Technology Development for the Sustainable Production of High-purity Chitosan Filament Yarns with High Performance and Functionality (Chion)

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Introduction and Objective

In the 21st century, society's high level of interest in using products that are manufactured in a sustainable way and minimize environmental impact grows constantly. In this context, the textile and fiber industry has the opportunity to accelerate the development of organic products from renewable raw materials, such as chitin and chitosan, in order to respond to the social, national and international demand for organic products.

The biopolymer chitin and its derivative chitosan are versatile and well-known materials used in (bio-)medicine and pharmacy. However, they are rarely available as a pure textile product. Chitin is the second abundant biopolymer after cellulose with $1.5\text{-}10^5$ t/a [1]. The semi-crystalline structure and stable network of molecular bonds limit the solubility of chitin significantly. Therefore, chitin derivative chitosan is being primarily addressed by research and material development. The chitosan class of materials demonstrates excellent biological and antibacterial properties as well as cell colonizability and biodegradability [2, 3]. In the last few years, considerable research efforts have been made to develop efficient chitosan products; nevertheless, the availability of pure chitosan multifilament yarns with long-term stability is currently extremely limited [4]. Likewise, a robust, scalable process for manufacturing of high-performance chitosan filament yarns is urgently needed, as current products are severely limited in terms of mechanical properties. Due to the natural provenance and variability of raw material properties, such as degree of deacetylation (DD), molecular weight (M_w), etc. There are still major challenges in producing of chitosan multifilament yarns using the acid- and alkali-dominated manufacturing processes established so far.

The aim of the IGF research project 'CHION' (21168 BR) was therefore to develop a robust wet-spinning process based on ionic solvents for manufacturing of multifilament yarns from 100 % chitosan with high performance and functionality.

Obtained Results

By using ionic liquids (IL), lower cost chitosans with lower M_w and DD < 90% became accessible to the wet-spinning process for the first time. A high content of acetamide groups in chitosan with low DD (< 90%) leads to the increase of intermolecular interactions, which resulted in improved mechanical performance with tensile strengths up to 28 cN/tex and proper textile processing of chitosan multifilament yarns. The extensive research of chitosan-IL-systems with different chitosan proveniences, M_w and DD 60 – 90% with imidazol-based IL was initially carried out on a laboratory scale for monofilaments. Based on the results, important process parameters and promising chitosan-IL combinations were obtained and the developed process was successfully transferred to the multifilament scale. A structural-mechanical adjustment of the properties of the chitosan multifilament yarns was a fundamental object of the research work: Each development step was systematically monitored by material and process characterizations and analyses. Further investigations included the solubility of chitosan in IL, viscosity studies, fiber morphology and geometry, chemical and physical material properties, crystallinity and degradation behavior, as well as on the influence of controlled fiber drawing during the spinning process according the adjustment of the textile-physical properties. By integrating acid- and temperature-sensitive agents into the spinning dope, the functionality of the chitosan multifilament yarns was demonstrated. As a result of the precise tailoring of the molecular fiber properties and the developed spinning process parameters, a robust, scalable wet-spinning process is now available for manufacturing of pure chitosan multi-filament yarns in pilot scale. Finally, the textile processability of the chitosan multifilament yarns was investigated and demonstrated by knitting, weaving and braiding processes.

Investigation of the solubility of chitosan in IL and spinning dope preparation

Initially, the dissolving ability of IL for chitosan was investigated and evaluated. Through systematic experiments, 19 commercially available chitosan materials of different qualities (e.g. medical grade chitosan, industrial grade chitosan, etc.), provenance (e.g. shrimps, crabs, fungal-based chitosan), degree of DD (60 – 90%) and M_w were characterized and their solubility evaluated in promising imidazole-based ILs. It was demonstrated that especially short-chain ILs in combination with acetate anions possess excellent solubility for all investigated chitosans (Figure 1). From the results of the dissolution tests, promising chitosan-IL combinations were defined for further process development steps.

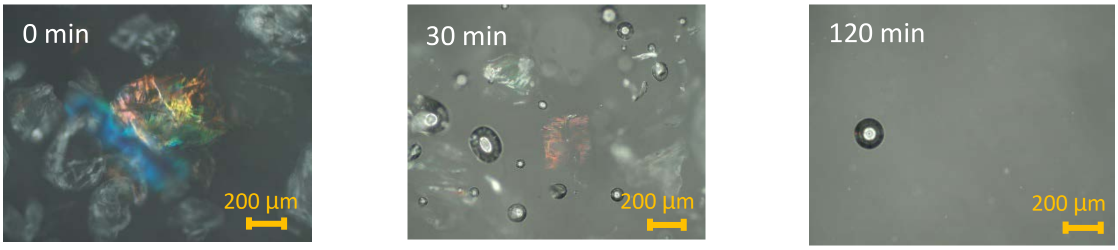


Figure 1: Light microscopic study of the dissolution process of a medical chitosan with degree of deacetylation of 75 % in IL at process temperature of 80 °C; complete dissolution after 120 min

The preparation of the chitosan-IL spinning dopes (Figure 2, left) was carried out using thermal processing in solids concentrations of up to 8 wt.-% and was monitored and evaluated by rheological investigations as a function of the temperature and shear rate (Figure 2, right). To investigate the stability, processability and spinnability of the homogeneous chitosan-IL-solutions, the spinning dopes were processed into monofilaments on a laboratory scale. In particular, fiber formation was analyzed as a function of the chitosan raw materials and process parameters, such as solid content, temperature, diffusion rate and residence time in the coagulation medium. The obtained results demonstrated, that all investigated chitosan-IL-combinations can be processed into pure chitosan fibers. Therefore, it was successfully proved that ILs are a suitable and promising solvent for the manufacturing of chitosan multifilament yarns.

