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Polypropylene nonwovens with natural polymers addition for filtration applications

Summary — Polypropylene composite nonwovens with microcrystalline cellulose (2 wt. %) and microbiological chitosan (3 wt. %) addition were processed by the melt-blown technique. The nonwovens were studied for filtration parameters and bio-destruction degree and the effect of chitosan on antibacterial properties of the polypropylene nonwoven was analyzed. The addition of modifiers resulted in impairing filtration parameters of polypropylene nonwovens but increased their biodestruction rate. Initial microbiological tests on nonwoven with chitosan indicated its anti-microorganisms effect towards selected colonies of bacteria and fungi.
Keywords: melt-blown technique, microbiological chitosan, composite nonwovens, filtration.

WŁÓKNINY POLIPROPYLENOWE Z DODATKIEM POLIMERÓW NATURALNYCH DO ZASTOSOWAŃ FILTRACYJNYCH

Streszczenie — Za pomocą techniki formowania włóknin metodą pneumatyczną ze stopu (melt-blown) wytworzono polipropylenowe włókniny kompozytowe z dodatkiem 2 % mas. celulozy mikrokrystalicznej lub 3 % mas. chitozanu mikrobiologicznego. Strużki stopionego polipropylenu rozdmuchiwano przy użyciu strumienia gorącego sprężonego powietrza i odbierano powstające włókienka w postaci runa (rys. 1). Otrzymane włókniny kompozytowe charakteryzowano wyznaczając przepuszczalność powietrza (rys. 3), opory przepływu powietrza (rys. 4) oraz efektywność filtracji (rys. 5). Zbadano także wpływ dodatku celulozy lub chitozanu na szybkość biorozkładu włókniny polipropylenowej (rys. 6). Obecność modyfikatora przyczyniła się do pogorszenia właściwości filtracyjnych włókniny polipropylenowej, przyspieszyła jednak jej biorozkład (we wszystkich przypadkach lepsze wyniki uzyskano w przypadku włókniny kompozytowej z dodatkiem chitozanu). Włókninę kompozytową z dodatkiem chitozanu mikrobiologicznego zanalizowano pod względem właściwości przeciwdrobnoustrojowych w stosunku do *Candida albicans*, *Bacillus subtilis*, *Staphylococcus aureus* i *Escherichia coli* (tabela 2). Wstępne badania mikrobiologiczne wykazały, że włóknina z dodatkiem chitozanu ogranicza rozwój wybranych kolonii mikroorganizmów.
Słowa kluczowe: technika melt-blown, chitozan mikrobiologiczny, włókniny kompozytowe, filtracja.

INTRODUCTION

Polypropylene nonwovens have been widely applied for many years as filtration materials due to their good parameters and low production costs [1, 2]. However, polypropylene usage is restricted as it depends on derivatives of crude oil or it causes slow degradation of materials based on polypropylene. Hence to improve the market effect and ecological aspects of filtration nonwovens, polypropylene can be replaced with biodegradable polymers [3] or polypropylene and biodegradable polymers can be combined in composite materials. Due to significant difficulties with biodegradable polymers processing [4] and their high cost it seems reasonable to add various modifiers to polypropylene to provide special properties (especially greater susceptibility to degradation).

Biodegradable polymers can be divided into two main groups:

— polysaccharides (starch, cellulose, chitin, chitosan) and other biopolymers (lignin, DNA, RNA, peptides);

— natural and synthetic polyesters [polyhydroxyalkanoates (PHA), polylactide (PLA), polycaprolactone (PCL)] and other synthetic polymers [poly(glutamic acid) (PGA), poly(vinyl alcohol) (PVA)] [5, 6].

In order to change low degradation rate of polypropylene its composites with natural polymers are produced, *e.g.* composites with starch [7] and with different types of cellulose [8—10] are known. The higher addition of

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modifier the higher degradation rate of composite material but also the worse mechanical parameters of it are observed, so it is necessary to find a balance between environmental and applied benefits.

In our earlier works we studied polypropylene composite nonwovens with addition of microcrystalline cellulose (2 wt. %) and microbiological chitosan (3 wt. %) with reference to photodegradation rate [11]. It was concluded that both modifiers increase photodegradation of composite nonwoven comparing with clean polypropylene nonwoven. Especially photodegradation rate of composite nonwoven with chitosan addition was significantly greater then photodegradation rate of polypropylene nonwoven without any modifier.

The aim of this work was to obtain composite polypropylene nonwovens and to examine the influence of cellulose and microbiological chitosan addition on filtration parameters and biodestruction degree of polypropylene composite nonwovens and the effect of chitosan addition on antibacterial properties of polypropylene composite nonwoven.

