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Stefan PETEREK, Thomas GRIES
Institute of Textile Technology at RWTH Aachen University, Aachen, Germany

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Sorumlu Yazara ait Orcid Numarası (Corresponding Author's Orcid Number) :
https://orcid.org/0000-0002-2480-8333

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CARBON FIBRE PRECURSOR PRODUCTION WITH NaSCN(aq.) AS A SUSTAINABLE SOLVENT

Stefan PETEREK[1]*
Thomas GRIES[1]
https://orcid.org/0000-0002-2480-8333
[1]Institute of Textile Technology at RWTH Aachen University, Aachen, Germany

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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 the industrial application. The organic solvents Dimethylformamide (DMF) and Dimethylacetamide (DMAc) are candidates for prohibition. To be prepared, the producers of carbon fibre precursors, 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.

The relevance of chemical regulations for the fibre industry and in particular for the carbon fibre precursor production process will be discussed and the major changes due to the use of inorganic solvents are shown. Some of the main characteristics and advantages of these solvents are considered. Appropriate spinning conditions and their effect on the process costs are in the focus of this work. The Institute of Textile Technology at RWTH-Aachen University (ITA) is one of the leading textile research institutes in Europe. The experience we gained during the trials on our wet spinning lines and from the collaboration with industry partners will be part of the work.

Keywords: Wet spinning, sodium thiocyanate, NaSCN, cost-saving, green process

SÜRDÜRÜLEBİLİR BİR ÇÖZÜCÜ OLARAK NaSCN (sulu çözelti) İLE ÜRETİLEN KARBON LİF BAŞLATICISI

ÖZET: 2007 yılında Avrupa ve Çinde çevreyi ve insanları, tüketim ürünlerindeki ve çalışma ortamlarındaki tehlikeli maddelerden korumak için bir kimyasal direktif talimatı kabul edildi. Tabiki bu dünyanın geri kalanının da ilgilendiren bir durumdu. Bazı maddelerin endüstri uygulamaları yasa ile engellendi. Organik çözücüler Dimetilformamid (DMF) ve Dimetilasetamid (DMAc) yasaklama için aday kimyasallardandırlar. Hazırlanacak olan içi boş lifler ve yaş çekim tekstil ürünleri için üreticiler karbon lifi başlatıcısı olarak üretim süreçleri için alternatif çözücüler aramaktadırlar ve sürece göre birikim kazanmaya çalışmaktadırlar. Bunun için İnorganik tuzların sulu çözeltileri en umut verici alternatiftir.

Bu çalışmada lif endüstrisi ve özellikle karbon lifi başlatıcısı üretim işlemi için kimyasal düzenlemelerin uygunluğu tartışılacak ve inorganik çözücülerin kullanımına bağlı olarak meydana gelen ana değişiklikler gösterilecektir. Bu çözücülerin temel özelliklerinden ve avantajlarından bazıları dikkate alınacaktır. Uygun lif çekmi koşulları ve işlem maliyetleri üzerindeki etkileri bu çalışmanın odak noktasındadır. RWTH-Aachen Üniversitesi'ndeki Tekstil Teknolojisi Enstitüsü (ITA), Avrupa'nın önde gelen tekstil araştırma enstitülerinden biridir. Yaş çekim hatlarımızdaki denemeleri sırasında ve endüstri ortaklarıyla işbirliğinden kazandığımız deneyim bu çalışmanın bir parçası olacaktır.

Anahtar Kelimeler: Yaş çekim, Sodyum tiyosiyanat, NaSCN, tasarruf, yeşil süreç

Sorumlu Yazar/Corresponding Author: *Stefan.peterek@ita.rwth-aachen.de*
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1. INTRODUCTION

Wet spun Polyacrylonitrile (PAN) fibres account for about 10.2 % of the worldwide 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 carcinogenic 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 NaSCN and ZnCl2 or the organic solvent Dimethylsulfoxide (DMSO).

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 paralyze 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.

2. EXPERIMENTAL SET-UP AND PROCEDURE

In the following, some basic experiences we made during our experiments with aqueous solutions of ZnCl2 and NaSCN will be presented. This can help to get an impression of the challenges and characteristics of the spinning process with inorganic salts. The process is compared with the DMSO process in Chapter 3 (Results). This can help to decide which solvent is better suited for which field of application. The focus is on the process handling and the process control.

2.1. Wet spinning trials

The trials were performed on a technical scale wet spinning line with one spinning bath, two washing baths, a hot air drying oven and a winder (Figure 2).