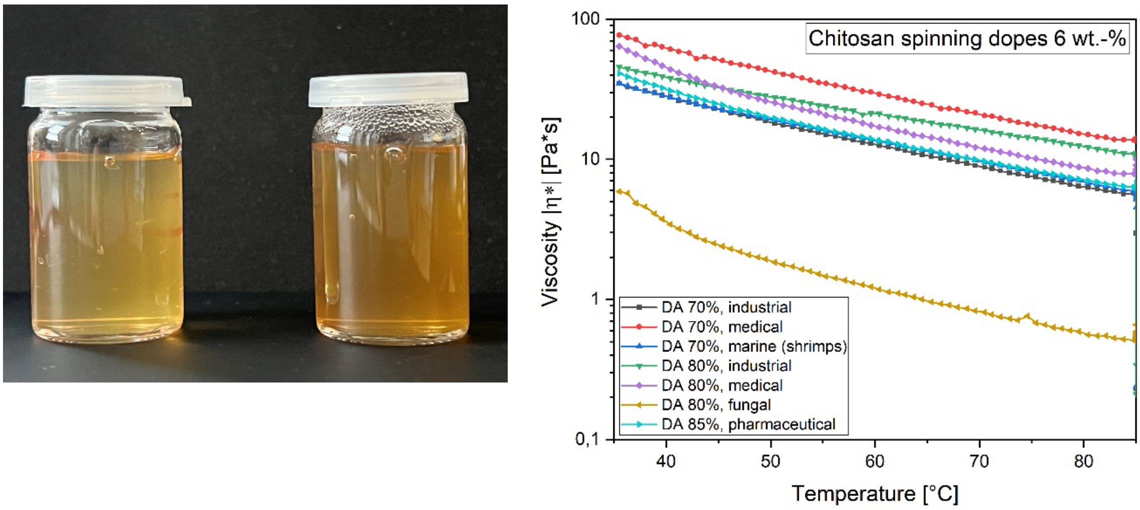
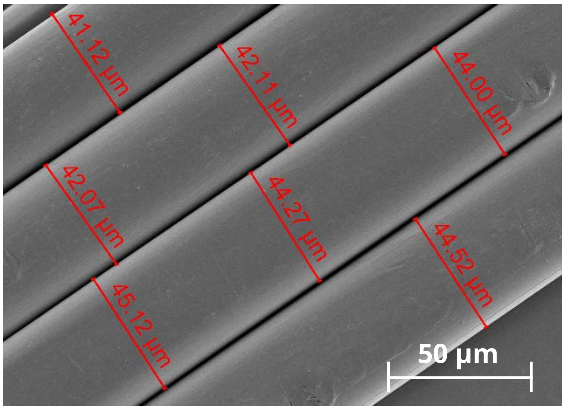


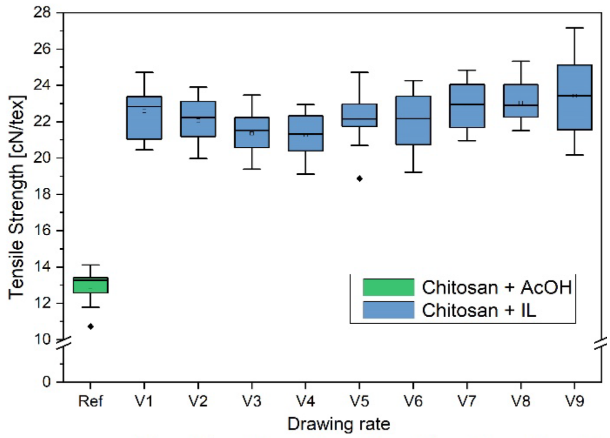
Figure 2: Spinning solutions of chitosan and IL (left) and results of rheological investigations of the chitosan-IL spinning dopes with 6 wt.-% solids content as a function of temperature and chitosan raw material (right).

Wet-spinning of the chitosan multifilament yarns

In the following step, the basic methods developed on the laboratory scale were successfully transferred to a wet-spinning process on a pilot scale. The chitosan multifilament yarns were spun on the wet-spinning plant (FOURNÉ MASCHINENBAU GMBH) of the ITM. The pilot spinning plant is specially designed for R&D process developments and enables, in particular, test trials with 2 – 60 liters of spinning dope.

