

RESEARCH ARTICLE

Chitin/cellulose blend fibers prepared by wet and dry-wet spinning

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We describe the wet and dry-wet spinning of multifilament cellulosic composite fibers, namely chitin/cellulose fibers. The direct solution process for the two biopolymers based on an ionic liquid as solvent represents an environmentally friendly and alternative technology to the industrially applied viscose and lyocell process. Both cellulose and chitin possess good solubility in 1-ethyl-3-methylimidazolium propionate ([C₂C₁Im][OPr]) and were spun into multifilament composite fibers. Moreover, for the first time, pure chitin multifilament fibers were obtained by dry-wet spinning. The effect of chitin addition on the filament properties was investigated and evaluated by microscopic, spectroscopic, and mechanical analyses.

KEYWORDS

blend fibers, cellulose, chitin, fiber spinning, ionic liquids

1 | INTRODUCTION

Multifilament spinning of cellulosic fibers is a complex process; traditionally, both derivatizing methods such as the viscose process and non-derivatizing processes such as the lyocell process are used on an industrial scale.^{1–3} The viscose process is a multistep procedure based on wet spinning and suffers from the disadvantages that it uses carbon disulfide as a cellulose-derivatizing agent and that highly toxic chemicals and gases are formed. The resulting fibers have pores and longitudinal as well as transversal rills on the fiber surface that reduce the tenacity of the fibers. By contrast, the lyocell process employs a direct cellulose solvent, namely *N*-methylmorpholine-*N*-oxide monohydrate (NMMO) and uses air-gap spinning. It is currently the only commercialized alternative to the viscose route. The NMMO-lyocell process represents a sustainable technology for the production of cellulose fibers, as the nearly full recovery of the solvent permits a closed-loop production process.⁴ However, due to several side reactions and by-products formed in the cellulose-NMMO-water system,

the lyocell process requires a stabilizer to reduce the chance of dangerous runaway reactions at the high process temperatures between 90 and 120°C. Unfortunately, this still does not fully guarantee for a risk-free process.⁵ Furthermore, lyocell fibers suffer from fibrillation, which limits their application in the market. Consequently, there still exists a strong need for a more flexible, cost-effective, and eco-efficient production method even though cellulose has already been utilized in man-made fiber and filament production for decades.

By contrast, the ionic liquid (IL) based direct dissolution approach provides a novel technology to manufacture cellulose-based fibers with superior properties.⁶ ILs were applied as direct cellulose solvent without using any auxiliaries for the first time in 2002 by Swatloski et al.⁷ In view of the low volatility and low toxicity of the ILs used, the IL-technology is a promising, environmentally friendly alternative to both the viscose and lyocell process.⁸ Moreover, ILs can also dissolve other biopolymers, such as chitin,⁹ lignin,¹⁰ and keratin.¹¹ As cellulose and chitin are the two most abundant biopolymers with a total production of 75 billion tons per year (10% of which is chitin), it seems

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promising to prepare the corresponding composite fibers for several reasons. First, cellulose and chitin have similar structures; the only difference is the presence of an *N*-acetyl amino group instead of a hydroxyl group on C-2 in cellulose. Consequently, chitin and cellulose are miscible and the resulting materials have improved properties benefiting from both polymers. Second, chitin itself is a promising raw material for the preparation of biomaterials with high potential in biomedical applications. It is biocompatible, non-toxic, suitable for wound and burn healing and is used in materials for tissue engineering and stem cell technologies. There is a high demand causing the Global Chitin Market value of \$803 million in 2016 to escalate, with a forecast to reach \$2940 million by 2027.¹² Beside the healthcare sector, which takes about \$309 million in 2016, chitin finds wide application in water and waste water treatment, for example, acts as a flocculating and a coagulating agent, removes metal and heavy ions from water, clarifies the water or reduces odors. In order to come up with a successful process, a clear and comprehensive classification of chitin is inevitable. The determination of material properties such as the origin of chitin, the purification performed the degree of acetylation, as well as the molecular weight and degree of polymerization is essential. Notably, the degree of acetylation¹¹ is essential to differentiate between chitin and chitosan. Unfortunately, most papers dealing with fiber spinning do not determine it. A degree of acetylation lower 70% is referred to chitosan. Chitosan is by far easier processed than chitin because chitosan has a lower degree of acetylation and is soluble in acidic media. There exist several studies dealing with the dissolution or extraction of chitin by ILs.¹³⁻¹⁷ Microwave radiation-assisted dissolution in ILs was successful accomplished leading to shorter dissolution times, for instance. A recent review covers different ILs, polymer types and dissolution conditions.¹² According to Shamshina et al.,¹⁸ the most promising ILs for chitin dissolution are imidazolium-based ILs such as 1-ethyl-3-methylimidazolium chloride, [C₂C₁Im][Cl], 1-ethyl-3-methylimidazolium acetate [C₂C₁Im][OAc], 1-butyl-3-methylimidazolium chloride [C₄C₁Im][Cl] and 1-butyl-3-methylimidazolium acetate [C₄C₁Im][OAc]. Most of these ILs possess also good solubility for cellulose and have already been used for fiber spinning.⁸ Recently, pure chitin fibers were prepared by electrospinning solutions of chitin in [C₂C₁Im][OAc].¹⁹ Materials with controllable and high specific surface area were prepared at the nanoscale using IL solutions of high-molecular weight chitin extracted with the same IL from shrimp shells. Roger et al synthesized chitin²⁰ and chitin/alginate monofilament fibers from [C₂C₁Im][OAc] that met the technical specifications (strength, water sorption) needed for wound care fibers.¹³

