

Jeremiasz Gorzędowski^{1,**},
Marcin Smiglak³,
Marcin H. Struszczyk^{2,*},
Michał Puchalski¹,
Izabella Krucińska¹

Chitin Fibre Formation by the Solution Blow Spinning Method, Using 1-butyl-3-methylimidazolium Acetate Ionic Liquid as a Solvent

DOI: 10.5604/01.3001.0014.0932

¹ Lodz University of Technology,
Faculty of Material Technologies and Textile Design,
Institute of Material Science of Textiles
and Polymer Composites,
S. Zeromskiego 116, 90-924 Lodz, Poland,
** e-mail: jeremiasz.gorzedowski@gmail.com

² Institute of Security Technologies "MORATEX",
M. Skłodowskiej-Curie 3, 90-505 Lodz, Poland,
* e-mail: mstruszczyk@morarex.eu

³ Poznan Science and Technology Park,
Adam Mickiewicz University Foundation,
Rubież 46, 61-612 Poznan, Poland

Abstract

Chitin is the second most abundant polysaccharide on the Earth after cellulose, therefore there is a tangible need for finding new environmentally-friendly solvents for the manufacture of useful forms of that polymer. Ionic liquids have been recently proposed as a possible type of solvent for chitin and cellulose. The possibility of the dissolution of chitin of various origin in six selected ionic liquids was investigated. Chitin samples were characterised by the main characteristic properties: degree of N-acetylation (by FTIR spectroscopy), degree of crystallinity (by WAXS), average molecular weight (by the viscometric method) and physical form. The studies performed allowed to find the optimum chitin-ionic liquid system based on 1-butyl-3-methylimidazolium acetate for the manufacture of chitin fibres by the solution blow spinning method. Final products were characterized by the same set of parameters as the initial materials.

Key words: chitin, ionic liquid, sustainability, chitin fibres.

Introduction

Chitin is a natural copolymer usually composed of major β -(1-4)-2-acetamido-2-deoxy-D-glucopyranose units and minor β -(1-4)-2-amino-2-deoxy-D-glucopyranose units, and having up to 1000-3000 repeating units. It is one of the most abundant biopolymers, just after cellulose [1, 2]. Chitin is characterised by a highly ordered structure, mainly in the α -chitin polymorphic form, where polymer chains are aligned anti-parallel. It has a strongly packed structure, with intra- and intermolecular hydrogen bonds, which makes chitin insoluble in most organic and inorganic solvents [3]. Due to that fact, only some derivatives e.g. dibutylchitin have been used for the formation of fibrous products, mainly by means of spinning methods [4-9]. Chitin is mainly extracted from marine organism e.g. crabs, shrimps and krill, but it can be also obtained from insects and fungi [10]. The usual procedure for chitin isolation from crustacean food product wastes involves acid hydrolysis, followed by alkaline treatment and decolourisation. The above-mentioned process may differ in order depending on the application of chitin envisioned. Moreover, it is also possible to use enzymatic treatment instead of alkali or acidic treatment [11]. However, the standard chitin isolation process is not environmentally friendly, since harsh chemical conditions are used. Moreover, it may cause a decrease in the

product molecular weight, the degree of N-acetylation, and crystallinity, and its processing can lead to environment pollution. Hence, there is a need for the development of new chitin manufacturing methods. In this light it has been reported that ionic liquids (ILs) may be a novel solvent for cellulose [12] and chitin [13, 14].

Ionic liquids (ILs) are a class of organic salts that generally melt at a temperature below 100 °C [15-17]. They have a number of interesting physical and chemical properties, most often in a unique combination within a single material. Ionic liquids are characterised by the following properties: high thermal and electrochemical stability, electrical conductivity, very low vapour pressure, customisable miscibility with other solvents, and non-flammability. Besides many other ways of utilisation, they are commonly considered as designer solvents, which means that they can be fine-tuned by the independent selection of cations and anions to be the optimum solvent for a given application [18]. Ionic liquids are also often referred to as "green" solvents due to their extremely low vapour pressure and high thermal stability, which gives, for example, ease of containment, product recovery and recycling ability [19-21].

From the beginning, ionic liquids were mainly considered as alternative, "environmentally friendly" solvents used in the process of catalysis. Currently ILs are used in many applications e.g.: conversion of energy [22], energy storage, lu-

bricants [23], electrolytes, applications in analytical methods [24], and as solvents for biomass [12-14]. In particular, in the example of using ionic liquids in the process of the dissolution of biomass, ILs are mainly known for their ability to dissolve cellulose [12, 25]. But their effectiveness in dissolving other biopolymers has also been proved [26]. However, the latest research indicates that some of the ionic liquids used in these processes do not remain inert towards the structure of biopolymers and cause their partial degradation [27].

The first example of using ionic liquids in the dissolution of chitin was presented by Rogers et al., where authors used ionic liquids to dissolve chitin samples that differed in molecular weight and form. Three ionic liquids were taken to compare their ability to dissolve chitin: 1-ethyl-3-methylimidazolium acetate (EMIMOAc), 1-butyl-3-methylimidazolium chloride (BMIM Cl) and 1-ethyl-3-methylimidazolium chloride (EMIM Cl). EMIMOAc turned out to have the best ability to dissolve chitin (15.2-80.0% load mass dissolved vs. 0-4% for the rest of ionic liquids). What is more, the authors claimed that they successfully extracted chitin directly from crustacean shells, obtaining chitin characterised by higher molecular weight than that from commercially available chitin [14]. Wang et al. found that the dissolution behaviour of chitin in ionic liquids is dependent on its origin, and hence on the degree of N-acetylation, the degree of crystallinity