For the spinning trials, chitosan-IL spinning dope was first filtered and degassed under specific temperature and pressure conditions. Different spinneret geometries were used for multifilament spinning, including 78 holes of 90 µm (90 µm/78f) and 24 holes of 160 µm (160 µm/12f), respectively. The prepared tempered spinning dope was extruded into a coagulation bath with deionized water as medium. Overall yarn counts of about 50 – 65 tex and filament diameters of about 30 – 50 µm were achieved depending on the spinneret geometry. In order to achieve tailored functionalities, such as high mechanical strength and crystallinity as well as improved molecular orientation, the influence of fiber drawing during the spinning process was systematically investigated. The produced yarns were analyzed for their mechanical and textile-physical properties and compared with conventionally produced acetic acid (AcOH) based chitosan yarns. The DD of the raw material has an important role in this context: a high content of acetamide groups in chitosan with low DD (< 90%) leads to an increase in intermolecular interactions, resulting in improved mechanical properties. The results obtained demonstrate a high functionality as well as significantly improved mechanical properties of the IL spun chitosan multifilament yarns compared to the conventional chitosan fibers (DD 90%) (Figure 3, right). By means of elaborated drawing parameters, tailor-made textile-physical properties, such as elasticity or tensile strength, can be adjusted according to defined requirements.





	V1	V2	V3	V4	V5	V6	V7	V8	V9
Jet-stretch	0,34	0,36	0,38	0,4	0,42	0,46	0,5	0,46	0,46
Total drawing	0,46	0,46	0,46	0,5	0,54	0,59	0,64	0,64	0,7

Figure 3: SEM images of the chitosan multifilament yarns from IL (left) and filament tensile strengths in cN/tex of the chitosan multifilament yarns from IL as a function of drawing rate (right)

Textile processing of the chitosan multifilament yarns

During the final phase of the project, the textile processing of the chitosan multifilament yarns from IL into knitted and woven patterns and braids was successfully implemented (Figure 4). The technical processing of conventional chitosan yarns on textile machines has always been a challenge due to insufficient mechanical strength and knot tearing forces. Trouble-free processing in weaving, knitting or braiding processes without special yarn pretreatment or machine adaptations could not be realized so far using conventional chitosan multifilament yarns. In contrast, the chitosan multifilament yarn produced by IL offers sufficient mechanical stability and flexibility to be processed into knitted, woven or braided structures in conventional textile processes on standard industrial production machines. Additional yarn functionalization, such as sizing, further improves the processability of the material and the quality of the finished product.

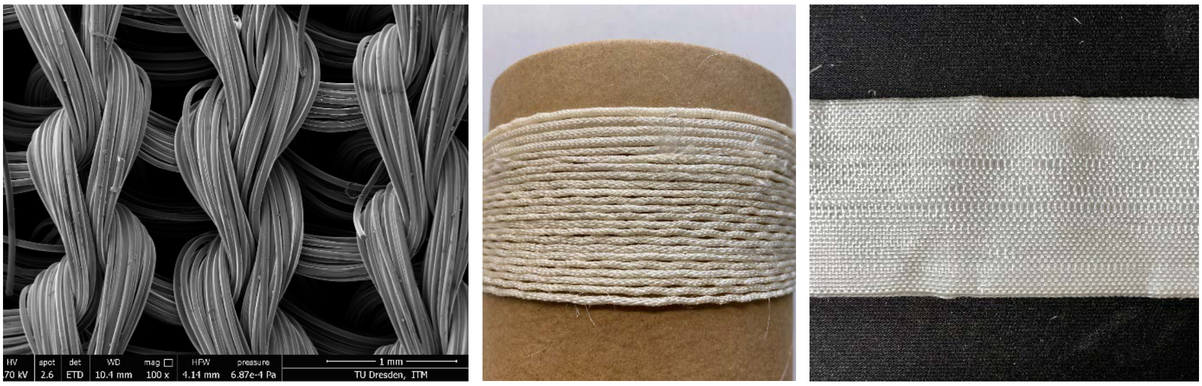


Figure 4: Examples of textile-technological implementation of chitosan multifilament yarns from IL: SEM images of chitosan knitted fabric (left), braiding process with chitosan multifilament yarn (middle) and blended fabric of chitosan (weft) and PES (warp) (right)

Conclusion

In the IGF project 21168 BR 'CHION', a technology for the manufacturing of chitosan multifilament yarns from ionic liquids was developed, enabling the tailoring of the yarn properties regarding their performance and functionality in all process stages. The material costs, the field of application and the functionalities achievable by the multifilament yarns are defined by the raw material selection. By using ionic liquids, it was possible for the first time to process lower-cost chitosans in various qualities and degree of deacetylation < 90%, previously unavailable with conventional spinning processes. From the achieved and extensively evaluated project results, required process parameters for the successful transfer of the elaborated fundamentals to a pilot scale as well as the process development for the spinning of chitosan multifilament yarns with high performance and strengths up to 28 cN/tex on a pilot solvent wet spinning plant were derived and implemented. To demonstrate the textile processability of the multifilament yarns, textile demonstrators were successfully fabricated for the first time in conventional textile weaving, knitting or braiding processes on standard industrial textile machines.

Acknowledgement

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