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A comparison of methods for obtaining nanocellulose using acid and ionic liquid hydrolysis reactions

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Abstract: *A comparison of methods for obtaining nanocellulose using acid and ionic liquid hydrolysis reactions.* In this study, two methods were compared, i.e. acid hydrolysis using sulphuric acid (VI) and ionic liquid hydrolysis using 1-methyl-3-butylimidazolium chloride to obtain nanocellulose from Sigmacell Cellulose Type 20. The efficiency of both processes was tested for weight loss of the material during the reaction. The study showed that much more material can be obtained using ionic liquid hydrolysis than using acid hydrolysis. A dynamic light scattering study was performed to determine material particle size before and after these processes. Particles of nanometric size were recorded only for cellulose after the reaction with an ionic liquid. In addition, Fourier transform infrared spectroscopy was performed to determine the chemical structure of the materials tested.

Keywords: 1-butyl-3-methylimidazolium chloride, sulphuric acid(VI), acid hydrolysis, ionic liquid hydrolysis, Dynamic Light Scattering, Fourier Transform Infrared Spectroscopy

INTRODUCTION

Nanometric size cellulose and the methods of its production are very popular research topics, as evidenced by the number of publications in recent years (Ribeiro et al. 2019). This is due to the increasing use of this material and attempts to develop a method that would be cost-effective and safe for the environment (Bhat et al. 2019). Nanocellulose may be obtained through affecting a factor capable of resolving strong interfibrillar hydrogen bonds within the molecule. This ability is found in strongly corrosive acids and bases, some ionic liquids, cellulose enzymes or mechanical forces (Jiang and Hsieh 2013).

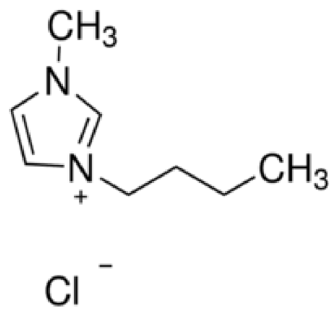

Figure 1. Chemical structure of [Bmim] [Cl]

Nickerson and Habrle (1947) were the pioneers of nanocellulose production by acid hydrolysis. It has been shown that sulphuric acid may be used for cellulose hydrolysis, but different nanoparticle dimensions (from 3 to 70 nm wide and from 35 to 3000 nm long) were obtained depending on the cellulose source and reaction conditions (Beck-Candanedo, et al. 2005; Elazzouzi-Hafraoui et al. 2008; Habibi et al. 2010). Strong acids, such as hydrochloric acid and hydrobromic acid, also hydrolyze but usually providing low yields of less than 30% (Jiang and Hsieh 2013). However, acids are dangerous for the environment and for its protection various methods are being developed not involving toxic substances.

Ionic liquids are considered non-toxic and eco-friendly. Additionally, thanks to their unique properties they have found numerous applications in new fields, including nanocellulose production (Shak et al. 2018). In 2002, Swatlowski and his team proved that 1-butyl-3-methylimidazolium chloride [Bmim] [Cl] is capable of dissolving cellulose with no need for other solvents. Since this discovery there has been a growing interest in the use of ionic liquids to dissolve and modify cellulose (Suzuki et al. 2014).

In this study two methods to obtain cellulose of nanometric size were compared. The acid hydrolysis method, first proposed for the chemical preparation of nanocellulose, was compared with hydrolysis of ionic liquid ([Bmim] [Cl]) (Figure 1). The experiments were conducted on microcrystalline cellulose: Sigmacell Cellulose Type 20 with 20 µm particle size.

MATERIALS

The research used microcrystalline cellulose – Sigmacell Cellulose Type 20 with 20 µm particle size (Sigma Aldrich). Moreover, the following chemical substances were used: sulfuric acid (VI) 95% (Sigma Aldrich) was diluted to 64% with water, anhydrous NaOH (Sigma Aldrich) for acid neutralization and 1-butyl-3-methylimidazolium chloride (≥98%) (Sigma Aldrich) as ionic liquid, phosphorus pentaoxide (P_2O_5) (Sigma-Aldrich), acetonitrile (Sigma-Aldrich), KBr (Sigma-Aldrich).

METHODS

Preparation of nanocellulose using acid hydrolysis reaction

Microcrystalline cellulose (Sigmacell) was mixed with H_2SO_4 (64%) at a 1:10 ratio (m/v). The suspension was subjected to constant magnetic stirring (ChemLand, Poland). The reaction was run at two temperatures (25 °C and 45 °C) for 1 min and 5 min. Cold water was added to terminate the reaction and sulfuric acid (VI) was neutralized by sodium hydroxide. The material was centrifuged and rinsed with water. The cellulose was dried in a dryer (Pol-Eko, Poland) and, in the final stage, placed in a desiccator over P_2O_5.