and the molecular weight [28]. Wu et al. and Kadokawa et al. used four ionic liquids: 1-allyl-3-methylimidazolium chloride (AMIM Cl), 1-butyl-3-methylimidazolium chloride (BMIM Cl), 1-butyl-3-methylimidazolium acetate (BMIM OAc) and 1-allyl-3-methylimidazolium bromide (AMIM Br) to dissolve chitin of different polymorphic form (α , β) and origin. The authors did not manage to dissolve all the samples, and the solubility obtained for the rest of the samples was from 3 to 12% (w/w) at 110 °C [13, 29]. Kadokawa in a separate work produced acetylated chitin using ionic liquids as a reaction medium. The author used three ionic liquids: 1-allyl-3-methylimidazolium bromide (AMIM Br), 1-methyl-3-propylimidazolium bromide (MPIM Br), and 1-butyl-3-methylimidazolium bromide (BMIM Br). For AMIM Br, a maximum concentration of ~4.8 wt% clear solutions of chitin was prepared, and <1 wt% solutions for MPIM Br and BMIM Br. Prior to N-acetylation, chitin was dissolved in AMIMBr (2.0 wt%) by heating the mixture at 100 °C for 24 h with stirring. Afterwards, 5-20 equiv. of acetic anhydride per repeating unit was added to the mixture, and then heated at a temperature between 60-100 °C for 24 h with stirring. The highest degree of the substitution value (1.86) was obtained for 20 equiv. of acetic anhydride at 80 °C [30]. Setoguchi et al., extracted chitin from dried shells of the red queen crab, using AMIM Br. The authors prepared a mixture of 2.0 g of crab shells and 20 g of AMIM Br, which resulted in obtaining a 0.15 g chitin sample. The average molecular weight of the extracted chitin was determined by viscometric analysis, applying the Mark-Houwink-Sakurada equation, and was calculated to be 2.2×10^5 Da [31]. Mundsinger et al. investigated the possibility of dissolving chitin and cellulose in ionic liquids to obtain multifilament cellulose/chitin blend yarn spun from one-pot spinning dope. The authors found that 1-ethyl-3-methylimidazolium propionate can be used to dissolve up to 12 wt% of cellulose and up to 4% of chitin [32]. Chakravarty et al. performed the dissolution of chitin using IL 1-ethyl-3-methylimidazolium acetate ([C2mim][OAc]) to produce chitin membranes. The authors produced several chitin-IL solutions with a concentration from 2 to 3 wt% chitin. The solutions prepared were used for membrane production by washing out the solvent with deionized water [33]. 1-ethyl-3-methyl-

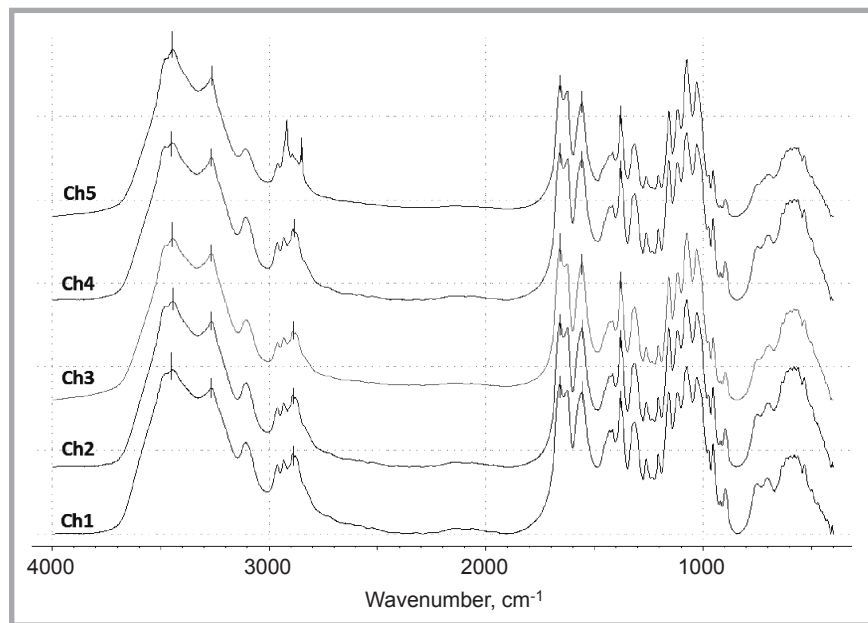


Figure 1. FTIR spectra of chitin samples Ch1-Ch5.

imidazolium acetate was also used by King et al. to dissolve from 2 wt% up to 3 wt% chitin. Solutions were used to cast a film by a simple casting method. It was found that 2.5% wt chitin solution resulted in films characterised by the best mechanical properties [34]. Another seven ionic liquids including EMIM Cl, EMIM Br, EMIM I, EMIM OAc, EMIM Lact, EPyr I and EMS BFSI, all having an ethyl group as a substituent in the cationic ring, were tested to dissolve chitin. Only EMS BFSI was determined not to have dissolution properties for chitin, while the rest of the ILs were found to have a different influence on the physical structure, particle size distribution and crystallinity of the chitins recovered³⁵. In another work, Barber et al. dissolved PG-chitin and shrimp shell extract in

EMIM OAc, obtaining 0.67 wt% chitin solution. It was used to produce nano and micron sized fibres by the electrospinning method. Higher concentrations were not used due to too high viscosity [36].

In this work, the authors chose 6 various ionic liquids and 5 chitins of various origin (crustacean and insect) and investigated the possibility of their dissolution. Initial chitin samples as well as final products regenerated from IL solutions were characterised by their chemical structure, degree of N-acetylation, average molar mass and degree of crystallinity.

On the basis of the reports above, the authors formulated a research hypothesis that the use of specially designated ionic liquid as a solvent effectively allows

Table 1. Samples of chitin used in the research.

Sample name	Producer	Usable form	Origin
Ch1	Sigma Aldrich (USA)	Powder	Shrimp shells (species not identified by manufacturer)
Ch2	Sigma Aldrich (USA)	Flakes	Shrimp shells (species not identified by manufacturer)
Ch3	Primex (Iceland)	Powder	Shrimp shells (<i>Pandalus borealis</i>)
Ch4	Primex (Iceland)	Flakes	Shrimp shells (<i>Pandalus borealis</i>)
Ch5	The Department of Material and Commodity Sciences and Textile Metrology, Faculty of Material Technologies and Textile Design, Lodz University of Technology (Poland)	Flakes	Honey bee (<i>Apsis mellifera</i>)

Table 2. Average molecular weight of chitin samples.