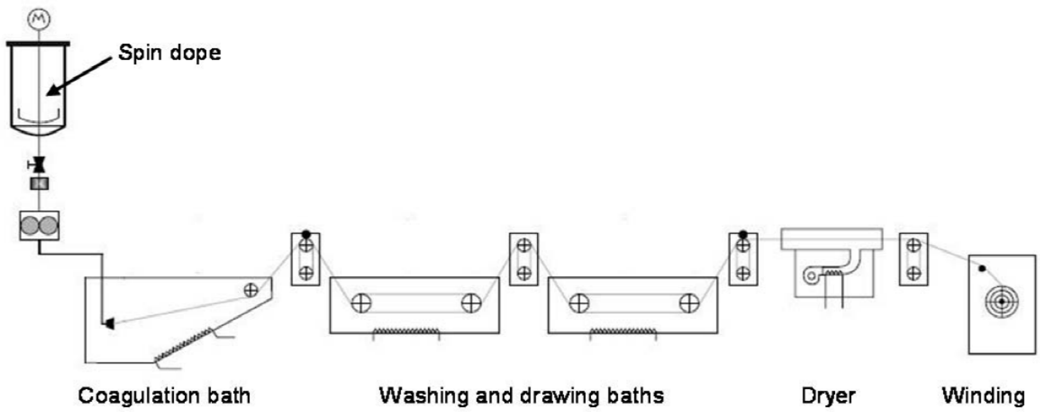

Figure 1. Schematic representation of the wet spinning process.

Figure 2. Technical scale wet spinning line at the Institute of Textile Technology at RWTH Aachen University

2.1.1 Spinning Dope preparation

The first step in the process is the preparation of the spinning dope. The inorganic salt is dissolved in deionized water with a concentration of 54 wt.-% of salt. Afterwards, the PAN-Polymer powder (8 wt.-% in case of ZnCl2, 13 wt.-% in case of NaSCN) is added while stirring until a homogeneous suspension is obtained (Figure 4, left). This suspension is filled into the storage tank of the spinning line and heated up to 75 °C. The spinning dope is held at this temperature for two days and continuously stirred until the PAN polymer powder is fully dissolved. To ensure, that there are no impurities in the spinning dope, it passes through a bundle of filters before it is spun to fibres.

2.1.2 Spinning process

For the spinning trials, the parameters listed in Table 1 were kept constant. The spinning bath temperature, the solvent concentration inside the spinning bath, the temperature of the spinning solution, the polymer content of the spinning solution and the solvent concentration inside the first washing bath were varied. One factor at a time was varied to observe the influence of the factor on the fibre quality. The aim was to find appropriate process conditions and a starting point for a full factorial experimental design. From these trials, general trends and effects can be derived and compared to the standard process with organic solvents. The total stretching degree from the exit of the coagulation bath to the winder is about 2.75, which is really low. Thus, the mechanical properties are not comparable to fully stretched fibres. In this study, the focus is on the coagulation conditions. That is why we consider and compare the properties of the fully coagulated, fully washed and nearly unstretched fibres to investigate this process step.

Table 1. Parameters kept constant within the trials with NaSCN[aq.] as solvent

Parameter	Value	
Pump rate (1,75 cm^3/round)	10 rpm	Jet stretch 0,52
Spinning jet	600 holes, 70µm	
Speed Duo 1 (v_1)	4 m/min	
Speed Duo 2 (v_2)	8,8 m/min	
Speed Duo 3 (v_3) (winding speed)	11 m/min	
Temperature drying oven	150 °C	
Temperature washing bath 1	75 °C	
Temperature washing bath 2	77 °C	

3. ANALYSIS

The fibre quality was evaluated by the single filament properties. For each investigated parameter set 30 filaments of the sample material were tested with a FAVIMAT+ from Textechno. The Strength, residual elongation, fineness and Young's modulus were considered as well as the standard deviation of each value. The testing parameters are shown in Table. 2.

4. RESULTS AND DISCUSSIONS

From Literature and own trials the following trends for the NaSCN process could be derived:

• The best fibre qualities could be obtained at polymer concentrations in the spinning dope of 16 wt.% PAN and a solvent concentration of 16 wt.% NaSCN in the spinning bath (Table 3, sample SP7). The sample SP7 shows good mechanical properties (high strength, moderate residual elongation, low variation coefficients). SP6 serves as an example of typical mechanical properties attained at a polymer concentration of 14 wt.% at comparable process conditions. These results are in accordance with the literature [3].

Nevertheless, at these high polymer concentrations in the spinning dope, the fibre homogeneity (CV-Values) gets worse over time, which is linked with an increase of the pump pressure. A PAN concentration of 16 wt.% seem to be near the critical solvability level of the solvent. Thus, undissolved polymer particles in the spinning solution are occurring, which increasingly block the spinning holes and filters over time. For a stable process, the PAN concentration should be below 16 wt.% for the used polymer grade.

During the trials, it could be observed, that the best spinning behavior and fibre properties could be obtained at spinning dope temperatures of about 25 °C. That means that the spinning solution does not have to be heated up, but can be extruded at room temperature. This helps to reduce production costs. Moreover, the spinning bath should be cooled down to temperatures of about 12 °C to achieve homogenous and good fibre properties. Similar results for the spinning bath temperature are found in [3, 4, 5]. Sample SP7 is produced with these conditions and shows low CV-values and good mechanical properties after the coagulation and washing of the fibres.

