Wet spinning PAN-fibres from aqueous solutions of ZnCl$_2$ and NaSCN

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Abstract. In 2007 a chemical regulation order was adopted in Europe and China, to protect the environment and human beings from hazardous substances in consumer goods and their working environment. It is a topic of interest for the rest of the world, as well. Some substances are banned by law from industrial application. The organic solvents Dimethylformamide (DMF) and Dimethylacetamide (DMAc) are candidates for prohibition. To be prepared, the producers of carbon fibres, hollow fibres and wet spun textile products are looking for alternative solvents for their production processes and try to gain according process Know-How. Aqueous solutions of inorganic salts are the most promising alternative. Within this work, the major differences between the organic and inorganic solvents are shown and the effects on the production costs are shown. This should show the chances which are linked with the use of the alternative solvents.

1. Introduction

Wet spun Polyacrylonitrile (PAN) fibres account for about 10.2 % of the world wide produced chemical fibres [1, 2]. Typical applications are textile products like jackets or shirts and home textiles. Moreover wet spun PAN fibres are the pre material for the production of high performance carbon fibres, which are used in technical applications like sports cars and wind turbines. For economic reasons, a large number of producers use toxic solvents for the production of PAN fibres, namely DMF and DMAc. These solvents are carcinogen and reproduction toxic and thus they have to be handled carefully. Moreover, the use of these solvents could be prohibited in the future. Less harmful alternatives are aqueous solutions of salts, like Sodium thiocyanate (NaSCN) and Zinc chloride (ZnCl$_2$) or the organic solvent Dimethylsulfoxide (DMSO). In this article the major characteristics of the wet spinning process with the inorganic salts are focused.

1.1. Wet spinning

For wet spinning of PAN, the polymer is dissolved in an organic or inorganic solvent and is then extruded into a bath of solvent and water. The polymer coagulates to solid fibres, which can be conducted to the washing and stretching step, before they are dried and winded up (Figure 1). During the process the fibres are stretched at high temperatures to paralyse the polymer chains and eliminate pores between the chains. As a result, the fibre properties are better and the strength of the fibres is higher. The type of solvent used for the dissolution and spinning of the polymer has a large influence on the fibre properties and affects the choice of parameters for the following process steps.
The type of solvent directly influences the process conditions and the production costs and has a major influence on the achievable fibre quality. In the following, the influence of the type of solvent on

- the fibre properties,
- the work safety,
- the production costs and
- the design of the production process

are further discussed.

2. Characteristics of wet spinning with aqueous NaSCN-solution

2.1. Fibre properties

NaSCN is an inorganic salt, which can be dissolved in pure water to receive an aqueous solution. This solution is capable to dissolve certain polymers like Polyacrylonitrile to bring them into fibre form in the wet spinning process. In comparison to organic solvents, like DMSO or DMF, the dissolution mechanism slightly differs from the mechanism of the inorganic aqueous solutions, which results in differences in the fibre formation process. In case of aqueous solutions of NaSCN and ZnCl₂, the salt changes the molecular structure of the water, which enables the water to dissolve the Polymer. As pure water is not able to dissolve PAN, the salt acts like an indirect solver for the polymer. [3,4,5,6] In the case of DMSO or DMF, we have an organic fluid, which is able to dissolve the polymer by itself [7]. This different dissolution mechanism has a big influence on the spinning process.

During the spinning process the dissolved polymer is spun into a coagulation bath and gets in contact with the coagulant (water). In case of the organic solvents the coagulant separates the solvent from the polymer because of the high bonding tendency of water and the solvent and thus the polymer goes into the solid state immediately. [7,8] To get a good fibre quality, the speed of the coagulation has to be controlled by the amount of water inside the coagulation bath. That means, you have to mix the water inside the coagulation bath with a certain amount of the organic solvent to decrease the speed of the coagulation. The slower coagulation speed usually result in better fibre properties and the formation of a dense microstructure. The amount of solvent inside the coagulation bath is usually far above 40 wt.%. [9] In case of the inorganic salts, the water itself works as the solving agent as far as it is in contact with the salt atoms. After extrusion of the polymer solution into the coagulation bath, the dissolved polymer gets in contact with the extra amount of water inside the bath. The coagulation takes place as the aqueous solution of the salt is diluted and the water loses its ability to dissolve the polymer gradually. The speed of this mechanism is much lower than the coagulation mechanism of the organic solvents. As consequence you can use pure water inside the coagulation bath or add only a small amount of salt < 14 wt.% to the coagulation bath to receive good fibre qualities. The process is thus much more resistant against the coagulation conditions than in case of the organic solvents.
2.2. Work safety and political regulations for the organic solvents