EXPERIMENTAL

Materials

Fiber-forming polypropylene granulate (produced by Borealis, type HL 612 FB, *MFR* = 1200 g/10 min) was used to produce nonwoven samples according to the melt-blown technique.

The structure of polypropylene nonwovens was modified by the addition of 2 wt. % of microcrystalline cellulose (Sigma-Aldrich product, particle size 20 μm) and by the addition of 3 wt. % of microbiological chitosan with 80 % degree of deacetylation from filamentous fungi *Absidia orchidis* (particle size ≤28 μm) [12]. These powdery modifiers are characterized by appropriately high thermal resistance so they could be applied in melt-blown process of polypropylene treatment [11].

Sample preparation

Polypropylene nonwovens were obtained using the melt-blown technique, which is an integrated nonwoven technology consisting in linking fiber-forming process with web-forming process [13]. The strings of molten polymer come out from the extruder head through the multi-hole nozzle where they are blown up by a stream of hot compressed air and set as fine fibers on a collecting drum (Fig. 1). Depending on the process parameters it is possible to produce monofilaments of different thickness, including superfine ones, below 1 μm in diameter.

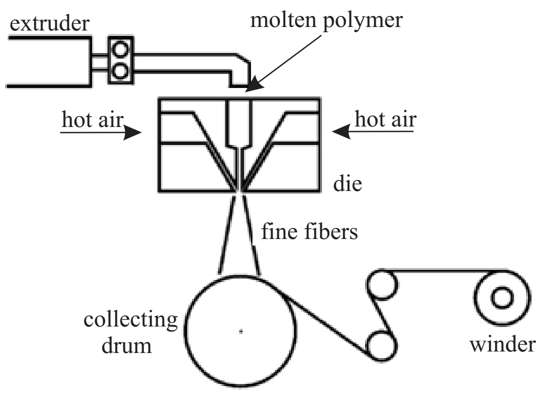

Fig. 1. Fibers formation according to the melt-blown technique

One of important advantages of this technique is the possibility to modify features of received nonwoven fabrics by insertion of additional powdery substances to their structures what provides new application possibilities for produced this way composite materials.

Polypropylene nonwoven without modifiers and composite polypropylene nonwovens (Fig. 2) were made using one-screw extruder (Axon product) and temperature parameters 240—285 °C were applied. The hot compressed air consumption was 7 m^3/h and the polymer

a)

b)

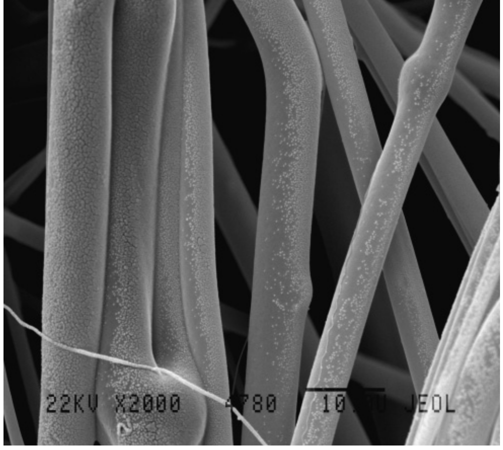

Fig. 2. SEM images (2000×) of polypropylene nonwovens: without modifier (a) and with 3 wt. % of chitosan addition (b)

consumption was 3 g/min. The mass per unit area of nonwovens (with and without modifiers) was 66 ± 3 g/m^2. Composite nonwovens were prepared using a two-step method — at the beginning regranulate of polypropylene and modifier was obtained and then it was processed by the melt-blown technique [14].

Methods of testing

— Filtration parameters (air permeability, air flow resistance and filtration efficiency) were determined for one layer of received clean polypropylene and composite nonwovens. Analysis were carried out at Institute of Textile Engineering and Polymer Materials of University of Bielsko-Biala.

— Air permeability was tested according to PN-EN ISO 9237:1998 standard; sample area 20 cm^2, pressure decrease 100 Pa.

— Air flow resistance and filtration efficiency were determined using filter tester TDA-100P. Measurement method consisted in spraying of cold oil particles (PAO); particles dimension 0,3 μm. Two rates of air flow were used in the tests — 20 dm^3/min and 50 dm^3/min.

— Bio-destruction degree was determined for achieved composite nonwoven samples and polypropylene nonwoven in composting conditions: temperature 58 ± 2 °C and humidity 59.9 % according to the test procedure of Institute of Biopolymers and Chemical Fibers in Lodz (elaborated based on PN-EN ISO 20200, PN-EN 14806 and PN-EN 14045 standards).

