# Properties of nanofibres modified with ionic liquid

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## Introduction

Broad application possibilities of nanofibres in many fields of the economy, including biomedical materials, packaging, filters, textiles and composite materials, force researchers to intensify their studies related to the modifications and the achievement of new properties. Nanofibres have fundamentally different properties than standard fibres, mainly due to the surface area/weight ratio, resulting in large specific surface area and ensuring great mechanical properties [1]. Biological cells also respond differently to the structure elements of nanometre sizes. Wettability is also different for nanofibres.

The current market and modern technologies seek for nanomaterials with a good strength, low weight, low production costs and biodegradability.

The most promising renewable materials are polylactides and poly(lactic acid) (PLA) [2]. These are thermoplastic, biodegradable and biocompatibile materials that are characterised by a good strength and elastic constant and that are easily processable. PLA has the greatest potential for commercial-scale production.

In recent years, a lot of attention has been paid to polyhydroxyalkanoates – biodegradable and biocompatibile thermoplastic polymers of high application potential. Poly(3-hydroxybutyrate) (PHB) is a natural thermoplastic polyester exhibiting mechanical properties comparable to synthetic polymers [3]. Moreover, it has a low steam permeability, similar to that of low-density polyethylene (LDPE).

Both PLA and PHB are non-toxic, biodegradable and biocompatible, and exhibit no bioactivity.

Biocides described in the literature, used for giving biocidal properties to nanofibres are based mainly on nano-scale silver compounds [4÷6]. There are also positive reports on the application of chitosan [7, 8]. Biodegradable nonwoven mats made from PLA and chitosan by means of the electrospinning process showed antibacterial activity against *Escherichia coli*.

A. Toncheva together with her team have described the use of benzalkanoate chloride, as a representative of quaternary ammonium salts, for the modification of PLA and PLA/PEG micro– and nanofibres [9]. The addition of a low molecular weight organic salt to the polymer solution, before the electrospinning process, resulted in the increase in the conductivity and helped to produce a membrane made of fibres arranged in the rotation direction of the collector. Apart from the hydrophobic surface, such membranes also exhibited an antibacterial activity against *Staphylococcus aureus*. The literature also describes nanofibres containing metronidazole obtained by means of the electrospinning process from polyvinyl alcohol, which showed a great activity against the following strains of microorganisms: *Escherichia coli*, *Pseudomonas aeruginosa*, *Aspergillus niger*, *Penicillium notatum* and *Aspergillus flavus* [10].

The aim of this paper was to study and evaluate the effect of ionic liquid, as a representative of quaternary ammonium salts, on the properties of PLA and PHB nanofibres.

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Quaternary ammonium salts are a well-known and widespread group of compounds used for example in the wood industry and construction as wood preservatives protecting it against microorganisms causing biological decomposition.

Moreover, positive results of microbiological studies were reported indicating possible applications of imidazole ionic liquids as potential biocides for protecting paper [11], wood [12] or fabrics made from natural fibres [13] against a destructive microbial activity.

The innovative nature of such research involves the use of ionic liquid, not used previously, for the modification of nanofibres.

## Material and methods

The studies included the production of nanofibres in a nonwoven form from poly(lactic acid) (PLA) and poly(3-hydroxybutyrate) (PHB) by means of the electrospinning process from the solution. PLA came from Hycail Oy, Finland, whereas PHB from Biomer, Germany. Both proposed thermoplastic polymers are non-toxic, biodegradable and biocompatible exhibiting no bioactivity. It was decided to achieve this property by adding the ionic liquid to the polymer solution prior to the electrospinning process. The ionic liquid – didecyldimethylammonium nitrate [DDA][$NO_3$] – was obtained from P.I.W. Delta, Poland whereas While chloroform used in the studies was from POCH, Poland.

The 4.5% PLA solution was obtained by dissolving the polymer in chloroform and stirring it for 24 h. The PHB solution (5% w/w) was obtained by heating the right amount of PHB in chloroform for 10 minutes. The solutions were mixed appropriately at the volume ratio 6:1. The ionic liquid was added in two concentrations: 0.5% and 1%. Then, the solutions were transferred to a syringe and were dosed at a specific rate (0.3 ml/min) through a plastic tube and a needle with an internal diameter of 0.8 mm and length of 50 mm. The amount of dosed solution was controlled with a syringe pump (KDS-100 KD Scientific Co., USA). High voltage (17 kV) was applied to the needle using high voltage supply. PLA/PHB/IL nanofibres were collected in the form of a membrane on grounded rotating metal plate located at distance of 15 cm from needle tip. Electrospinning in all experiments was conducted at a constant temperature (23°C±2°C) and humidity (35% ± 5%). The nanofibres were collected for 15 minutes.

The obtained nanofibres were assessed microscopically regarding potential changes in their morphology using the scanning electron microscopy (Hitachi S-3400N).

