New Developments in Dissolving and Processing of Cellulose in Ionic Liquids

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Summary: Ionic liquids (IL) are new direct dissolving systems for cellulose characterized by unique dissolving properties and simple technical handling. Selected IL-systems are non toxic and chemically as well as physically neutral which represents an advantage as compared to the commonly used direct solvent N-methylmorpholine-N-oxide (NMMO). Fibres can easily be prepared by coagulation in water. The BASF company as a leading producer of ionic liquids investigates the technical conversion of the preparation of cellulosic fibres using ionic liquids in cooperation with the Institut für Textilchemie und Chemiefasern (ITCF), Denkendorf and the Thüringisches Institut für Textil- und Kunststoff-Forschung (TITK), Rudolstadt. The major targets of this project are the selection of appropriate IL-systems, the IL recycling, rheology of spinning dopes and the charcterization of resulting fibre profiles. Essential results of this work and the potential for establishing a technical-scale process are summarized.

Keywords: cellulose; fibre production; ionic liquid; man made cellulosics

Introduction

Cellulose has immense importance as a renewable raw material. Only around 200 million tons of the 40 billion tons renewed anually are used as raw materials (pulps) in the manufacture of materials and goods such as textile fibres, packaging, paper and body care products. The main obstacle to the more extensive use of cellulose until now was a lack of suitable solvents for the chemical dissolution process. Cellulose is not soluble in water or conventional organic solvents because of its well developed intermolecular hydrogen bonding. Therefore technical processing of cellulose requires either chemical derivatization or physical dissolution in a suitable solvent. As a result, processing has traditionally been complex and in many cases more expensive than is the case with comparable, synthetically manufactured products (e.g. polyester fibres).

The most important, and also the oldest, process currently used to manufacture cellulose fibres is the viscose process, which involves derivatizing the cellulose with carbon disulphide to cellulose xanthate followed by dissolution in sodium hydroxide. This method currently accounts for approximately 95% of annual production volumes. Despite continuous improvement in the past decades, more than 2 tons of auxiliaries (e.g. carbon disulphide, sodium hydroxide, sulfuric acid) and significant volumes of fresh water are required per ton of cellulose fibre produced. Although carbon disulphide is approx. 70–75% recyclable, waste water and exhaust air treatment is complex owing to tough environmental requirements. The concentrations of cellulose in solution are in the range of 8–12 wt.-% with this process.

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Due to the economic and ecological drawbacks of the viscose process, scientists have long been engaged in efforts to make cellulose fibre production more cost effective and ecoefficient.[1,2] One of the main alternatives for fibre production is the NMMO process (N-methylmorpholine-N-oxide) developed since the late 1960s and commercialized in the early 1990s. The NMMO process is a direct dissolution process which produces cellulose solutions at concentrations of 10–15 wt.-% and is used to manufacture socalled Lyocell fibres characterized by good mechanical properties. Despite many advantages, the NMMO process has not replaced the viscose process to date. The main reason is the severe fibrillation of the fibres manufactured and the fibre profile which is closer to cotton. Moreover, the use of NMMO - a thermally unstable solvent – requires a major investment in safety technology. This is where ionic liquids (IL) come into play as a new type of cellulose direct solvent with superior dissolving power for cellulose: Selected ILs produce cellulose solutions of 20 wt.-% and more without pre-treatment.

Ionic Liquids, Definition and Properties

By definition, ionic liquids are low melting salts with melting points of less than 100 °C. Like common salt, they consist of 100% cations and anions.[3] However, they are large volume organic ions, whose low melting points are due to ''softening'' of the crystal lattice. On account of their interesting dissolving properties for organic and inorganic compounds and polymers, they can replace conventional solvents in many applications. Furthermore, they have excellent stability and are neither volatile nor readily flammable, which gives them advantages when this class of compound is used in a production process. The choice of cations and anions contained in an ionic liquid is crucial in tailoring its physical and chemical properties in order to meet the requirements of a given production process.

