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Multifilament cellulose/chitin blend yarn spun from ionic liquids

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ABSTRACT

Cellulose and chitin, both biopolymers, decompose before reaching their melting points. Therefore, processing these unmodified biopolymers into multifilament yarns is limited to solution chemistry. Especially the processing of chitin into fibers is rather limited to distinctive, often toxic or badly removable solvents often accompanied by chemical de-functionalization to chitosan (degree of acetylation, DA, <50%). This work proposes a novel method for the preparation of cellulose/chitin blend fibers using ionic liquids (ILs) as gentle, removable, recyclable and non-deacetylating solvents. Chitin and cellulose are dissolved in ethylmethylimidazolium propionate ([C2mim]$^+$[OPr]$^-$) and the obtained one-pot spinning dope is used to produce multifilament fibers by a continuous wet-spinning process. Both the rheology of the corresponding spinning dopes and the structural and physical properties of the obtained fibers have been determined for different biopolymer ratios. With respect to medical or hygienic application, the cellulose/chitin blend fiber show enhanced water retention capacity compared to pure cellulose fibers.

1. Introduction

Cellulose as most abundant renewable organic material produced in the biosphere is a linear homopolymer composed of D-anhydroglucopyranose units (AGUs), which are linked by β-(1-4)-gylcosidic bonds. The second most abundant organic material of very similar chemical structure compared to cellulose is chitin, which can be isolated from manifold biological sources, e.g., from shrimp-shells or fungi. Chemically, chitin can be seen as a derivative of cellulose, acetamidated at the C2-carbon with varying total amount and distribution (β-(1-4)-N-acetyl-D-glucosamine).

Both biopolymers are well known and all their specific properties, their processing as well as the resulting materials have been summarized in various reviews (Jayakumar, Menon, Manzoor, Nair, & Tamura, 2010; John & Thomas, 2008; Khor, 2002; Klemm, Heublein, Fink, & Bohn, 2005; Qiu & Hu, 2013; Vroman & Tighzert, 2009).

Very important classes of materials based on cellulose are textile multifilament fibers, well established in clothing, hygienic/medical applications, and fully or partially bio-based composites or in technical filtration. There, the technical fabrication of cellulose fibers is almost exclusively based on processing derivatives or solutions of cellulose from specific solvents.

Cellulosic blend fibers are also well known and well established in textile industry. In fact, most current textile fabrics are mixtures containing cellulose, viscose and chemical fibers. Chitin itself also has most appealing properties such as acceleration of wound healing and tumour cell growth suppression. It is also chemically very stable, yet easily biodegradable because of widespread chitinases. All together, these features render chitin a highly attractive progenitor biopolymer for fibers. Processing and direct applications of chitin (DA > 50%) are limited due to its insolubility in usual organic solvents. In contrast, its derivative chitosan, obtained by (partial) deacetylation of chitin, can be processed into films, coatings and fibers using conventional carbon-based solvent systems and is widely used because it inherits most of chitins pharmacological properties like antimicrobial and hemostatic activity. (Kumar, 2000; Rinaudo, 2006) Overcoming the solubility problem of chitin, several solvent systems have been tested and developed for the direct processing into films, coatings and fibers, which often resemble common solvents for the processing of cellulose, e.g., DMAc/LiCl or saturated $CaCl_2$/MeOH-solution (Agboh & Qin, 1997; Aiba, Izume, Minoura, & Fujiwara, 1985) as well as the preparation of biopolymer derivative analog to cellulose (Feng-Jian, Chun-Ju, & Qing-Rui, 2003). These solvent systems also allowed the

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preparation of cellulose/chitin blend fibers for the first time (Feng-Jian et al., 2003; Shuai, Fa-Xue, & Jian-Jong, 2009). However, most solvents systems exhibit significant toxicity or cannot be removed completely after biopolymer processing. A review on chitin and chitosan polymers, their chemistry, solubility and fiber formation can be found elsewhere (Pillai, Paul, & Sharma, 2009).

Scientific activities around biopolymer processing with non-toxic, easily removable and recyclable solvents led to the processing of poorly soluble polymers from ionic liquids (ILs) (Setoyama, Kato, Yamamoto, & Kadokawa, 2013). This general class of compounds is by this time used in many scientific and technical applications; these compounds are based on specific compositions of different cations and anions, which lead to a liquid state at room temperature, exhibit low viscosities, are often stable against thermal load and, most remarkably, show a considerable capability to interrupt strong H-bond interactions and are easily removable. Some ILs were found to be promising solvents for chitin and chitin/cellulose blends (John & Thomas, 2008; Kadokawa, 2013; Klemm et al., 2005) and have been used to prepare various chitin/cellulose and chitosan/cellulose blend materials like gels, foils, coatings and fibers with varying structures and for different applications (Bochek et al., 2012; Kadokawa, Hirohama, Mine, Kato, & Yamamoto, 2012; Kuzmina, Heinze, & Wawro, 2012; Ma, Hsiao, & Chu, 2011; Pillai et al., 2009; Shamsuri & Daik, 2015; Takegawa, Murakami, Kaneko, & Kadokawa, 2010) as well as nanofiber-reinforced materials thereof (Kadokawa, Endo, Hatanaka, & Yamamoto, 2015). However, up to now all applied ILs, e.g., $[C2mim]^+[Cl]^-$ (1-ethyl-3-methylimidazolium-chloride), cannot simultaneously dissolve sufficient amounts of chitin and cellulose, often exhibit toxicity and corrosivity and are therefore not suitable for establishing a multifilament wet spinning process for the above-mentioned biopolymer blend/IL systems.