Sample name	Ch1	Ch2	Ch3	Ch4	Ch5
$M_w, \times 10^5, \text{ Da}$	1.77	2.37	0.61	3.35	3.56

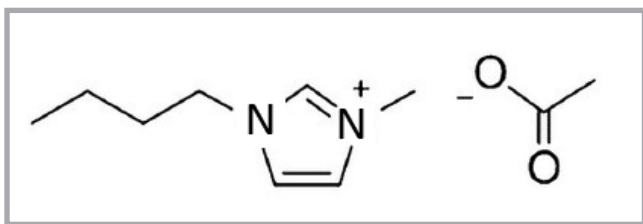


Figure 2. Chemical formula of 1-butyl-3-methylimidazolium acetate (BMIM OAc).

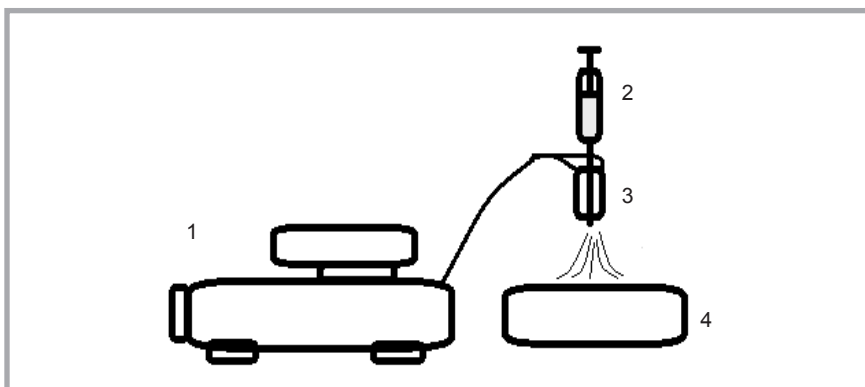


Figure 3. Schema of the solution blow spinning stand used in the laboratory scale trail: 1 – air compressor, 2 – syringe with polymer solution, 3 – head with an inner nozzle for polymer drawing and an outer nozzle for high velocity gas flow, 4 – cuvette with coagulation bath.

Table 3. Degree of N-acetylation evaluated from FTIR spectra of chitin samples – A_{1650}/A_{3450} .

Sample	Ch1	Ch2	Ch3	Ch4	Ch5
Degree of N-acetylation, %	80.1	78.3	86.4	82.3	74.5

Table 4. Results of WAXS numerical calculation of chitin samples Ch1 – Ch5.

Sample	Ch1	Ch2	Ch3	Ch4	Ch5
X_c , %	71.2	73.0	72.7	72.0	64.0

to perform the process of formation of chitin fibres by the direct-solution blow spinning method, characterised by desired properties from both a scientific and application point of view (strength, preserved natural bioactivity, etc.). The novelty of this work is using solution blow spinning as a method for chitin fibre production from its ionic liquid solution, since in the literature review only electrospinning method examples were found.

Materials and methods

Materials

Chitin

Chitin from various origins and in various usable forms were used in the study (Table 1).

The average molecular weight (M_w) value of chitin samples is presented in Table 2, whereas FTIR spectra of chitin are listed in Figure 1.

The degree of N-acetylation values for each chitin sample are presented in Table 3. According to the method of determination of the degree of N-acetylation used, the most acetylated sample was Ch3 (86.4%), while the most deacetylated was Ch5 (74.5%). The difference of 11.9% in the degree of N-acetylation is probably not significant for the dissolution, since chitin in that range of the N-acetylation level is characterised by similar characteristics from a chemical point of view.

According to data presented in Table 4, the most different supramolecular structure is observed for sample Ch5. This sample is characterised by a lower degree of crystallinity and smaller average size of crystalline areas (L_{AVE}), which may be the result of different chitin origin or its production method. Samples Ch1–Ch4 were obtained from shrimp shells, while Ch5 was from the honeybee [37]. Analysing the differences between sam-

ples from the shrimp, it is worth noting that the ordering of the crystal structure is similar; sample Ch2 is observed to be insignificantly higher.

One is generally expected to observe lower chemical activity for substances of a higher degree of crystallinity. Therefore, sample Ch5 may be more susceptible to dissolving in ionic liquid. The crystalline structure is tightly packed, thus it is harder to dissolve.

Ionic liquids

N,N-dimethylacetamide (DMAc, 99.8% anhydrous) and lithium chloride (LiCl, 99.0% anhydrous) were purchased from Sigma-Aldrich (United States). LiCl was lyophilised for 24 h before dissolving it in DMAc. 6 various ionic liquids were obtained from Poznan Science and Technology Park, Adam Mickiewicz University Foundation (Poland): 1-ethyl-3-methylimidazolium acetate (EMIM OAc), 1-butyl-3-methylimidazolium acetate (BMIM OAc, Figure 2), 1-butyl-3-methylimidazolium chloride (BMIM Cl), 1-butyl-3-methylimidazolium bromide (BMIM Br), and 1-ethyl-3-methylimidazolium chloride (EMIM Cl), 1-allyl-3-methylimidazolium chloride (AllMIM Cl).

Methods

Preparation of chitin solutions

Dissolving chitin in ILs was performed by taking 20 g of IL and 0.5 g of chitin, followed by heating for 4 h at 80–100 °C, and then stirring for 1 h with heating. The procedure was repeated twice: after 24 h and 48 h to dissolve a higher amount of chitin [38, 39]. Reaction mixtures were put into distilled water to precipitate the dissolved chitin. Precipitates were isolated by filtration, washed with distilled water, and then lyophilized for 24 h.