— Antibacterial properties were tested using microbiological chitosan from filamentous fungi *Absidia orchidis* (80 % degree of deacetylation, particle size ≤28 μm), quantitative screening method according to PN-EN ISO 20645 standard (plate method) and according to AATCC Test Method 147 (linear inoculation method). The growth of microorganisms on the tested sample and the range of area around the sample where the growth of microorganisms was inhibited were evaluated. Six types of microorganisms were used: bacteria Gram (+) *Bacillus subtilis*, Gram (+) *Staphylococcus aureus* and Gram (–) *Escherichia coli*, molds *Aspergillus niger* and *Penicillium chrysogenum* and yeast *Candida albicans*. Antibacterial properties were tested at Institute of Microbiology of Technical University of Lodz.

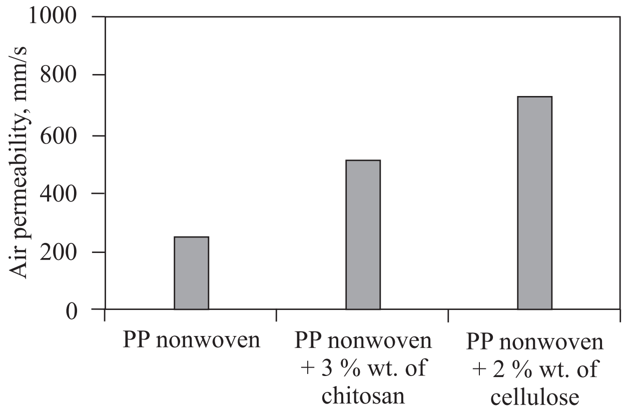

Fig. 3. The air permeability of polypropylene (PP) nonwovens without and with modifiers

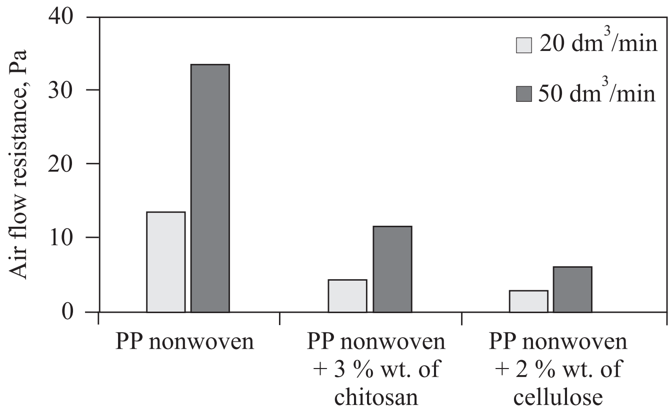

Fig. 4. The air flow resistance of polypropylene (PP) nonwovens without and with modifiers

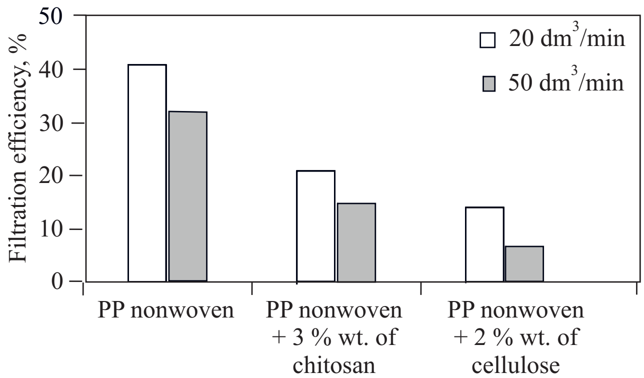

Fig. 5. The filtration efficiency of polypropylene (PP) nonwovens without and with modifiers

RESULTS AND DISCUSSION

The air permeability, air flow resistance and filtration efficiency were detected for clean polypropylene nonwoven and composite polypropylene nonwovens with 2 wt. % of microcrystalline cellulose and 3 wt. % of microbiological chitosan addition (Fig. 3—5).

All these results indicated that addition of any modifier impairs filtration parameters of polypropylene nonwoven. It was also noticed that the effect of modifiers is different — addition of 3 wt. % of chitosan downgraded filtration parameters about two times and addition of 2 wt. % of cellulose downgraded filtration parameters about three times. Results achieved for nonwoven with the addition of chitosan indicated that among composite nonwovens this material is recommended for filtration applications.

The composite nonwovens with 2 wt. % of cellulose and 3 wt. % of chitosan addition were analyzed with reference to biodestruction degree (Fig. 6). The figure shows that both modifiers accelerated biodestruction of the