To enhance a better protection for human beings and nature towards hazardous chemicals, the European Union has adopted a substantial reform for the use and distribution of chemical substances in Europe. This Reform is named REACH (Registration, Evaluation, Authorization and Restriction of Chemicals). Currently, 163 substances are placed on the SVHC (Substances of Very High Concern) list because of their carcinogenic, mutagenic and reproduction toxic properties. DMAc and DMF, which are commonly used for the production of wet spun fibres are placed on the list in 2011 and 2012, respectively. Both solvents will be proved in a second step, where it will be decided to ban them from industrial application. Then it will be forbidden to use and sell these chemicals in larger amounts. [10]

In China a similar regulation program, the so called “China REACH”, has been adopted in 2010. Both chemicals are not restricted yet but registered and classified as hazardous substances [11]. The evaluation of the chemicals is based on the REACH reform of the European Union and performed by the CIRS (Chemical Inspection and Regulation service), which collaborates with European research groups. Thus, it is probable that the evaluation and restriction of chemicals follows the decisions of the European Union.

2.3. Production costs and design of the production line

The described coagulation mechanism of the aqueous solutions of inorganic salts NaSCN or ZnCl₂ has an effect on the design of the spinning line. In case of the organic solvents you have to slightly increase the amount of water in the first baths from < 60 % to 100% to control the coagulation speed. For this reason you usually have at least 2 coagulation baths in the line. In case of the inorganic salts, you do not need a second or third coagulation bath, which influences the investment costs for the spinning line. Moreover you can use solution polymerization for the production of the spinning solution and reverse osmosis in combination with industrial distillation for the recovery of the solvent. Other saving potentials can be realized in the ventilation system and the explosion protection equipment, because of the hazardous and inflammable nature of the organic solvents in contrast to the inorganic aqueous solutions. On the other hand, the polymer throughput is higher with the organic solvents, because of a better solvability for the PAN Polymer. All in all the production costs with NaSCN are comparable or even lower than the production costs with DMSO.

3. Conclusion

PAN fibres for textile and technical applications represent a big market with good future prospects. In Europe and China the producers will have to meet strict regulations regarding the use of harmful chemical substances in their production processes. In other countries similar approaches are considered. These political interferences mean extra costs and investments for the producers concerned in the first place, but the regulations do not have to be of disadvantage for the producers in the longer term. Better fibre properties at similar or even lower production costs are attainable. In carbon fiber production sector, some of the leading producers are already working with NaSCN and DMSO. Besides, the use of alternative solvents, especially in case of inorganic salts, is advantageous in regard to health protection of the workers and environmental effects.

References

[1] Numbers from industry association chemical fibers e.V. Industrievereinigung Chemifasern e.V. 25 Mar. 2015 <https://www.ive-ev.de/live/index.php?page_id=42>
[2] Massons J C 1995 Acrylic Fiber Technology and Applications. New York, Basel, Hong Kong: Marcel Dekker Ink.,
[3] Caplin M 2015 Hofmeister Series, URL: http://www. Isbu.ac.uk/water/hofmeister_series.html, 13.12.2015
[4] Edwards G G M, Hoskins A R and Johnson A F 1993 Raman Spectroscopic Studies of the Polyacrylonitrile-Zinc Complexes in Aqueous Solutions of Zinc Chloride and Bromide, Polymer International 30, S. 25-32

[5] Valiev M, Deng S and Wang X B, How Anion Chaotrope Changes the Local Structure of Water: Insights from Photoelectron Spectroscopy and Theoretical Modeling of SCN Water Clusters

[6] Xu L and Qiu F 2015 Unusual viscosity behaviour of polyacrylonitrile in NaSCN aqueous solutions, Polymer 64, S. 130-138

[7] Ehrenstein G P and Pongratz S 2007 Beständigkeit von Kunststoffen, Band 1, München: Hanser

[8] Henrici-Olive G and Olive S 1979 Molecular Interactions and Macroscopic Properties of Polyacrylonitrile and Model Substances, Advances in Polymer Science 32, S. 123-152

[9] Kobashi T and Takao S, Polyacrylnitrilfaser DE 3535368 A1, publication day: 17.04.1986

[10] Website of the European Chemicals Agency (ECHA), Helsinki. 01 Feb. 2016 <http://echa.europa.eu/de>

[11] Website of the Chemical Inspection & Regulation Service. 01 Feb. 2016 <http://www.cirs-reach.com/China_Chemical_Regulation/IECSC_China_REACH_China_New_Chemical_Registration.html>