The results showed that an effective dissolution process occurred for only one pair of chitin and ionic liquid samples – chitin 3 and BMIM OAc. For the rest of the chitin samples and ionic liquids, chitin was observed to be swelled; but the solution concentration did not exceed 2 wt%. As the IL samples were always used as received, the high hygroscopicity of the ILs used and, thus, the increasing water content during the sample preparation are most likely responsible for the low values of chitin dissolution, especially in the case of EMIM OAc IL, known for good chitin dissolution properties. Hence, the

authors repeated the above-mentioned procedure to obtain chitin 3 in BMIM OAc solution up to 10 wt%.

Preparation of chitin fibres

Fibre formation trials were performed only for one designated pair of chitin and ionic liquid that revealed the best dissolution properties, i.e. chitin 3 and BMIM OAc. Due to the high viscosity of the solution, it was not possible to use a concentration higher than 2.5 wt%. The solution blow spinning method was undertaken for fibre fabrication. This technique is for making non-woven webs of micro- and nanofibres with diameters comparable with those made by electrospinning. In that method a polymer solution is delivered by a syringe to an apparatus with a nozzle (or multiple nozzles), pumped through the inner nozzle while a constant high velocity gas flow is sustained to draw a stream of fibres from a droplet of the polymer. A schema of the equipment is shown in **Figure 3**.

Since ionic liquid cannot be evaporated during a stream flight, it is collected in a cuvette with distilled water. Since the chitin is insoluble in water, a fibre is formed, while the ionic liquid is solubilised [40, 41].

Analytical methods

Optical microscopy

The fibres obtained were imaged with an optical microscope from PZO (Poland) equipped with a CCD Elemis KK 35 camera (Poland), using LUCIA G software (Czech Republic).

Scanning Electron Microscopy (SEM) imaging

A high resolution scanning electron microscope – Nova nanoSEM 230 from Fei Co. (The Netherlands) was used to determine the morphology of fibres obtained.

Molecular weight

Prior to analysis, the chitin was dissolved in 5% (w/v) LiCl/N,N-dimethylacetamide (DMAc) solutions (1 mg/ml) [42].

The molecular weight (M_w) value of chitin samples was determined by viscometric analysis of the chitin solutions using the Mark–Houwink–Sakurada **Equation (1)** [24]:

$$[\eta] = K\overline{M}_v^a \quad (1)$$

Where, η is the intrinsic viscosity, and K & a are constants that are independent

Figure 4. Macroscopic image of chitin fibres produced by the solution blow spinning method.

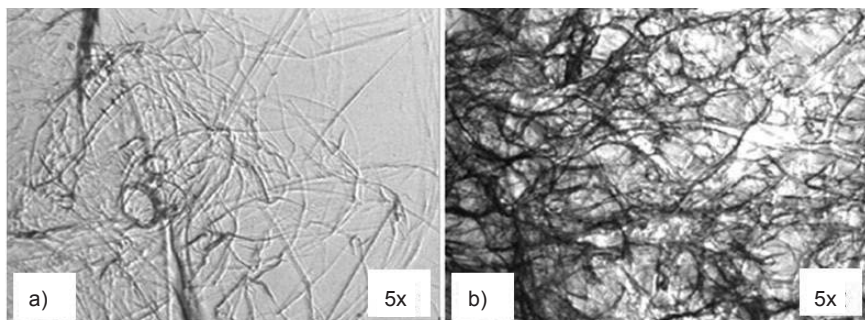
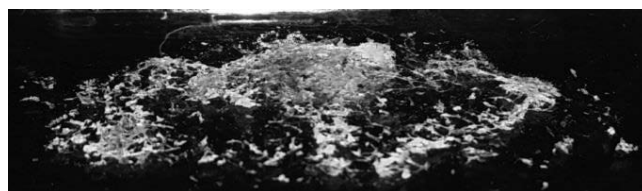


Figure 5. Microscopic images of chitin fibres (Ch3) produced by the solution blow spinning method: (a, b) mag.: 5x, fibre diameter: 0.3-30 μm ; (b) mag.: 5x, fibre diameter: 0.3-30 μm .

of the molecular weight over a considerable range of molecular weights for a given polymer. For the DMAc–LiCl solvent system, the values are as follows [42]:

$$K = 2.4 \times 10^{-1} \text{cm}^3 \text{g}^{-1}, a = 0.69 \quad (2)$$

Viscosity measurements of diluted polymer solution ($c < 1.2\%$) were carried out on an Ubbelohde viscometer. The flow times were recorded with an accuracy of ± 0.1 s, and the bath temperature was constant (25.0 ± 0.1 °C).

Degree of N-acetylation

The chemical structure as well as the degree of N-acetylation of the samples studied were determined using FTIR spectra of the chitin samples. For the analysis, an FTIR-Nicolet 6700 spectrophotometer from Thermo Scientific (USA) was used within the wavelength range of 4000-600 cm^{-1} . All chitin samples were lyophilised and made into KBr discs (2 mg of lyophilized chitin into 200 mg of KBr).

The degree of N-acetylation (DA) value was then determined by a method reported by M. Ratajska et al. [43]. In this method the $\lambda = 3450$ cm^{-1} absorption (OH + Amide I) band is used as a reference band and the amide I band at $\lambda = 1650$ cm^{-1} as a measurement band. The 3450 cm^{-1} and 1650 cm^{-1} absorption bands were measured on the baseline from 3800 cm^{-1} to 3000 cm^{-1} and from 1800 cm^{-1} to 1600 cm^{-1} , respectively [44].

Crystallinity

The degree of crystallinity and crystallite size of the samples studied were determined by the wide angle X-ray diffraction scattering (WAXS) method, using a X'Pert PRO diffractometer (CuK α source, $\lambda = 0.154$ nm) from PANalytical (The Netherlands). Diffractograms for the powdered samples were recorded in the 2θ angle range from 5° to 60°. Numerical analysis of the WAXS data obtained was performed by means of WAXSFIT software [45].