Here, purified shrimp shell-based chitin with a high degree of acetylation (DA > 80), from which minerals and proteins have been removed, was used for the preparation of blend fibers together with cellulose. As natural materials show variations in their composition, a defined and fully characterized chitin was chosen as starting material. Both, [C₂C₁Im][OAc] and 1-ethyl-3-methyl imidazolium propionate ([C₂C₁Im][OPr]) have already been identified as appropriate solvents allowing for the preparation of homogenous chitin/cellulose multifilament films and fibers with increased water retention capacities via wet spinning.^{9,21} Fiber formation during wet spinning mainly occurs in the nozzle and in the coagulation bath while in dry-wet spinning pre-

orientation occurs in an air-gap and allows for higher stretching values compared to wet-spinning. This has a strong influence on the mechanical properties as a higher orientation of the crystallites is achieved. Cellulosic fibers spun by this technique revealed excellent mechanical properties such as high tenacity (up to 50 cN/tex) at high modulus values (2000-2500 cN/tex).^{6,8} Herein, our latest research findings in the wet and dry-wet spinning of chitin/cellulose composite fibers are presented. Multifilament cellulose/chitin fibers were continuously spun both via wet and dry-wet spinning and showed excellent water retention capacities and filament tenacities allowing the preparation of non-woven, knitted fabrics and yarns.

2 | EXPERIMENTAL

2.1 | Materials

Chitin powder was purchased from Aldrich (shrimp shells, degree of polymerization, DP = 4400, degree of acetylation, DA = 88%). The purification process was performed in 1 kg batches including demineralization and deproteinization. A detailed description is reported elsewhere.^{9,21} α -Chitin with a DA of 86% and DP of 680 was used for all spinning trials. Linters cellulose with a DP of 1400 was used as received for wet spinning; Sappi cellulose (DP 590) was used as received for dry-wet spinning. [C₂C₁Im][OPr] was purchased from Iolitec.

2.2 | Preparation of the spinning dope

Cellulose pulp sheets were sliced and milled to a fineness of 0.5 mm by Retsch ZM1000 mill. Spinning dopes were prepared inside a two-necked round-bottom flask equipped with a KPG stirrer. Chitin and cellulose were subsequently added in small portions at room temperature to the IL. The solution was heated to 110°C and kept for 30 to 90 minutes until a clear solution was obtained. For degassing, the solution was kept for 2 hours at 100 mbar at that temperature prior to transfer to spinning vessel.

2.3 | Spinning trials

Two different fiber spinning technologies were applied in order to optimize fiber performance and develop a suitable spinning process for cellulose/chitin blend fibers, namely wet and dry-wet spinning.

For wet spinning, the prepared dopes were spun through a 200-hole spinneret with an orifice diameter of 50 μ m into a water coagulation bath with a bath temperature of 95°C. Stable, continuous multifilament wet spinning was established at a feed rate of 9.6 g min⁻¹ and an injection speed of 9.8 m min⁻¹, respectively. The first godet was run at 6.3 m min⁻¹ resulting in 35% shrinkage in the aqueous coagulation bath. The second godet was run at 6.4 m min⁻¹ to achieve a 35% draw ratio in the following heating channel at 90°C.