Preparation of nanocellulose using ionic liquid hydrolysis reaction

Microcrystalline cellulose (Sigmacell) was added to the molten ionic liquid [Bmim] [Cl] at a 1:10 ratio (w/w). The reaction was run for 9 hours at 90 °C, with intensive magnetic stirring (ChemLand, Poland). After hydrolysis the reaction product was filtered and washed thoroughly with acetonitrile to remove the ionic liquid. In the next stage of the study, the cellulose material was left to dry at a room temperature and, in the final stage, it was placed in a desiccator over P_2O_5.

Fourier transform infrared spectroscopy (FTIR)

The samples were mixed with KBr (Sigma Aldrich) at a 1:200 mg ratio and, in the form of pellets, were analyzed by FTIR. Spectra were registered at a range of 4000-500 cm^{-1}, at a resolution of 2 cm^{-1} and registering 16 scans using a Nicolet iS5 spectrophotometer (Thermo Fisher Scientific, USA).

Dynamic light scattering analysis (DLS)

DLS was used to determine the particle size (hydrodynamic diameter) of the materials. The samples were previously mixed (2 mg) with 5 ml deionized water, treated using an ultrasound system (Polsonic, Poland) for 25 min and next centrifuged using an incubated shaker (Jeio Tech, Korea) in order to remove the micrometric fraction of cellulose. Finally, the hydrodynamic diameter of samples was determined with a Zetasizer Nano ZS-90 (Malvern Instruments Ltd., UK) at room temperature, with the results presented as size distribution by intensity.

RESULTS

The dried material was weighed to calculate the efficiency of the hydrolysis reaction process. The results are shown in Table 1.

The efficiency of nanometric cellulose production in the hydrolysis reaction was higher in milder reaction conditions. After a reaction of 1 min at 25°C, the reaction yield was 60%, while after a reaction of 5 min. at 25°C and 1 min at 45°C, the yield was close to 30%. The lowest result was registered for the 5 min reaction at 45°C (5%). A much higher yield was obtained during hydrolysis with the ionic liquid (89%), despite a longer reaction time and a higher temperature.

Another test was performed using FTIR spectra to determine the chemical structure of the resulting materials (Figure 2).

Additional bands were recorded in the cellulose spectrum after hydrolysis with an ionic liquid, which are not present in the spectra after acid hydrolysis. Wave numbers of 1575 cm^{-1} are due to C=N stretchings. The peak at the wave number of 757 cm^{-1} is due to C–N stretching vibration. These bands correspond to the ionic liquid 1-butyl-3-methylimidazolium chloride, which was not eluted from the cellulose sample, similarly as in a study of Dharaskar et al. (2013). An increase in the intensity of the "crystallinity band", which corresponds to CH_2 bending vibrations, was recorded at 1466 cm^{-1} for cellulose after hydrolysis with the ionic liquid. At the same time, a decrease in the intensity of the "amorphous band" was recorded at 815 cm^{-1}, which corresponds to the C-O-C tensile vibration at β- (1 → 4) -glycosidic bonds.

Table 1. The efficiency of the acid and ionic liquid hydrolysis reactions

Hydrolysis reaction	Conditions	Efficiency [%]
Acid	1 min, 25°C	60
	5 min, 25°C	35
	1 min, 45°C	28
	5 min, 45°C	5
Ionic liquid	24 h, 90°C	89

This indicates an increase in the crystallinity of the cellulose sample after hydrolysis with the ionic liquid (Adsul et al. 2012). In the case of the cellulose sample after acid hydrolysis, no changes in intensity were recorded in these areas, therefore it may be concluded that cellulose crystallinity did not change, either.

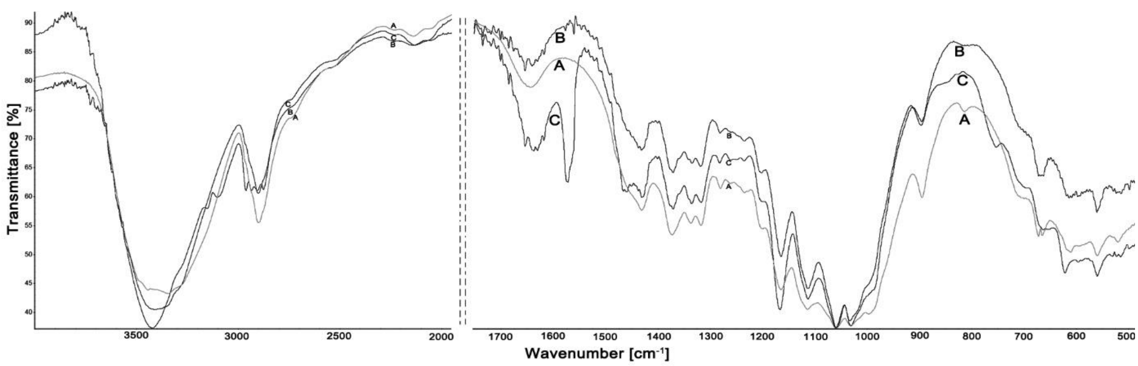

Figure 2. FTIR spectra of cellulose (A); cellulose after the acid hydrolysis reaction (B) and the ionic liquid hydrolysis reaction (C)