According to Hindeleh and Johnson's method, the X-ray profiles were resolved into crystalline and amorphous components. The content of the crystalline phase (χ_c – crystallinity degree) was calculated according to the **Equation (3)** [46]:

$$\chi_c = \frac{A_c}{A_c + A_a} \quad (3)$$

Where, A_a , and A_c – calculated integral intensity under the amorphous and crystalline curves obtained, respectively.

The size of crystalline areas perpendicular to lattice planes (hkl) ($L_{(hkl)}$) was determined by measuring the width of the diffraction peak using Scherrer's **Equation (3)** [45]:

$$L_{(hkl)} = \frac{K\lambda}{B \cos \theta} \quad (4)$$

Where, θ – Bragg angle for planes (hkl), λ – wavelength of X-ray radiation (for CuK α $\lambda = 0,154$ nm), B – half width of the diffraction peak for planes (hkl),

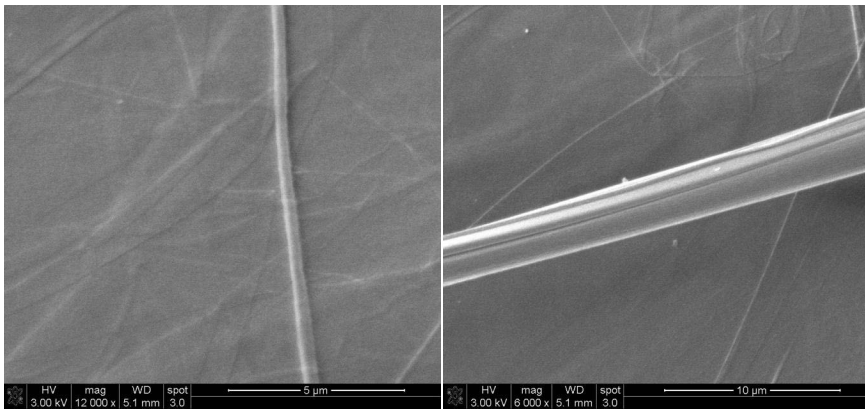


Figure 6. SEM microphotographs of chitin fibres produced by the solution blow spinning method; HV 300 kV, magnification 6 000 x – 12 000 x.

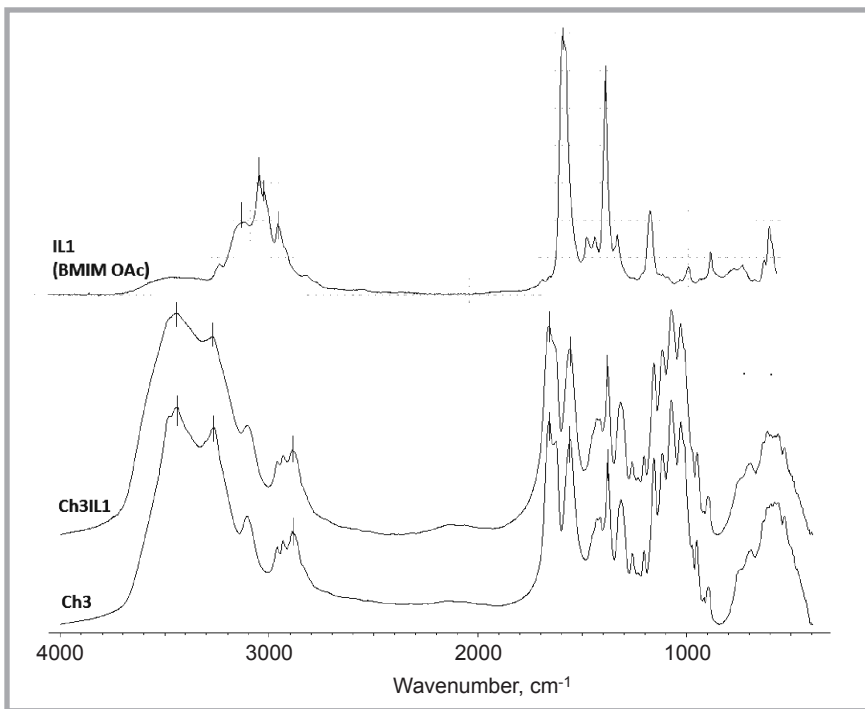


Figure 7. FTIR spectra of chitin, sample Ch3, regenerated Ch3IL1 and ionic liquid – BMIM OAc.

K – Scherrer’s constant, which is equal to 0.9 for the polymer.

■ Results and discussion

Chitin regenerated from ionic liquid solution

As described in previous sections, only one pair of chitin and ionic liquid was

designated for fibre formation trials. The preparation procedure for 2.5% solution of Ch3 in BMIM OAc was described in the previous section. The solution blow spinning method was used to fabricate dispersed chitin microfibrils, whose diameter ranged from 0.3 to 70 µm. A 5% ethanol solution was used as a coagulation bath.

Table 5. Average molecular weight, degree of N-acetylation, and degree of crystallinity of Ch3 and its regenerated form from BMIM OAc.

Sample name	Ch3	Ch3IL1
Average molecular weight, Da, $\times 10^5$	0.61	0.55
Degree of N-acetylation, %	86.4	91.7
L_{ave} , nm	9.6	8.5
Degree of crystallinity, %	72.73	69.25

The chitin non-woven product of regenerated chitin 3 (**Figure 4**) was washed 3 times in distilled water, and then dried in an oven for 2 h at 100 °C.

The images in **Figure 5** show a large range of diameters of fibres: from 0.3 µm up to 30 µm. The fibres of higher diameter reveal wrinkled morphology, while the others are characterised by a smooth surface, which suggests that fibres are stretched differently.

SEM microphotographs revealed the fibrous structure of chitin, with diameters of about 0.5 µm (**Figure 6**).

Regenerated samples are denoted by Ch3IL1. They were investigated by the same methods as for the initial samples to observe the influence of ionic liquid on chitin properties (**Table 5**).