After two washing steps, to prevent filament stickiness, the multi-filament was coated with surfactant before drying on two heated twin-godets at 90°C.

Dry-wet spinning was performed with a laboratory piston spinning system (Fourné Polymertechnik, Germany) through 64-hole spinnerets with a diameter of 150 µm and a length: diameter ratio of the spinneret capillary (L/D) of 4:1 (Enka Tecnica, Germany). The cylinder pressure was measured with a sensor and limited with a torque-limiting coupling. The spinning cylinder was heated to 70°C and loaded with a piece of the solidified dope (250 g), softened by slight heating. Filaments were spun over a 1 cm airgap into a water bath (25°C), where the formed filament was led over a teflon guide roller (at 20 cm depth) and via another guide onto a godet couple. The extrusion velocity was varied between 3.1 and 5.3 m min⁻¹, and the draw ratio (DR) varied between 1.3 and 2.3 by adjusting the take-up speed (7–10 m min⁻¹). Zero-shear viscosities higher than 500 Pa s are suitable for dry-wet spinning according to our experience and spinning line modification.

The IL recycling was done by rotary evaporator allowing the almost complete recycling of the IL (>99.5%).

2.4 | Characterization

Rheological measurements of the spinning dopes were accomplished on a Rheometrics (SR 500) rheometer equipped with parallel plate geometry and a Peltier temperature control system. Shear rates varied between 0.5 and 100 seconds⁻¹. The diameter of the plate was 25 mm and the gap between them 1 mm. The viscoelastic properties of the spinning dopes were studied by dynamic oscillatory experiments at temperatures between 30 and 100°C, which allow for the determination of the storage (G') and the loss modulus (G'') as well as of the complex viscosity $|\eta|$. Using the principle of frequency-temperature superposition, master curves were obtained. The zero-shear viscosity (η^0) was calculated by the Carreau model.²²

Scanning electron micrographs were recorded on a Zeiss Auriga field emission scanning electron microscope equipped with an Everhart-Thornley secondary-electron detector and an in-lens secondary-electron detector. Both fiber surface structure and fractures were analyzed.

X-ray diffraction patterns were measured by the WAXD instrument D/Max Rapid II from Rigaku. The instrument has a curved imaging plate area detector, which is able to collect the complete Debye rings of samples measured in transmission. The 2D images of blank tests were removed from the 2D images of fiber diffraction to reduce the effect of background diffraction. The degree of preferred relative orientation of the crystallites (P.O.) was calculated according to Equation (1)

$$\text{P.O.} = (180^\circ - \text{FWHM})/180^\circ. \quad (1)$$

Mechanical fiber properties were measured on a Textechno Favimat tensile tester at 20°C with an average result from 20 different

single filaments. Fineness was obtained as weight in gram per 10 000 m in length (dtex).

Tendency to split was evaluated according to the following method: Single filaments (2.5 cm length) were fixed on a frame and put in a beaker containing 20 mL distilled water and 9 g zirconia balls (0.75–1 mm). Testing was performed in a Labomat over 3 hours at 30°C and a circulate rate of 50 U min⁻¹. Depending on the number of fibrils determined by light microscopy, marks ranging from 1 to 6 were assigned (1 = no fibrillation, 6 = strong fibrillation). Total number of investigated areas/fibers was 16 per sample.

Water retention capacity was determined according to DIN 53814. Four samples at 100 mg each were weighed in spinning tubes. The tubes were put into demineralized H₂O for 2 hours and afterwards centrifuged for 20 minutes at 4000 rpm. The tubes were weighed to determine the weight of the wet samples, then dried at 105°C until constant weight to determine the dry weight of the samples. The WRV was calculated as follows: $\text{WRC} [\text{wt}\%] = (m_{\text{wet}} - m_{\text{dry}})/m_{\text{dry}} \times 100$.

3 | RESULTS AND DISCUSSION

3.1 | Rheological behavior and fiber spinning

Independent of the cellulose/chitin ratio, a total polymer concentration of 8 wt% was found suitable to establish a stable wet spinning process with both ionic liquids. A basic requirement for the performance of spinning trails is the exact knowledge of the viscoelastic behavior of the spinning dope. In earlier studies, [C₂C₁Im] [OAc] and [C₂C₁Im] [OPr] were identified being both excellent solvents for chitin, among which [C₂C₁Im] [OPr] allowed for achieving higher biopolymer concentrations.⁹ Several solutions of chitin and cellulose in [C₂C₁Im] [OPr] were investigated. Figure 1 shows the frequency sweep of 25:75 and 50:50 chitin/cellulose blend solutions in [C₂C₁Im] [OPr] at $T = 100^\circ\text{C}$. With increasing shear rate, both the loss and storage modulus increased and a viscoelastic behavior was observed. Zero-shear viscosities of 152 and 77 Pa s were achieved for biopolymer blends in [C₂C₁Im][OPr] using chitin: cellulose ratios of 25:75 and 50:50, respectively. For any further increase in the chitin content, a reduction in DP would be necessary in order not to sacrifice on the high degree of acetylation.