Dissolving and Processing of Cellulose

The processing of cellulose by its dissolution in ionic liquids is an entirely new industrial application.[3] The use of ionic liquids as a solvent system enables fibre manufacture in a manner very similar to the NMMO process in a direct dissolution process. Ionic liquids are almost entirely recovered (>99.5%) after use in the process and can be reused. The requisite amount of auxiliaries and the volume of waste water produced is much lower than in the viscose process and is similar to the NMMO process.

If ionic liquids are intended for use in a direct dissolution process, other requirements ideally also need to be met:

- low melting point <20 °C) and high decomposition point (>200 °C)
- no cellulose decomposition
- stable and storable spinning dopes
- easy processing
- easy cellulose regeneration (e.g. with water)
- uncomplicated recovery of ionic liquids
- no toxicity and no odours
- more cost effective process than the NMMO or viscose process
- fibre properties at least as good as with the NMMO or viscose process

The first step towards technical conversion of the fibre processing performed by Röder et al.[4] and Laus et al.[5] seems to be promising. In these studies BMIM CI (1-butyl-3-methylimidazolium chloride) was found as the favourable solvent. Our own studies[6] using BMIM Cl showed that spinning dopes containing up to 16.5 wt.-% cellulose could be produced. Wet spinning and air gap spinning were feasible. However, the corrosion profile, the severe cellulose decomposition and handling of the ionic liquid with its fairly high melting point at 70 °C were technical drawbacks and prompted a search for more suitable ionic liquids. A detailed screening with different types of IL selected and synthesized at

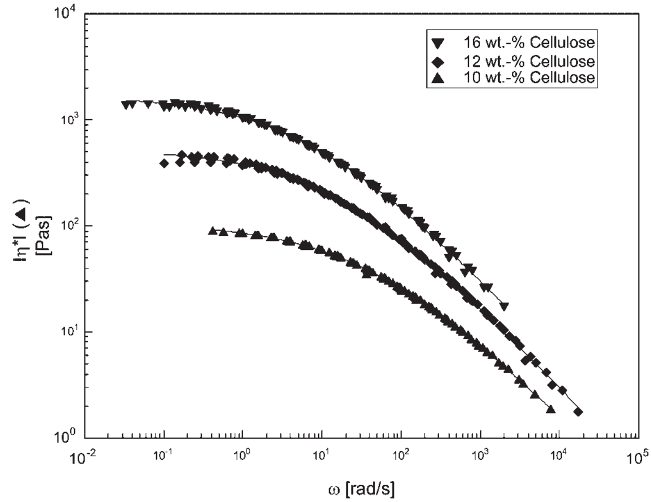

Figure 1.
Rheology master curves of 10, 12 and 16 wt.-% cellulose (Linters, DP 795) dissolved in EMIM acetate (reference temperature 95 °C).

BASF was performed searching for Ils matching all the requirement for technical conversion of the spinning process.

EMIM acetate (1-Ethyl-3-methyl-imidazolium acetate) is one of a number of promissing alternatives. The following results focus on this selected IL.

EMIM acetate is non-corrosive. It is also non-toxic. Solutions with high cellulose concentrations (as high as 20 wt.-%) can be obtained without gel formation and chain decomposition through hydrolysis. Additionally, the viscosity of the spinning dopes can be modified either through temperature or cellulose concentration within a broad range (50–3000 Pas), giving high flexibility in the spinning process. Figure 1 illustrates rheology curves of 10, 12 and 16 wt.-% cellulose solutions (Linters DP 795) in EMIM acetate. The shape of the