A drop of 10% in the average molecular weight is observed for the regenerated chitin. It may suggest some degradation of chitin macromolecules during the dissolution process or be caused by the lack of dissolution of chitin macromolecules of the highest average molecular weight and by them being washed out during the regeneration process.

An increase of 5.3% in the degree of N-acetylation is observed for the regenerated chitin, which may occur due to temperature conditions or because of the loosening of intermolecular H-bonds between chains and the better access of ions of the ionic liquid to the structure of the chitin, including its acetyl amine groups; thus promoting N-deacetylation. It is important to stress that the mechanism of chitin dissolution is widely discussed in the literature [28, 47, 48], and it is suggested that the character of the dissolution process is similar to the one governing the dissolution of cellulose in ionic liquids and progresses through the loosening of intermolecular hydrogen bonds between chitin chains.

The other explanation is that some macromolecules of a lower N-acetylation degree are washed out during the regeneration process, consequently the average degree of N-acetylation increases. This should be taken into consideration in further studies. Also, it was noted for chitin 3, which was characterised by the highest degree of N-acetylation among the chitins investigated, that after the dissolution the value even increased, which

may suggest that some of the chitin with a much lower degree of N-acetylation was washed away during sample processing. The regenerated chitin was characterised by a lower ordering of the crystal structure than the initial chitin, as presented in **Figure 8**, where the crystalline peaks of α -chitin are definitely clearly visible, mainly in the case of the diffraction peak corresponding to the (130) lattice plane. The degree of crystallinity of the regenerated chitin as well as the average size of crystalline areas (L_{AVE}) testify that they are clearly lower than in the case of the initial sample (Ch3). This change in the supramolecular structure may result from the recrystallisation of chitin after dissolving in ionic liquid. Recrystallisation during solidification of the dissolved natural polymer is energetically too low to obtain a supramolecular structure similar to that of the raw material. However, the crystalline structure of the regenerated chitin is the same as that of the raw material – α -chitin.

The comparison of FTIR spectra of Ch3 and regenerated Ch3, i.e. Ch3IL1 and BMIM OAc (chemical formula in **Figure 7**) suggests that there is no ionic liquid in the regenerated chitin. The FTIR spectra gathered are similar besides the absorption bands around $\lambda = 1630\text{ cm}^{-1} - 1655\text{ cm}^{-1}$, where for Ch3IL only one peak is visible, instead of two, as in the case of Ch3 (**Figure 7**). The difference is related to a change in the degree of N-acetylation and the crystallinity [49].

As shown in **Table 6**, there is a shift from $\lambda = 2890\text{ cm}^{-1}$ to $\lambda = 2879\text{ cm}^{-1}$ for the absorption band assigned to C-H stretching for regenerated chitin, suggesting some changes in the regenerated chitin structure. Moreover, the shift from $\lambda = 3264\text{ cm}^{-1}$ to $\lambda = 3272\text{ cm}^{-1}$ for a band assigned to NH_2 symmetrical stretching was also detected, which may be related to the higher N-deacetylation degree, resulting in an increase in hydrogen bonds.

A decrease in the intensity of crystalline peaks (2θ angle around 10° and around 20°) is observed in the pattern of regenerated chitin (**Figure 8**), which was also observed in the literature [50]. It reflects the lower degree of crystallinity of chitin after regeneration.

Summary

The authors investigated the possibility of dissolving chitin in ionic liquids and

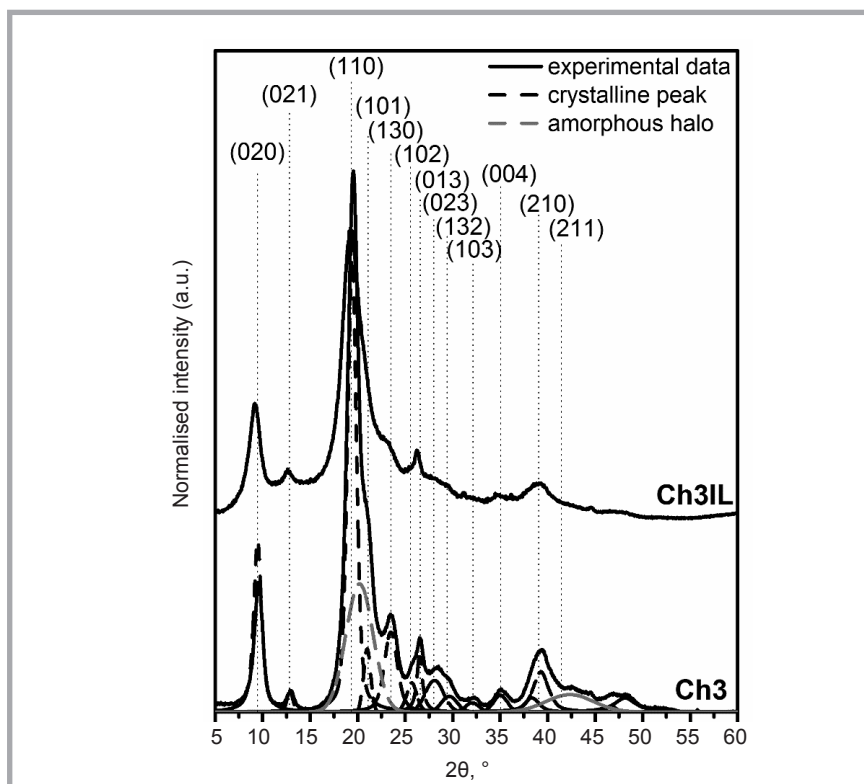


Figure 8. WAXS patterns of chitin (Ch3) and regenerated chitin (Ch3IL1).

Table 6. Characteristic absorption bands (cm^{-1}).