For dry-wet spinning, the total biopolymer concentration could be increased up to 12 wt% as higher zero-shear rates (around 500 Pa s) are acceptable. In parallel, a lower molecular weight cellulose (DP 590) was used allowing for these high concentrations. Higher dope concentration resulted in higher take-off speeds, higher process rates and an overall increased resource efficiency of the process. Apart from higher polymer concentrations in the spinning dope, a higher chitin content (>50 wt%) in the fibers could be realized. Indeed, 100% chitin fibers were successfully spun; nevertheless, the spinning process had to be modified in order to establish stable spinning conditions. To the best of our knowledge, these are the first pure chitin multifilament fibers produced by dry-wet spinning from ILs. Detailed

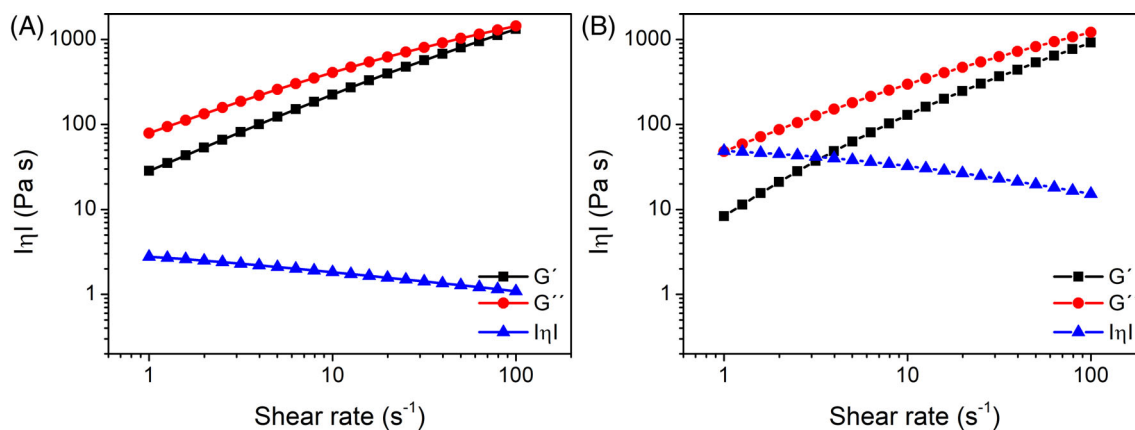


FIGURE 1 Storage modulus G' , loss modulus G'' and complex viscosity $|\eta|$ of 75:25 (left) and 50:50 (right) chitin/cellulose blend solutions in IL (8 wt% total concentration) at 100°C [Colour figure can be viewed at wileyonlinelibrary.com]

TABLE 1 Spinning parameters and conditions used for wet and dry-wet spinning of the chitin/cellulose blend fibers

Process	Chitin/cellulose blend ratio	Dope temperature (°C)	Dope concentration (wt%)	Total draw ratio (%)
Wet spinning	0/100	100	8	30 ^a
	25/75	95	8	35
	50/50	95	8	30
Dry-wet spinning	0/100	68	12	126
	25/75	68	12	126 ^a
	50/50	68	12	126
	100/0 ^b	90	8	26

^aHigher stretching possible.

^bNo continuous spinning trail.

spinning conditions are summarized in Table 1. For chitin/cellulose composites, fibers draw ratios up to 126% were realized instead of 35% draw ratio for wet-spun fibers.

3.2 | Structural analysis of the fibers

The crystalline structure of the fibers obtained was analyzed by X-ray diffraction; diffraction patterns are shown in Figure 2. The cellulose fibers displayed a typical cellulose II structure independent from the spinning procedure.