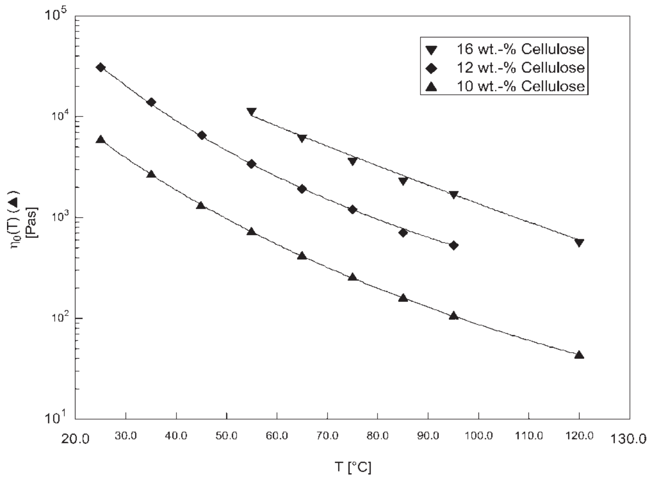

Figure 2.
Zero viscosity values of 10, 12 and 16 wt.-% cellulose (Linters DP 795) solutions in EMIM acetate.

curves is typical for polymer solutions characterized by a Newtonian area at low shear rates and reduced viscosity with increasing shear rate.

The range of zero viscosities of these spinning dopes as a function of temperature is summarized in Figure 2.

Another advantage is that EMIM acetate melts at temperatures well below room temperature (melting point $<-20\,^{\circ}C$), allowing the processing of spinning dope with excellent stability at moderate temperatures (80–90 °C) and with no need to add stabilizers. Cellulose can be directly dissolved in EMIM acetate by stirring. A specific activation or predrying of the pulps is not necessary. The preparation time of a 10 wt.-% cellulose spinning dope is about 45 - 60 min. In order to quantify the stability of the spinning dopes the cellulose molecular weight as a function of temperature and storage time was investigated. The results are summarized in Table 1. A slight decrease of molecular weight can be determined after spinning dope preparation which is caused by the mechanical shearing during stirring. The dopes are stable up to storage temperatures of 120 °C which is above the processing temperature. This is very important with respect to technical conversion of the process.

Table 1.
Stability of spinning dopes (12 wt.-% Linters, DP795 in EMIM acetate).

Storage temp. [°C]	Storage time [h]	av. DP
95	8	620
95	24	611
95	48	614
120	8	607
120	24	601
120	48	610
150	2	620
150	4	625
150	8	562
150	24	543

According to the wide range of viscosity fibres could be produced with different spinning technologies. The fibre properties that could be achieved so far differ significantly depending on the spinning technology chosen. For instance, the conventional wet spinning process according to the vicose technology developed at ITCF produces fibres with properties close to those of standard viscose fibres (Figure 3).

These fibres can be processed without any difficulty to textile yarns and fabrics. At TITK the processing in a dry-wet spinning process was developed and adapted to EMIM acetate.[7] This spinning technology is derived from the NMMO process and gives fibres with higher tenacities that are

Figure 3.
Cellulose fibres manufactured by conventional wet spinning process using EMIM acetate as direct solvent.

produced by conventional wet spinning comparable to Lyocell fibres. Another remarkable feature was an increase in loop tenacity peaking at a range of 30–35 cN/tex.

Another important requirement for technical conversion is the recycling of the ionic liquid used in the process. Recycling of EMIM acetate is achieved by collecting process fluids and evaporation of water. The EMIM acetate was then reused without further purification. Fibre properties such as tenacity and elasticity remain intact even after a number of process cycles. Also, filterability and stability of the spinning dope remained unchanged. Further tests are necessary both to optimize the recycling process and to investigate the formation of by-product formation and to monitor the accumulation of pulp impurities during the process.

Conclusion

Ionic liquids have great promise and great potential in the manufacture of cellulose fibres. The results show that the use of ionic liquids enhances the efficiency of processing cellulose. Compared with the NMMO process, the direct dissolution is more easily controlled, the process is inherently safer, and it enables the production of fibres with very different properties. Cellulose fibres manufactured with ionic liquids are already displaying similar properties in terms of tenacity and elasticity compared to fibres manufactured by the NMMO and viscose process. In addition, the process can be designed such that both fibrillating and non-fibrillating fibres can be manufactured specially for textile applications. This flexibility in designing fibre properties gives this new technology the potential for wide-scale use in future textile and technical applications.

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