Ch3	1378	1558	1660	2890	3264	3446
Ch3IL1	1378	1558	1660	2879	3272	3446
BMIM OAc	1377	1574	2873	2934	2958	3040

producing fibres by the solution blow spinning method. Five various chitin samples as well as six ionic liquids were used: 1-ethyl-3-methylimidazolium acetate (EMIM OAc), 1-butyl-3-methylimidazolium acetate (BMIM OAc), 1-butyl-3-methylimidazolium chloride (BMIM Cl), 1-butyl-3-methylimidazolium bromide (BMIM Br), 1-ethyl-3-methylimidazolium chloride (EMIM Cl), an 1-allyl-3-methylimidazolium chloride (AMIM Cl).

It was possible to prepare a chitin solution with a concentration higher than 2 wt% for only one type of chitin (Ch3) with one ionic liquid (BMIM OAc). The Ch3 sample was characterised by the lowest average molecular weight (0.61×10^5 Da) and the highest degree of N-acetylation (86.4%) among all chitin samples. It was possible to fabricate fibres from 2.5 wt% chitin/IL solution by the solution blow method.

Regenerated chitin in the form of fibres was characterised by a higher degree of N-acetylation (5.3%), a lower degree

of crystallinity (3.48) and a lower average molecular mass (0.55×10^5 Da), than the initial sample. The analysis of FTIR spectra suggests that there is no ionic liquid in the regenerated chitin after washing coagulated fibres in distilled water 3 times. Therefore, the thesis that specially designated ionic liquid as a solvent will effectively allow to perform the process of formation of chitin fibres by the direct-solution blow spinning method was confirmed.

Further research will be aimed at the investigation and characterisation of the properties of the fabricated fibres.

References

- Li Q, Dunn ET, Grandmaison EW, et al. Applications and Properties of Chitosan. *J Bioact Compat Polym* 1992; 7: 370-397.
- Struszczyk MH. Chitin and Chitosan: Part I. Properties and production. *Polymer* 2002; 47: 316-325.
- Minke R, Blackwell J. The Structure of α -Chitin. *J Mol Biol* 1978; 120: 167-181.