Table 2. Parameters for single filament testing

Property	Pre-load[cN/tex]	Clamping length[mm]	Testing speed [mm/min]
Fineness	0,75	25	0,625; 1,25; 1,88; 2,5
Strength and residual elongation	0,5	25	6,25; 12,5; 18,8; 25

Table 3. Parameters and relating mechanical properties for different samples to see the influence of PAN concentration and process Temperatures on the fibre properties

	PAN Konz.	T Dope	T KB	NaSCN KB	NaSCN WB1		strength [cN/tex]	-CV-	Residual elongation	-CV-	Titer	-CV-
SP6	14	25	18	15,9%	9,3%		7,88	7,09	35,84	11,03	5,45	6,84
SP7	16	25	12	16,3%	9,0%		14,58	2,65	27,55	7,02	5,81	3,22
SP8	16	25	12	16,5%	8,2%		12,52	6,19	26,34	11,08	5,47	6,69
SP9	16	25	12	15,5%	8,1%		13,07	17,71	25,79	21,84	5	16,36

• A high solvent concentration in the spinning bath decreases the coagulation speed and allows a higher stretching degree inside the spinning bath (jet stretch) [2]. Thus higher NaSCN concentrations have a positive effect on the fibre quality and process stability. The comparison between samples produced with 13 wt.% to 15.5wt.% NaSCN inside the coagulation bath reveals that the higher solvent concentration has an advantage in dependence on the degree of jet stretch and the used polymer grade (see Table 4). At the given jet stretch of 0.52, the residual elongation of the fibre samples increases with increasing NaSCN concentration of the coagulation bath (Table 4, sample A, B, C). At the same time, the strength of the fibres decreases. This indicates, that the fibres get orientated by the jet stretch inside the coagulation bath. At lower NaSCN concentrations inside the coagulation bath, the fibres coagulate quicker because of the"harder" coagulation conditions and the orientation of the fibres can not relax before the solidification of the polymer.

4.1. Effects on production costs

Based on these findings, a model process was developed in cooperation with partners from industry (EPC Engineering & Technologies GmbH). A cost analysis was performed according to the assumptions in Table 5. As a result of this process cost scenario, production costs of 4.83 € per kilogram of manufactured precursor yarn are determined for the NaSCN process. Similar considerations were performed for DMSO and DMF as the solvent. In case of DMSO, the calculation resulted in a price of 6.59/kg precursor and for DMF in a price of 6.49€. Thus the use of NaSCN offers cost advantages of about 25%. The production costs are highly sensitive to changes in acrylonitrile prices, electricity prices and labor costs.

Table 4. Parameters and relating mechanical properties for different samples to see the influence of NaSCN concentration in the spinning bath on the fibre properties

	PAN Konz.	T Kessel	T KB	NaSCN KB	NaSCN WB1		Festigk. [cN/tex]	-CV-	Restdehnung	-CV-	Titer	-CV-
B	14	23,3	18	13,1%	5%		11,39	3,42	25,69	18,3	5,15	16,99
C	14	33,5	16,9	14	5 %		9,88	3,78	30,15	16,17	5,1	2,35
D	14	22,8	18	15,4%	8,5%		8,91	7,45	35,07	12,12	5,36	5,53

Table 5: Assumptions for the model process and cost analysis

Characteristic	**values**
Production capacity	3400 t/a Precursor
PAN-concentration in spinning dope	15 wt% PAN
Temperature spinning dope	20 °C
Temperature coagulation bath	10 °C
Production waste	5 %
Maintainance costs	3,5 % of Investment for plants
Production time	24 h/d; 330 d/a
Men power	10 plant operators, 1 Shift supervisor
Produktionsstandort	Germany

5. CONCLUSIONS

Carbon fibres are one of the most interesting and promising materials for different fields of application like transportation, construction and electricity. About 90 % of all carbon fibres are based on PAN [6]. Thus, the improvement of this process route is important to bring down production costs and make carbon fibres available for more fields of application. This can help to reduce emissions and accelerate the technological progress in many fields of industry.

In the past, the use of the toxic and environmental unfriendly organic solvents was more economic especially if the companies produce both textile and technical fibres. This is the reason, why most of the producers work with these solvents until today. But the technical progress in related fields like the wastewater treatment and new political regulations changed this situation. The traditional process route with DMF or DMAc does not seem to be more economic anymore.

Modern reverse osmosis plants work 60 times more efficient than the commonly used distillation plants. This technology is not suited for organic solvents but can be used with the inorganic solvents NaSCN or $ZnCl_2$. Moreover, work safety and health protection becomes more important in all countries of the world. In Europe and China, the allowed limiting values of the reprotoxic solvents in the consumer goods have been seriously reduced. The industrial use of these solvents will be forbidden in Europe from 2020. The import of consumer goods is also tightly controlled. Producers have to meet these limits if they want to sell their goods to Europe or China. Thus, the inorganic solvents become more attractive and more cost-efficient in the future.

In the paper, some of the main characteristics of the spinning process with NaSCN[aq.] as solvent have been presented. The process differs from the spinning process with organic solvents but leads to a more efficient and economic production. The resulting fibre price is about 25 % lower than in case of DMSO or DMF.

The process parameters for appropriate fibre characteristics differ from the process with organic solvents and there is only a little Know-How available from the literature. For this reason, the process has to be investigated in more detail to develop adjusted equipment and a more cost efficient carbon fibre production process to bring down carbon fibre price in the future.

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