The most significant diffraction peaks of cellulose were observed at $2\theta = 12.2^\circ$ [−110], 20.2° [110], 21.4° [020], and 28.3° [−113].²³ Chitin crystallizes in the α -chitin structure typically for shrimp-based chitin²⁴; the major diffraction peaks of chitin were $2\theta = 8.8^\circ$ [020], 12.8° [101], 19.4° ([040]/[110]), 23.0° [130], and 26.2° [013]. Additional minor signals at 32° , 34.6° , and 38.7° correspond to the [113], [152], and [063] reflexes, respectively. In case of chitin/cellulose composite fibers the diffraction peaks overlapped strongly with each other, so the exact determination of the phase composition by X-ray diffraction was impossible. Nevertheless, it can be clearly seen that even a low amount of chitin within the composite fibers contributes to a change

of the diffraction pattern. The [020] and [013] reflexes of chitin appeared for a chitin content of 25 wt%, while no significant changes of the [110] reflex of cellulose were observed. By a further increase of the chitin content to 50 wt% the main peaks of the cellulose at $2\theta = 12.2^\circ$ and 28.3° decreased and completely disappeared, as shown in Figure 3. Evaluation of the azimuthal scan of the [110]/([040]/[110]) reflex between 19.4 and 20.2° allowed for determining the preferred orientation (P.O.) of the crystalline fraction (Table 1). While wet spun cellulose fibers had P.O. values between 80% and 86%, P.O. values of the dry-wet spun cellulose and chitin/cellulose composite fibers ranged from 75% to 77%. In contrast, 100% chitin dry-wet spun fibers again possessed a high orientation of 86%. Since high orientation is usually a result of higher stretching, higher values should in principle be achieved for dry-wet spun fibers. Accordingly, differences in orientation must result from the different spinning conditions. Thus, lower stretching during wet spinning allows for a better alignment of the chitin crystallites during spinning and coagulation while higher polymer concentration and higher feed rates in case of the chitin/cellulose composite system result in lower orientation.

Characterization of the fiber surface and fracture break by SEM revealed homogenous, nonporous composite fibers. Figure 3 shows wet and dry-wet spun composite fibers with a chitin content of

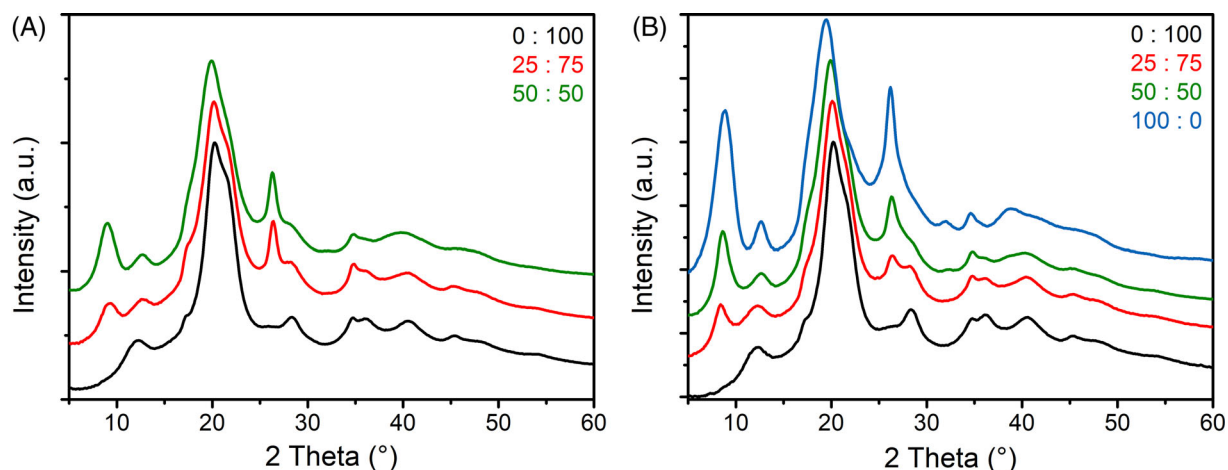


FIGURE 2 Diffraction patterns of chitin, cellulose, and cellulose/chitin blend fibers obtained by wet spinning (left) and dry-wet spinning (right) [Colour figure can be viewed at wileyonlinelibrary.com]

