, and so on. It is known that the key to success in a spinning process is the quality of the spinning solution. This includes its viscosity and rheological properties, content of air bubbles and undissolved particles as well as its stability over time. All these factors must be considered when developing technical fibers from e.g. cellulose-lignin blends. In addition, the solvent must be safe to handle and recyclable for environmental and economic reasons.

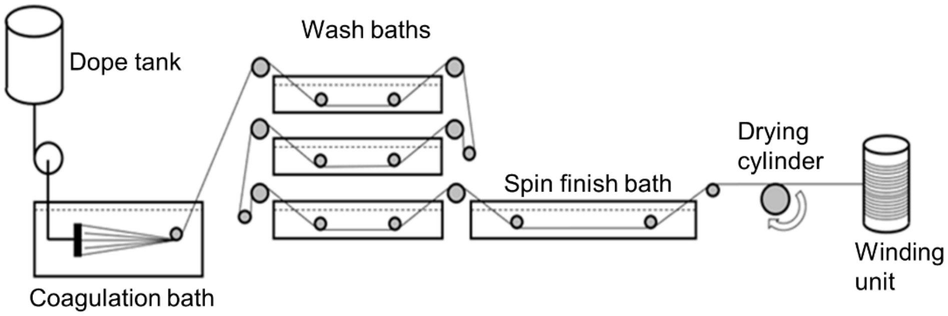

Figure 4. Illustration of a wet spinning process.

NMMO is capable of co-dissolving cellulose and lignin at high concentrations which suggests robust spinning and there is an existing recycling process developed for its recovery. However, NMMO is not completely unproblematic due to its chemical and thermal instability, which may lead to dangerous runaway reactions. In parity with NMMO, EmimAc and [DBNH][OAc] can co-dissolve cellulose and lignin at high concentrations. Unfortunately, they lack an established process for solvent recovery. It should also be noted that all these solvent systems yield spinning solutions with high viscosity that needs to be pre-heated to 40-95 °C for robust spinning. Their high viscosity also makes filtration and removal of air bubbles (deaeration) complicated.

The DESs suffers from poor capability of dissolving cellulose, which implies a high solvent consumption per mass unit of fiber produced. This may also give a low viscosity of the spinning solution which may result in a low wet strength of the fiber during spinning and thus low robustness. In addition, there is no existing recovery process for recycling of DESs.

The cold alkali solvent system is an environmentally friendly water-based solvent system. However, when compared to NMMO and ILs, it is moderately effective in dissolving cellulose and lignin, meaning that less material can be dissolved and that the cellulose needs to have a lower DP. This may still be acceptable for certain applications. The issue with poor stability of the spinning solution can be minimized by the addition of minor amounts of ZnO or urea. Pilot studies at RISE have shown the possibility for large scale spinning and with a technology to recover solvent and coagulant, making it an interesting candidate to act as a solvent system for co-dissolution of cellulose and lignin.

The way forward

Direct co-dissolution of cellulose and lignin is a recent and emerging technological field of interest, having its importance in the production of bio-based reinforcing fibers such as carbon fibers. The solvents that are able of co-dissolving cellulose and lignin are NMMO, ILs, DESs and cold alkali. Each solvent has its intrinsic advantages and disadvantages, and more research is needed to fully elucidate which has the highest potential for commercial use. We propose that a generic strategy for the further development of solvent systems for cellulose-lignin fiber spinning includes work on four topics.

- Increasing the **dissolution capacity** to lower solvent use and cost.
- Improving the **processability** for dope and spinning stability as well as fiber performance.
- Developing an efficient process for **solvent recovery** to lower cost.
- **Safety** improvement while maintaining sustainable production.

The future fiber must allow production of fibers in a robust, safe and economically feasible way, while still meeting the technical requirements for the desired application.

Further reading

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