LYOCELL FIBRES BASED ON DIRECT DISSOLUTION OF CELLULOSE IN N-METHYLMORPHOLINE N-OXIDE: DEVELOPMENT AND PROSPECTS

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The scientific principles of direct dissolution of cellulose in the NMNO—water system demonstrate the major possibility of obtaining concentrated spinning solutions and spinning hydrated cellulose fibres from them. The specific features of the properties of NMNO (high boiling point and insufficient thermal stability) that dissolves the NMNO—water system (narrow concentration range, optimum for dissolution of cellulose) makes it necessary to recycle the washing water by evaporating it, which causes high power consumption for this process. It is expedient to examine the possibilities of membrane technologies, including electrodialysis, for solving problems of recycling the solvent and cutting power consumption. However, this path only allows partially concentrating used washing water; since there is the danger of crystallization of NMNO di- and monohydrate. Spinning through an air gap from highly viscous solutions with long relaxation times at high spinneret draw ratios results in highly oriented fibres with high tensile rigidity (high deformation modulus). Fabrication of fibres whose properties correspond to ordinary viscose fibres will perhaps require “going away” from highly viscous solutions to a lower concentration and spinning by the ordinary wet method, but the volume of solvent used increases significantly, recycling it is more difficult, and power consumption increases. For the same reason of high orientation, the fibres exhibit important fibrillation when wet, and a “peach skin” effect is formed in the finished textiles. To reduce fibrillation, special treatments of the fabrics must be used, biofinishing, for example. During use of the articles, fibrillation can reappear, in laundering, for example. The technology for fabricating fibres of the Lyocell type requires solving many problems. Developing research on selecting alternative solvents and dissolving systems for direct dissolution of cellulose to obtain concentrated spinning solutions is simultaneously useful.

An important part of the scientific and engineering legacy of A. I. Meos is dedicated to cellulose and cellulose fibres. In his lectures to students on man-made fibre technology, he spoke of the dream of researchers of “finding a direct solvent of cellulose practically suitable for creating technology for fabrication of hydrated cellulose fibres.” This dream came true, but only after he was no longer with us.

Direct dissolution of cellulose to obtain concentrated solutions and spin fibres and films from them has been the object of research to develop the corresponding technologies for many years. The extremely tempting conversion to technologies with direct dissolution of cellulose could allow reducing consumption of chemicals by ten times in comparison to consumption in viscose and cuprammonium processes, facilitating recycling, and decreasing and improving the cleanliness of harmful industrial discharges. Attempts to reach these goals have been examined in many publications [1-10].

Many substances have been tested as solvents of cellulose:
– caustic soda solution, which causes significant swelling of cellulose and dissolves it, but only at a maximum degree of polymerization (DP) of 150-200; such a DP is totally insufficient for manufacturing fibres;
– zinc chloride solution of 65% concentration, which allows obtaining sufficiently concentrated solutions of cellulose; this process could not be developed due to its rapid breakdown;

St. Petersburg State University of Technology and Design. Translated from Khimicheskie Volokna, No. 2, pp. 58-64, March—April, 2007.
Fig. 1. Vapor pressure as a function of temperature: 1) monohydrate (13.5% water); 2) dehydrated NMMO.

Fig. 2. Phase diagram of NMMO—water system. Regions of existence of:
- L — liquid; L + DH — liquid + dihydrate; L + MH — liquid + monohydrate;
- DH + MH — dihydrate + monohydrate; L + AH — liquid + anhydrous crystals; MH + AH — monohydrate + anhydrous crystals.

- saturated sodium thiocyanate solution, which causes strong swelling of cellulose but does not allow obtaining concentrated solutions;
- solutions of polyvalent metal complexes, which also cause swelling and dissolution of cellulose, but the use of these substances is restricted by the insufficient DP of cellulose; the best results are obtained in dissolving cellulose in cadoxen and SITA (sodium-iron tartaric acid solution), but this method of dissolution has also not fulfilled hopes;
- different N-amino oxides and other organic compounds; however, the dissolution conditions and properties of the solutions, as well as the properties of the solvents themselves, were technologically and economically unacceptable.

As a result of the studies conducted by many scientists, including in our country, in the 1980s-1990s, it became clear that the process based on use of N-methyl N-oxides as the solvent could be a possible technology for direct dissolution of cellulose and spinning of hydrated cellulose fibres.

The advances of many firms and research organizations in creating alternative methods of obtaining hydrated cellulose fibres based on direct dissolution of cellulose without chemical transformations allowed finding a promising version of this process. Thanks to these advances, the scientific principles of direct dissolution of cellulose were created, using N-methylmorpholine N-oxide (NMMO) as the most promising solvent and spinning fibres from the solutions obtained.

In discussing the history of this process, several fundamental dates should be mentioned:
- 1936-1939 — a method of direct dissolution of cellulose in amino oxides was proposed [Ch. Granacher and R. Sallmann, DR Pat. No 713486 (1936); US Patent No. 2179181 (1939)];
- 1979 — research and development began on fabrication of a new kind of hydrated cellulose fibre by Courtauld in Great Britain; the fibre as called “Tencel;”
- 1983-1984 — a pilot unit was constructed for fabricating Tencel staple fibre in Coventry, Great Britain, and commercial production was begun;
- 1988 — industrial production of Tencel fibres began in Grimsby, Great Britain;
- 1989 — the specific name “Lyocell” was given to hydrated cellulose fibres made by direct dissolution of cellulose in N-amino oxides;
- 1990 — pilot production of Lyocell fibres by direct dissolution of cellulose in an aqueous solution of NMMO was created by Lenzing in Austria;
- 1992 — production of Tencel fibres by Courtauld began in Mobile, Ala. USA;
- 1992-1994 — research on Lyocell fibres began at the Textile and Man-Made Fibre Research Institute in Rudolstadt and was subsequently organized by Aclercu Schwarzga GmbH; the fibre was called “Aclercu;”
- 1993-1997 — an industrial Lyocell plant was built and started up by Lenzing in Heiligenkreuz, Austria;