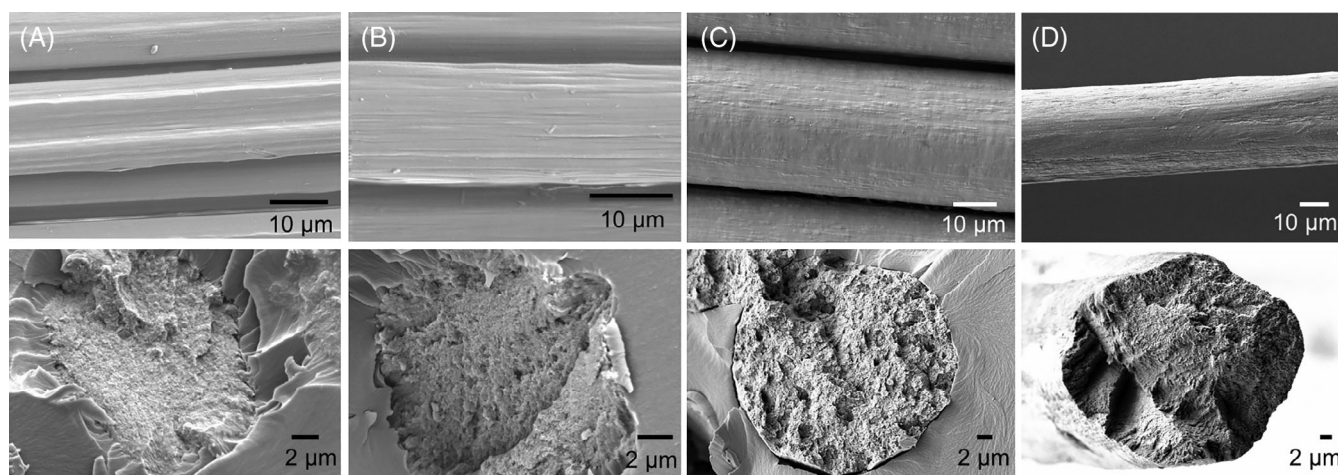


FIGURE 3 SEM micrographs of 25:75 (A, C) and 50:50 (B, D) chitin/cellulose composite fibers: wet (A, B) and dry-wet spun (C, D)

25 and 50 wt%, respectively. Fiber diameters ranged from 13 to 31 μm . In agreement with X-ray diffraction measurements no phase separation was observed. Compared to results reported in earlier work,²¹ the fiber surface obtained by coagulation in water was rough and structured compared to those using a sucrose/water bath. Here, the surface structure was again strongly influenced by the coagulation conditions. Water as coagulation media resulted in fibrous, structured fiber surfaces instead of smooth surfaces obtained by the sucrose/water mixtures. Up to a chitin content of 50 wt%, the spherical shape of the fibers was preserved, while the pure chitin fibers exhibited irregular fiber fractures due to instable spinning conditions, as shown in Figure S1.

3.3 | Mechanical properties of the blend fibers

Generally, the spinning conditions have a significant influence on the mechanical properties of the fibers. First, wet spinning resulted in a

lower fineness of the cellulose and composite fibers compared to fibers prepared by dry-wet spinning. Filament fineness of the wet spun and dry-wet spun fibers were 2.0 to 2.5 and 9 to 12.5 dtex, respectively. Usually, due to a higher polymer orientation, man-made cellulose fibers obtained by dry-wet spinning (lyocell) possess higher tenacities than those prepared by wet spinning (viscose). Accordingly, the tenacity of the pure cellulose fibers prepared by dry-wet spinning (20 cN/tex) was higher than the one for wet spun fibers (12.5 cN/tex). In case of chitin/cellulose composite systems, two different trends were observed for each spinning process (Figure 4).

While for the wet spun composite fibers the tenacity increased slightly to 15 cN tex^{-1} up to a chitin content of 50 wt%, the addition of chitin resulted in a decrease to 12 to 13 cN tex^{-1} in dry-wet spinning, independent of the chitin content. Thus, addition of chitin to cellulose decreases the intermolecular interaction at the interface of the structural elements, since the acetamide groups of chitin impede the packing of the cellulose macromolecules. With increasing chitin content, the E-modulus of wet spun fibers increased to 1000 cN