A susceptibility test was performed for nanofibres against biodeterioration, including resistance to mould fungi. The tests were performed according to the standard PN-EN ISO 846:2002 Plastics – Evaluation of the Action of Microorganisms. 4 samples of each non-modified and modified nanofibres were tested and subjected to the action of mixture of fungi (*Aspergillus niger*, *Chaetomium globosum, Aureobasidium pullulans, Paecilomyces variotii*, *Penicillium funiculosum*). Fungal strains came from the Pure Culture Collection of the Institute of Fermentation Technology and Microbiology, Lodz University of Technology. Nanofibre samples were placed on the agar plates and inoculated with the suspension of the test fungi mixture. The test samples were incubated for 4 weeks at 29±1°C and relative humidity of 90%. After this period, a visual assessment of the level of mould fungi growth on the test sample surface was performed using the following grade:

0 – no visible growth under the microscope;
1 – growth not visible with the naked eye, but clearly visible under the microscope;
2 – growth visible with the naked eye, covering up to 25% of the tested surface;
3 – growth visible with the naked eye, covering up to 50% of the tested surface;
4 – significant growth, covering over 50% of the tested surface;
5 – intensive growth, covering the entire tested surface.

Moreover, thermal parameters of the modified nanofibres were tested by determining the heat release rate as a function of temperature using the pyrolysis-combustion flow calorimeter (PCFC). The test had the following temperature:
– temperature increase rate 1°C/s; pyroliser temperature range 75–750°C; combustion temperature 900°C; $O_2/N_2$ atmosphere at 20/80 $cm^3$/min ratio; sample weight 5 (±0.01) mg.

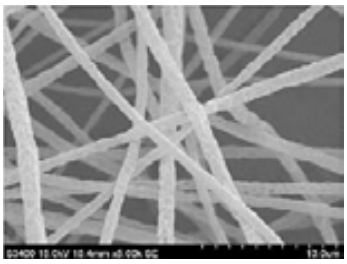
**Results**

Poly(lactic acid) (PLA) and poly(3-hydroxybutyrate) (PHB) nanofibres were formed in a nonwoven form by means of the electrospinning process from the solution. A mixture of polymer solutions in chloroform containing 4.5% PLA and 5% PHB was prepared. [DDA][$NO_3$] was added in two concentrations: 0.5% and 1% before the electrospinning process. Time parameters of the electrospinning process and the weight of the obtained nanofibre samples are presented in Table 1.

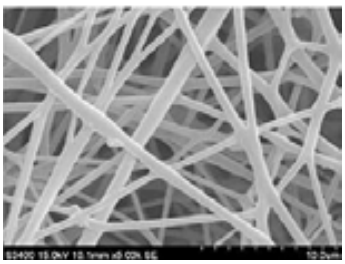
**Table 1**

**Parameters of the electrospinning process and obtained nanofibres**

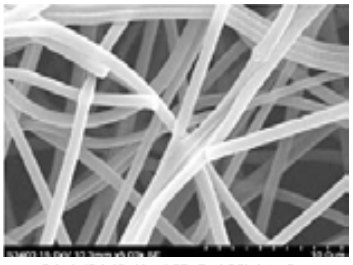
| | Control sample PLA/PHB | PLA/PHB + 0.5%[DDA][$NO_3$] | PLA/PHB + 1%[DDA][$NO_3$] |
|---|---|---|---|
| Electrospinning time, min | 15 | 15 | 15 |
| Surface mass, g/$m^2$ | 0.0019 | 0.0026 | 0.0028 |



PLA/PHB



PLA/PHB/0.5%[DDA][$NO_3$]



PLA/PHB/1%[DDA][$NO_3$]

**Fig. 1. SEM images of PLA/PHB nanofibres unmodified and modified with [DDA][$NO_3$]**

The microscopical assessment showed that nanofibres modified with [DDA][$NO_3$] have a much more regular and smooth structure in comparison to the unmodified nanofibres (Fig. 1).

Microbiological tests showed that nanofibres modified with 1% [DDA][$NO_3$] are resistant to the test mould fungi. No visible fungi growth was observed on the surface of the test samples. The test results are presented in Table 2.

Microscopic tests using SEM for the PLA/PHB/1%[DDA][$NO_3$] nanofibres carried out after the microbiological test showed that there were no changes in the morphology that could have been caused by the test microorganisms. In case of nanofibres with 0.5% of [DDA][$NO_3$], a limited 3rd level of fungi growth covering less than 50% of the tested surface area was observed. Microscopic tests using SEM for these nanofibres also showed no changes in the morphology. Whereas, in case of the unmodified nanofibres, a significant growth of test fungi covering over 50% of tested surface area was found. Microscopic tests using SEM for the unmodified nanofibres showed changes in the morphology after the exposure to fungi.