However, we now succeeded in preparing one-pot polysaccharide solution containing relevant amounts of biopolymers in a non-toxic solvent. This one-pot polysaccharide approach bears remarkable potential for further processing, for example into films and coatings on textile substrates (cotton, viscose, polyurethane). Here we outline in detail the chemistry and physics of cellulose/chitin biopolymer solutions in ILs with suitable viscoelasticity and sufficient stability versus gelation for processing into multifilament yarns through a conventional wet-spinning process. In comparison to synthetic additive polymers, chitin has the advantage of being a natural, renewable, biocompatible as well as biodegradable material with the above-outlined unique property profile. Chitin-based materials are both hydrophilic and antibacterial. Consequently, aiming on fibrous materials, cellulose/chitin blend fibers are of utmost interest. Here we report on the realization of the first continuous wet-spinning process of cellulose/chitin blend fibers with up to 25 wt% of chitin. Multifilament yarns with single fiber diameters of 15 μm could be prepared. Promising results in terms of water retention capacity solely obtained by blending the two readily available biopolymers have been achieved.

2. Experimental

2.1. Materials

Cellulose linters (degree of polymerization, DP = 911, viscos. (DMAc·5LiCl)) were used as received. Lab grade powdered chitin (Sigma Aldrich, DP = 4.400, viscos. (DMAc·5LiCl), DA = 88%, crystallinity index CI = 68%). was purified as described below. If necessary, the chitin's molecular weight was adjusted by wet-chemical degradation. All ILs were supplied by BASF SE and used without further purification.

2.2. Chitin purification

Chitin was purified prior to use with regards to calcified and protein impurities. For these purposes, chitin was demineralized by stirring for 2 h at room temperature in 1.2 M HCl and washed until neutral (pH ~7) with demineralized water. Purification from potential protein impurities was done at 80 °C in 0.3 M NaOH for 1 h and washed with demineralized water until all excess base was removed. This procedure was repeated until the washing water was colorless. Following this procedure, purified chitin was received as a colorless powder without detectable protein (*Note*: as detectable by elemental analysis) or mineral (ash content) impurities and a degree of acetylation DA = 75 ± 5% (DP = 3.000, viscos. (DMAc·5LiCl), crystallinity index (CI)=70%).

Furthermore, the DP was reduced to the desired value by stirring the purified chitin in concentrated formic acid (Th. Geyer, Chemsolute, p.a.) at 80 °C. Reaction times depended on the target DP. Formic acid was removed using a rotary evaporator and the pasty residue was quenched in 0.3 M NaOH at 80 °C for 1 h, washed with demineralized water, dried (6 h, 110 °C, atmospheric pressure) and ground.

2.3. Degree of acetylation

To specify the degree of acetylation (DA), IR- and ^{13}C CP-MAS NMR spectroscopy were used. Chitin/KBr pellets were prepared for 12 h at 120 °C to minimize the influence of adsorbed water and all pellets were stored under vacuum. Prepared KBr pellets were measured with a Perkin Elmer Spectrum 2000 FT-IR and the DA was calculated from specific ratios of characteristic bands according to the methods described in references (Bauch, 2009; Brugnerotto et al., 2001; Duarte, 2002; Huang, Moon, & Pal, 2000).

Reference bands: IR (KBr): 3450 cm^{-1} (OH), 2878 cm^{-1} (CH_{str}), 1420 cm^{-1} (CH_{def}),

Measured bands: IR (KBr): 1655 cm^{-1} (C=O), 1661 cm^{-1} (C=O Amide), 1625 cm^{-1} (C=O Amide), 1550 cm^{-1} (C=O Amide), 1320 cm^{-1} (C—N Amide)

$$\text{Method IR} - \text{V} : \text{DA}(\%) = 31.918 \cdot (1320/1420) - 12.2 \quad (1)$$

$$\text{Method IR-I} : \text{DA}(\%) = 35.461 \cdot (1550/2878) \quad (2)$$

$$\text{Method IR} - \text{VI} : \text{DA}(\%) = 85.5 \cdot (1661 + 1625/3450) - 0.13 \quad (3)$$

The DA values obtained from IR-analysis were correlated with those derived from CP-MAS NMR spectroscopy. A correlation factor of $R = 88\%$ based on the equation

$$\text{DA}(\%) = 0.331 \cdot \text{DA(I)} + 0.261 \cdot \text{DA(V)} + 0.221 \cdot \text{DA(VI)} + 2.386 \quad (4)$$

was acquired.

2.4. Degree of polymerization

The DP of chitin was determined by viscosimetry using a type Vi Ubbelohde viscometer and an automated Schott AVS 360 measuring device. A concentration series of chitin in 5 wt% LiCl in *N*-*N*-dimethylacetamide (DMAc) was measured to provide the intrinsic viscosity $[\eta]$ and to calculate the degree of polymerization according to Eq. (2):

$$[\eta] = KM_n^{\alpha};\ M_n = [\eta]/k \cdot e(1/\alpha) \quad (5)$$

13C solid state NMR

^{13}C CP-MAS NMR spectra were recorded at 30 °C on a Bruker Biospin Avance III 400 WB spectrometer at 100 MHz resonance frequency using a 4 mm MAS BB/1H specimen holder spun at 5 kHz MAS-frequency.