4. Wawro D, Stęplewski W, Komisarczyk A, Krucińska I. Formation and Properties of Highly Porous Dibutylchitin Fibres Containing Nanoparticles. *FIBRES & TEXTILES in Eastern Europe* 2013; 21, 4(100): 31-37.
5. Chilarski A, Szosland L, Krucińska I, et al. Non-Wovens made from Dibutylchitin as Novel Dressing Materials Accelerating Wound Healing. In: H. Struszczyk, A. Domard, M. G. Peter HP (ed) *Proceedings of 6th International Conference of the European Chitin Society, EUCHIS'04*. 2004.
6. Błasińska A, Krucińska I, Chrzanowski M. Dibutylchitin Nonwoven Biomaterials Manufactured Using Electrospinning Method. *FIBRES & TEXTILES in Eastern Europe* 2004, 12, 4(48): 51-55.
7. Błasińska A, Mikołajczyk T. Wet Spinning of Dibutylchitin Fibres from Ethanol Solution. *FIBRES & TEXTILES in Eastern Europe* 2005, 13, 6(54): 36-40.
8. Błasińska A, Trębska I, Krucińska I. Preliminary Assessment of Sorption Capabilities of Nonwoven Dressing Materials. *Prog Chem Appl Chit Deriv* 2003; IX: 169.
9. Chilarski A, Krucinska I, Kiekens P, et al. Novel Dressing Materials Accelerating Wound Healing Made from Dibutylchitin. *FIBRES & TEXTILES in Eastern Europe* 2007 15, 4(63): 77-81.
10. Struszczyk MH. Chitin And Chitosan: Part III. Some Aspects of Biodegradation and Bioactivity. *Polimery* 2002; 47: 619-629.
11. Shahidi F, Abuzaytoun R. Chitin, Chitosan, and Co-Products: Chemistry, Production, Applications, and Health Effects. *Adv Food Nutr Res* 2005; 49: 93-135.
12. Swatloski RP, Spear SK, Holbrey JD, et al. Dissolution of Cellulose with Ionic Liquids. *J Am Chem Soc* 2002; 124: 4974-4975.
13. Wu Y, Sasaki T, Irie S, et al. A Novel Biomass-Ionic Liquid Platform for the Utilization of Native Chitin. *Polymer (Guildf)* 2008; 49: 2321-2327.
14. Qin Y, Lu X, Sun N, et al. Dissolution or Extraction of Crustacean Shells Using Ionic Liquids to Obtain High Molecular Weight Purified Chitin and Direct Production of Chitin Films and Fibers. *Green Chem* 2010; 12: 968-971.
15. Wasserscheid P, Welton T. *Ionic Liquids In Synthesis*. John Wiley & Sons, 2008.
16. Aparicio S, Atilhan M, Karadas F. Thermophysical Properties of Pure Ionic Liquids: Review of Present Situation. *Ind Eng Chem Res* 2010; 49: 9580-9595.
17. Hallett JP, Welton T. Room-Temperature Ionic Liquids: Solvents for Synthesis and Catalysis. 2. *Chem Rev* 2011; 111: 3508-3576.
18. Freemantle M. Designer Solvents. *Chem Eng News Arch* 1998; 76: 32-37.
19. Mallakpour S, Dinari M. Ionic Liquids as Green Solvents: Progress and Prospects BT – Green Solvents II: Properties and Applications of Ionic Liquids. In: Mohammad A, Inamuddin D (eds). Dordrecht: Springer Netherlands, pp. 1-32.
20. Welton T. Room-Temperature Ionic Liquids. Solvents for Synthesis and Catalysis. *Chem Rev* 1999; 99: 2071-2083.
21. Wasserscheid P, Keim W. Ionic Liquids – New 'Solutions' for Transition Metal Catalysis. *Angew Chemie Int Ed* 2000; 39: 3772-3789.
22. Wishart JF. Energy Applications of Ionic Liquids. *Energy Environ Sci* 2009; 2: 956-961.
23. Minami I. Ionic Liquids In Tribology. *Molecules (Basel, Switzerland)* 2009; 14: 2286-2305.
24. Anderson JL, Armstrong DW, Wei G. Ionic Liquids in Analytical Chemistry. *Anal Chem* 2006; 78: 2892.
25. Stolarska O, Pawłowska-Zygarowicz A, Soto A, et al. Mixtures of Ionic Liquids as More Efficient Media for Cellulose Dissolution. *Carbohydr Polym* 2017; 178: 277-285.
26. Chowdhury ZZ, Bee S, Hamid A, et al. Catalytic Role of Ionic Liquids for Dissolution and Degradation of Biomacromolecules. *BioresourcesCom* 2014; 9: 1787-1823.
27. Clough MT, Geyer K, Hunt PA, et al. Ionic Liquids: not always Innocent Solvents for Cellulose. *Green Chem* 2015; 17: 231-243.
28. Wang W-T, Zhu J, Wang X-L, et al. Dissolution Behavior of Chitin in Ionic Liquids. *J Macromol Sci Part B* 2010; 49: 528-541.
29. Kadokawa J, Takegawa A, Mine S, et al. Preparation of Chitin Nanowhiskers Using an Ionic Liquid and their Composite Materials with Poly(Vinyl Alcohol). *Carbohydr Polym* 2011; 84: 1408-1412.
30. Kadokawa J-I. Ionic Liquid as Useful Media for Dissolution, Derivatization, and Nanomaterial Processing of Chitin. *Green Sustain Chem* 2013; 03: 19-25.
31. Setoguchi T, Kato T, Yamamoto K, et al. Facile Production of Chitin from Crab Shells Using Ionic Liquid and Citric Acid. *Int J Biol Macromol* 2012; 50: 861-864.
32. Mundsinger K, Müller A, Beyer R, et al. Multifilament Cellulose/Chitin Blend Yarn Spun from Ionic Liquids. *Carbohydr Polym* 2015; 131: 34-40.
33. Chakravarty J, Rabbi MF, Bach N, et al. Fabrication of Porous Chitin Membrane Using Ionic Liquid and Subsequent Characterization and Modelling Studies. *Carbohydr Polym* 2018; 198: 443-451.
34. King C, Shamshina JL, Gurau G, et al. A Platform for More Sustainable Chitin Films from an Ionic Liquid Process. *Green Chem* 2017; 19: 117-126.
35. Jaworska MM, Górak A, Zdunek J. Modification of Chitin Particles with Ionic Liquids Containing Ethyl Substituent in a Cation. *Adv Mater Sci Eng*; 2017. Epub ahead of print 2017. DOI: 10.1155/2017/3961318.
36. Barber PS, Griggs CS, Bonner JR, et al. Electrospinning of Chitin Nanofibers Directly from an Ionic Liquid Extract of Shrimp Shells. *Green Chem* 2013; 15: 601-607.
37. Stawski D, Rabiej S, Herczyńska L, et al. Thermogravimetric Analysis of Chitins of Different Origin. *J Therm Anal Calorim* 2008; 93: 489-494.
38. Muzzarelli RAA. Biomedical Exploitation of Chitin and Chitosan via Mechano-Chemical Disassembly, Electrospinning, Dissolution in Imidazolium Ionic Liquids, and Supercritical Drying. *Mar Drugs* 2011; 9: 1510-1533.
39. Jaworska M, Górak A. Modification of Chitin Particles with Chloride Ionic Liquids. *Mater Lett* 2016; 164: 341-343.
40. Medeiros ES, Glenn GM, Klamczynski AP, et al. Solution Blow Spinning: A New Method to Produce Micro- and Nanofibers from Polymer Solutions. *J Appl Polym Sci* 2009; 113: 2322-2330.
41. Krucinska I, Komisarczyk A, Paluch D, et al. The Impact of the Dibutylchitin Molar Mass on the Bioactive Properties of Dressings Used to Treat Soft Tissue Wounds. *J Biomed Mater Res Part B Appl Biomater* 2012; 100B: 11-22.
42. Roberts GAF. *Chitin Chemistry*. London: Macmillan Education UK, 1992.
43. Ratajska M, Struszczyk MH, Boryniec S, et al. The Degree of Acetylation of Chitosan: Optimization of the IR Method. *Polimery/Polymers* 1997; 42: 572-575.
44. Kasaai MR. A Review of Several Reported Procedures to Determine the Degree of N-Acetylation for Chitin and Chitosan Using Infrared Spectroscopy. *Carbohydr Polym* 2008; 71: 497-508.
45. Rabiej M. A Hybrid Immune-Evolutionary Strategy Algorithm for the Analysis of the Wide-Angle X-Ray Diffraction Curves of Semicrystalline Polymers. *J Appl Crystallogr* 2014; 47: 1502-1511.
46. Hindeleh AM, Johnson DJ. Crystallinity and Crystallite Size Measurement in Polyamide and Polyester Fibers. *Polymer (Guildf)* 1978; 27-32.
47. Uto T, Idenoue S, Yamamoto K, et al. Understanding Dissolution Process of Chitin Crystal in Ionic Liquids: Theoretical study. *Phys Chem Chem Phys*. Epub ahead of print 2018. DOI: 10.1039/c8cp02749h.
48. Ma Q, Gao X, Bi X, et al. Dissolution and Deacetylation of Chitin in Ionic Liquid Tetrabutylammonium Hydroxide and its Cascade Reaction in Enzyme Treatment for Chitin Recycling. *Carbohydr Polym*. Epub ahead of print 2020. DOI: 10.1016/j.carbpol.2019.115605.
49. Paulino AT, Simionato JI, Garcia JC, et al. Characterization of Chitosan and Chitin Produced from Silkworm Crystals. *Carbohydr Polym* 2006; 64: 98-103.
50. Jaworska M, Tomasz K, Andrzej G. Review of the Application of Ionic Liquids as Solvents for Chitin. *Journal of Polymer Engineering* 2012; 32: 67.

Received 19.10. 2018 Reviewed 15.05.2019