**Table 2**

**Assessment of mould fungi growth on the surface of tested nanofibres**

| | Mould fungi growth level on the scale from 1 to 5 | | |
|---|---|---|---|
| | Control sample PLA/PHB | PLA/PHB + 0.5%[DDA][$NO_3$] | PLA/PHB + 1%[DDA][$NO_3$] |
| *Aspergillus niger* | 5 | 3 | 1 |
| *Chaetomium globosum* | 5 | 3 | 1 |

Thermal parameters of the obtained nanofibres were also tested. PCFC results (Fig. 2) indicate that 1% [DDA][$NO_3$] modification caused the decrease in the combustion intensity of the test sample and a 30% decrease in the heat release rate (HRR) in comparison to the results obtained for the unmodified nanofibres.

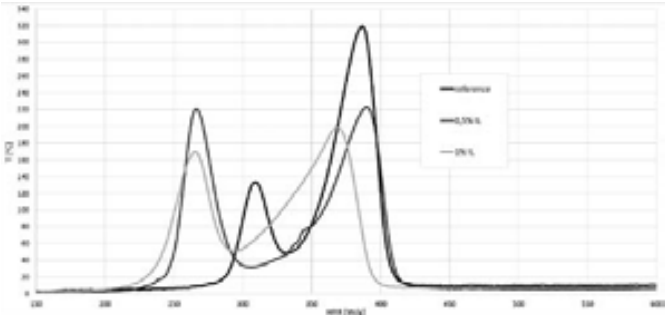


**Fig. 2. Heat release rate curves for PLA/PHB nanofibres unmodified and modified with [DDA][$NO_3$]**

The nanofibres were used for air filtration, making use of their positive structural properties. The results prepared together with the team from the Institute of Atmospheric Sciences and Climate (ISAC-CNR), Bologna, Italy, were described in the publication [14]. They proved that the addition of [DDA][$NO_3$] had a positive effect on both the filtration efficiency (E), as and the quality factor ($Q_F$) of the filters made of the modified nanofibres (Tab. 3). In case of filters made of the nanofibres unmodified with [DDA][$NO_3$], a pressure drop was observed due to the increase in the particle penetration rate (ΔP).

**Table 3**

**Parameters of air filtration process using filters made from the nanofibres**

| | Control filter made of PLA/PHB | Filter made of PLA/PHB + 0.5%[DDA][$NO_3$] | Filter made of PLA/PHB + 1%[DDA][$NO_3$] |
|---|---|---|---|
| ΔP, Pa | 130 | 200 | 330 |
| E, % | 93.2 | 98.4 | 99.9 |
| $Q_F$, Pa-1 | 0.02 | 0.02 | 0.02 |


**Summary**

The modification with an ionic liquid improved the functional properties of the tested PLA/PHB nanofibres.

The addition of [DDA][$NO_3$] to PLA and PHB solution resulted in the electrospun nanofibres having a much more regular and smooth structure than the nanofibres produced from the solutions without the addition of the ionic liquid.

The modification also helped to increase the nanofibre resistance to mould fungi. The incorporation of 1% [DDA][$NO_3$] into the structure of nanofibres resulted in no visible growth of test fungi on the surface of test samples. In contrast to the unmodified nanofibres, no changes in the morphology were observed after the exposure to mould fungi.

The modification also proved to be successful in the reduction of the PLA/PHB nanofibre flammability. The combustion intensity decreased, whereas the maximum heat release rate was reduced by 30% in comparison to the results obtained for the unmodified nanofibres.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**Synthos zostanie europejskim liderem w produkcji EPS**

26 sierpnia br. Komisja Europejska zatwierdziła zakup INEOS Styrenics na rzecz Synthos SA Transakcja zakupu jednostki biznesowej Ineos Styrenics European Holding BV została z powodzeniem sfinalizowana 31 sierpnia 2016. Tym samym oświęcimska firma chemiczna stanie się europejskim liderem rynku polistyrenu spienialnego (EPS). Wartość transakcji wyniosła 80 mln EUR, a jej realizacja jest kolejnym krokiem rozwoju firmy w obszarze EPS. Wraz z zakupem INEOS Styrenics, Synthos SA przejmie trzy zakłady produkcyjne, z których dwa znajdują się w północnej Francji (Wingles i Ribécourt) a trzeci w Holandii (Breda). Dodatkowo w Bredzie funkcjonuje nowoczesne centrum technologiczne, w skład którego wchodzą specjalistyczne laboratorium badawcze oraz zakłady pilotażowe, w których testowane są innowacyjne produkty wdrażane przez spółkę.

Zakup INEOS Styrenics pozwoli Synthos SA na dostarczanie najwyższej jakości polistyrenu spienialnego (EPS) a także utrzymanie pozycji lidera produktów styropianowych wśród materiałów izolacyjnych.

*(https://synthosgroup.com, 1 września 2016 r.)*

**Synthos na targach K Show 2016**

Synthos S.A. jako jeden z największych producentów surowców chemicznych w Polsce i w Europie - numer jeden w Europie producent kauczuków emulsyjnych i wiodący producent polistyrenu do spieniania będzie obecny na targach w hali numer 8a , na stoisku B19, 19 do 26 X Dusseldorf.

*(https://synthosgroup.com 20 września 2016)*