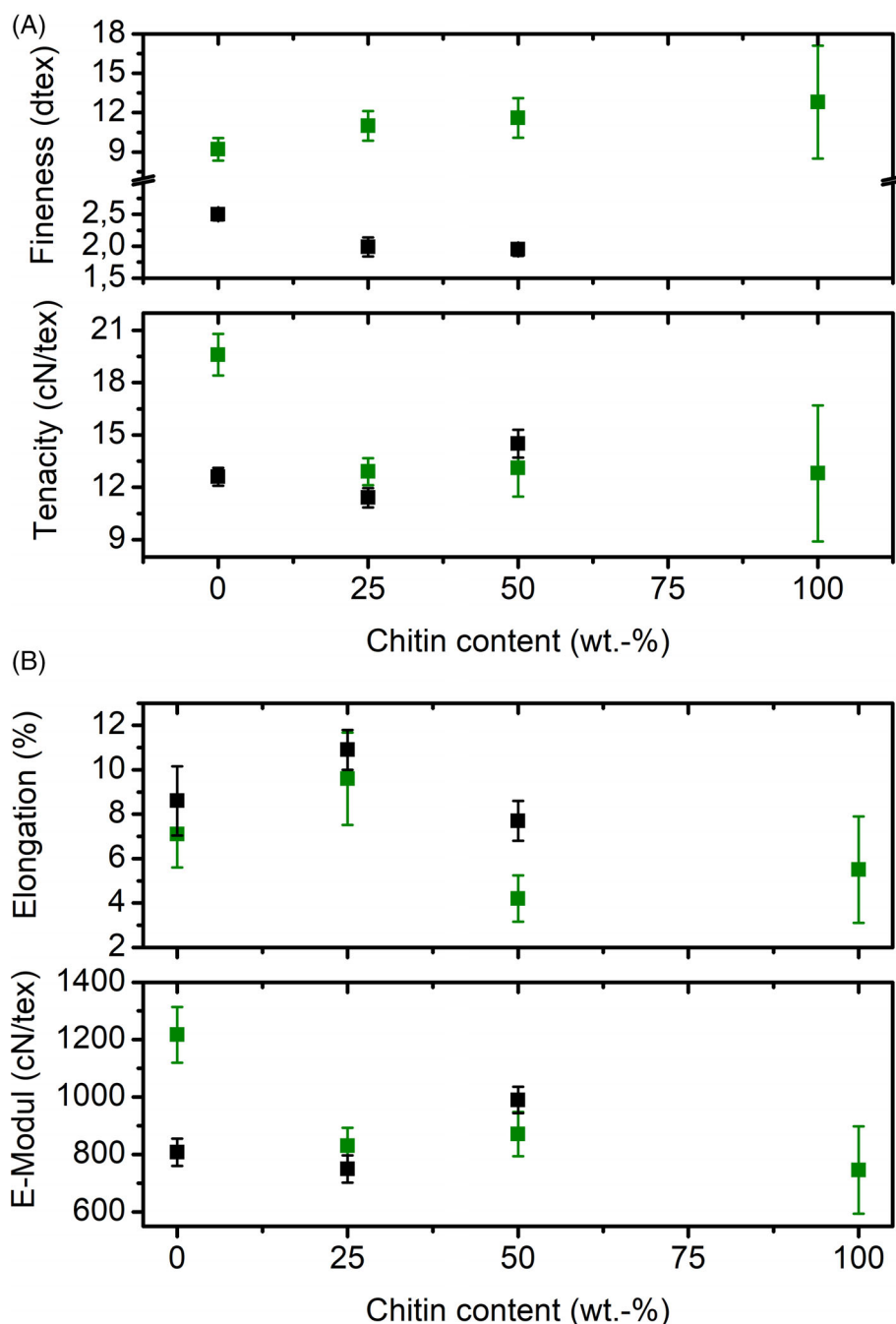


FIGURE 4 Tensile properties of the blend fibers obtained by wet spinning (black) and dry-wet spinning green) [Colour figure can be viewed at wileyonlinelibrary.com]

tex^{-1} , while for the dry-wet spun it decreased from 1200 to 750 cN tex^{-1} . Table 2 provides a comparison of the properties of fibers obtained by wet and dry-wet spinning, respectively, with literature data. Highest tenacities up to 436 MPa have been reported for fibers 50 μm in diameter spun from DMAc/LiCl as solvent.²⁵ Dry-wet spun monofilament chitin fibers, using $[\text{C}_2\text{C}_1\text{Im}][\text{OAc}]$ as solvent reportedly possess tenacities between 80 and 260 MPa, though again with large fiber diameters between 55 and 130 μm .^{13,16,20,26} Overall, all reported fibers have too large fiber diameters while the chitin/cellulose composite fibers reported here have diameters in the range of 13 to 31 μm . Equally important, the chitin/cellulose composite multi-filament fibers reported here have tenacities between 190 and

250 MPa, thereby outrivaling most existing systems. They also show much higher elongation between 6% and 11% compared to published IL-based fibers, which have elongations in the range of 2.9% to 5%.