Another study was performed to determine the particle size of the materials. The results are shown in Figure 3.

For samples following acid hydrolysis, no particles below 100 nm were recorded. The result for cellulose after a reaction of 5 min. at 45°C was very similar to that for the native material, while the particle size after hydrolysis with an ionic liquid was below 100 nm. This showed that the ionic liquid hydrolysis was a better choice for obtaining cellulose nanometre sizes. The limited weight loss of cellulose during this process further strengthens this belief. Mao and his co-workers reported a very similar size of nanocellulose molecules using an ionic liquid with the same cation, but at a much lower yield (Mao et al. 2015).

CONCLUSIONS

After analyzing the amounts and particle size of the material recovered after the hydrolysis reaction, it may be concluded that the use of an ionic liquid to obtain nanocellulose was more favourable than the use of sulphuric acid(VI).

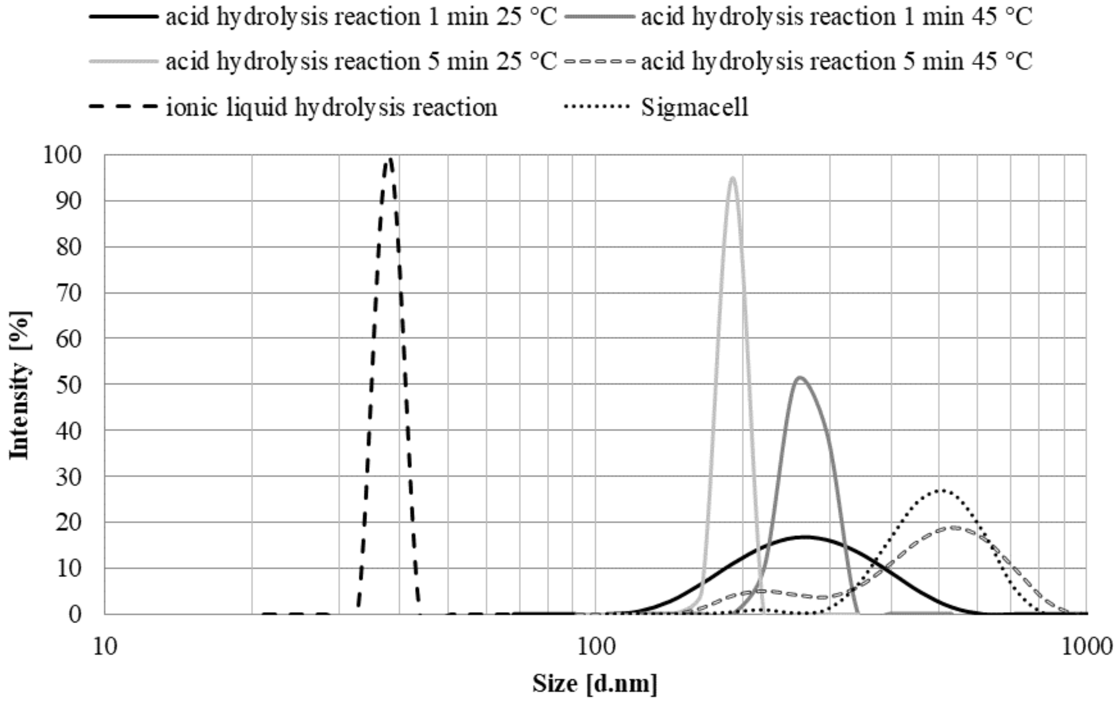

Figure 3. The average particles size of the cellulose before and after treatment with ionic liquid and acid

The yield for the ionic liquid reaction was higher than in all the acid tests. Nanometric particles were registered only for the material after ionic liquid hydrolysis. Based on the analysis of FTIR spectra, it may be stated that the degree of cellulose crystallinity after the ionic liquid hydrolysis increased, while no changes were recorded for cellulose after the acid hydrolysis. In the FTIR spectra of samples after hydrolysis with ionic liquid, bands corresponding to the ionic liquid were recorded, which may be due to insufficient washing of the material.

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