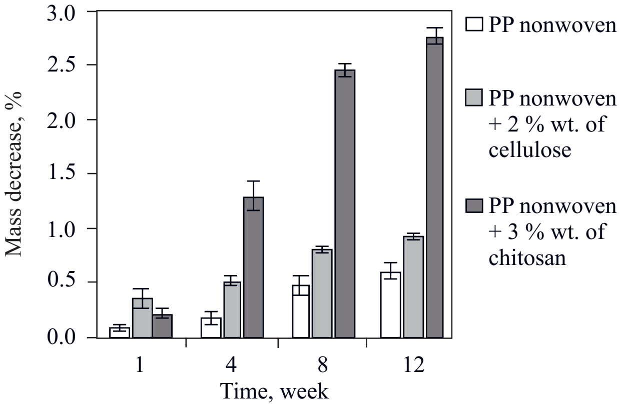

Fig. 6. The biodestruction rate of the clean polypropylene (PP) nonwoven and composite nonwovens with 2 wt. % of cellulose and 3 wt. % of chitosan addition

polypropylene nonwoven. The mass loss of the nonwoven sample with cellulose addition was about 1.5 times higher and the mass loss of the sample with chitosan addition was about 4.5 times higher than clean polypropylene nonwoven after 12 weeks of degradation.

Chitosan is known as an efficient antibacterial agent. The antibacterial properties of chitosan from filamentous fungi *Absidia orchidis* were determined (Table 1). The results show that chitosan is strongly bactericidal towards *Staphylococcus aureus* and *Escherichia coli* and inhibits the growth of *Candida albicans* and *Bacillus subtilis*. The growth of molds *Aspergillus niger* and *Penicillium chrysogenum* was also inhibited but to a lesser degree.

Bacteria *Bacillus subtilis*, *Staphylococcus aureus* and *Escherichia coli* and yeast *Candida albicans* were chosen to determine antimicroorganisms properties of the composite nonwoven with 3 wt. % of chitosan addition. While testing the nonwoven it was observed that it inhibits the growth of colonies of all chosen microorganisms (Table 2). The activity of composite nonwoven towards *Bacillus subtilis*, *Staphylococcus aureus* and *Candida albicans* is of special importance because these microorganisms are found in air and the composite nonwoven is analyzed from the point of filtration applications.

In the case of polypropylene melt-blown nonwovens with chitosan addition its antibacterial properties are not so strong compared to chitosan alone. The reason is the structure of the nonwoven — some chitosan molecules are on the surface of fibers, but many are inside them. Only these molecules which are on the surface can show antibacterial properties.

T a b l e 1. Anti-microorganisms properties of microbial chitosan from filamentous fungi *Absidia orchidis* (plate method, culture medium: TSA or wort 7°Blg)

Analyzed micro-organism	Time h	Diameter of microorganisms colony, mm	
		control sample	chitosan micro-biological 0.2 g
Aspergillus niger	24	8	2
	48	20	3
	120	46	15
Penicillium chrysogenum	24	8	5
	48	17	8
	120	47	9
Candida albicans	24	3	0
	48	5	3
	120	9	4
Gram (+) *Staphylococcus aureus*	24	4	0
	48	6	0
	120	8	0
Gram (–) *Escherichia coli*	24	6	0
	48	9	0
	120	10	0
Gram (+) *Bacillus subtilis*	24	5	1
	48	10	4
	120	12	0

CONCLUSION

Our researches led to obtaining of composite polypropylene nonwovens with the 2 wt. % of cellulose and 3 wt. % of chitosan addition which are characterized by better biodestruction degree than clean polypropylene nonwoven which allows for its better utilization and disposal.

Obtained results indicated that it is possible to maintain the basic functions and wear properties of polypropylene nonwovens in spite of addition of modifiers (especially it refers to nonwovens with microbiological chitosan). In this situation polypropylene composite non-

T a b l e 2. Anti-microorganisms properties of the polypropylene nonwoven with 3 wt. % of chitosan addition towards *Candida albicans*, *Bacillus subtilis*, *Staphylococcus aureus* and *Escherichia coli* (linear inoculation method)

Analyzed nonwoven	Microorganism growth symptoms			
	Candida albicans	Gram (+) *Bacillus subtilis*	Gram (+) *Staphylococcus aureus*	Gram (–) *Escherichia coli*
Polypropylene nonwoven	limited activity	insufficient activity	limited activity	limited activity
Polypropylene nonwoven with addition of 3 wt. % of microbiological chitosan	good activity	limited activity	good activity	good activity

woven with microbiological chitosan addition is recommended for filtration applications.

Initial microbiological tests on the composite nonwoven with chitosan indicate its antimicroorganisms effect against *Candida albicans*, *Bacillus subtilis*, *Staphylococcus aureus* and *Escherichia coli*; hence such nonwoven can be applied as a layer in multi-layer filtrating systems for air purification in high class of clean rooms.

The study was financed by Polish Ministry of Science and Higher Education within research project no. PBZ-MNiSW- 01/II/2007 (2007—2011).

ACKNOWLEDGMENTS

The authors are grateful to Dr Eng. Małgorzata Jaworska from the Faculty of Chemical and Process Engineering at Warsaw University of Technology for microbiological chitosan from filamentous fungi Absidia orchidis.

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Received 18 VII 2012.