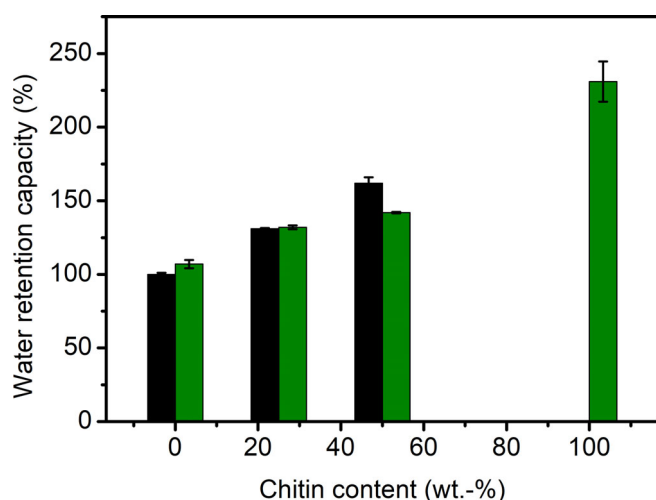
3.4 | Water retention capacity and fiber splitting

As reported earlier, chitin/cellulose composite fibers possess an increased water retention capacity (WRC) compared to pure cellulose fibers.²¹ Results for the composite fibers presented here are shown in Figure 5.

TABLE 2 Comparison of fiber properties of chitin-based fibers from the literature with fibers of this work

Chitin: cellulose blend ratio/used IL	Spinning process	Diameter (μm)	Fineness (dtex)	Tenacity (MPa)	Elongation (%)
25:75 [C ₂ C ₁ Im][OPr] ²¹	Wet, multifilament	15	2.4	294	5
25:75 [C ₂ C ₁ Im][OPr]	Wet, multifilament	13	2.0	179	11
50:50 [C ₂ C ₁ Im][OPr]	Wet, multifilament	13	2.0	218	8
75:25 [C ₂ C ₁ Im][OPr]	Dry-wet multifilament	31	11.0	194	10
50:50 [C ₂ C ₁ Im][OPr]	Dry-wet, multifilament	33	13.1	197	5
0:100 [C ₂ C ₁ Im][OPr]	Dry-wet multifilament	20-50 ^a	12.8	192	6
0:100 [C ₂ C ₁ Im][OAc] ¹⁶	Dry-wet, monofilament	130	n.d.	80	5.0
0:100 [C ₂ C ₁ Im][OAc] ¹³	Dry-wet, monofilament	80	n.d.	256	4.5
0:100 [C ₂ C ₁ Im][OAc] ²⁶	Dry-wet, monofilament	55	n.d.	146	4.3
0:100 DMAc LiCl ²⁵	Wet, multifilament	50	n.d.	436	2.9

^aIrregular fiber fractures.

**FIGURE 5** Water retention capacities of wet spun (black) and dry-wet spun fibers (green) [Colour figure can be viewed at wileyonlinelibrary.com]

With increasing chitin content, the WRC increased linearly independent of the spinning process. Similar values were obtained and ranged from 130% to 160% for fibers containing 50 wt% chitin. Notably, the WRC of pure chitin fibers reached 230%.

Finally, the tendency to split, which is important for textile and technical application of cellulosic fibers, was investigated. Lyocell fibers tend to split, which is unfavorable and leads to a peach skin effect in textiles. Figure S2 shows the microscopic images of both cellulose and chitin/cellulose composite fibers. For all wet spun fibers, no fibrillation was observed at all. The same results were observed for the dry-wet spun composite and chitin fibers.

4 | CONCLUSIONS

IL-based chitin/cellulose spinning dopes were successfully processed into multifilament fibers by dry-wet and wet spinning, respectively. Chitin, which is usually a waste product, was

successfully transferred into blend fibers containing up to 50 wt% chitin. The effect of chitin addition on the filament properties of cellulose was investigated by microscopic, spectroscopic, and mechanical analysis. The received fibers exhibit textile mechanical properties that rival those of conventional cellulosic fibers, such as viscose. New, interesting and promising intrinsic properties have been realized through biopolymer blending, in particular high water-retention capacity and no fibrillation. The IL-based process allows for a facilitated and efficient access to natural biopolymers such as chitin and cellulose and for establishing a product technology platform based on these renewable sources.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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