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Antimicrobial Functionalization of Textile Materials with Copper Silicate

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Abstract
A biofunctionalization of nonwoven fabrics was carried out with 0.1 - 4 wt.% of copper silicate. Polypropylene (PP), polyethylene (PE) and biodegradable polymers [poly(lactic acid) (PLA), polyhydroxyalkanoates (PHA)] or their mixtures were used as polymer components. Mostly liquid oligomers of ethylene glycol (PEG) or copolymers of ethylene oxide and propylene oxide (2.5 - 5 wt.%) were applied as plasticizers. New composite nonwovens containing $CuSiO_3$ were prepared by the melt-blown technique [1]. They showed very good antibacterial and antifungal properties against colonies of gram-negative bacteria (Escherichia coli), gram-positive bacteria (Staphylococcus aureus) and a yeast fungus (Candida albicans). Nonwovens containing ≥ 0.5 wt.% of $CuSiO_3$ can be used, e.g. as hygienic and bioactive filter materials in air-conditioning systems. The application of PLA and PHA affects the ability of these hybrid nonwovens to biologically decompose. DSC analysis indicated that the incorporation of additives in PLA and PP nonwovens significantly affected their melting and crystallization processes.

Key words: *biofunctionalization, textile materials, nonwovens, antimicrobial properties.*

Introduction

Textile materials with antibacterial and antifungal properties are very important common goods and find huge practical applications, particularly in the manufacturing of sanitary materials and protective clothing components.

Metal ions, e.g. silver [2], zinc [3] and copper [4, 5] exhibit strong antibacterial activity. For a long time, the antimicrobial properties of Ag have been known, which are very useful both in the textile industry and medicine [6 - 13]. In recent years many examples of the antibacterial activity of ZnO [14 - 19], TiO_2 and other metal oxides have been described in literature [19 - 24]. It was demonstrated that the highest activity against bacteria was exhibited by Ag nanoparticles (NPs) with dimensions of 1 - 10 nm [25] and also by titania (TiO_2) NPs [26].

Copper oxide also has good antibacterial, antiviral and antifungal properties [27 - 32]. Although compared to most microorganisms, small concentrations of copper are sufficient, quite often, higher doses are used to inhibit the growth of certain microorganisms and achieve bactericidal activity [33]. Permanent biocidal properties of textiles containing 3 - 10% of copper were described in [34]. In recent years new antibacterial materials based on copper nanoparticles have been developed [5, 35 - 37].

Ren [29] found that the minimum bactericidal concentration of CuO nanoparticles in relation to *bacteria Pseudomonas aeruginosa* is ~5000 μg/ml. They also suggested that the releasing of copper ions into the local environment was necessary for preserving microbial activity. However, by applying the atomic absorption spectroscopy method (AAS), it was revealed that there was no simple correlation between the amount of copper released from the polymer matrix and the inhibition of bacterial growth. Most likely, this effect was caused by other factors such as the smoothness of the surface. Another reason could be the release of organic polymer compounds.

Trapalis [38] established that thin composite silicate coatings containing copper on glass plates (Cu/SiO_2) showed high antibacterial activity against *Escherichia coli* strains, which increased together with an increase in metal concentration, and decreased with an increase in heat treatment temperature during the process of forming Cu nanoparticles.

Copper nanoparticles deposited on the surface of spherical silica NPs showed a hybrid structure of the $Cu\text{-}SiO_2$ nanocomposite [39]. SiO_2 nanoparticles served as a substrate for the continuous deposition of copper. Copper NPs homogeneously formed on the surface of SiO_2 nanoparticles did not undergo aggregation and exhibited excellent antibacterial activity with respect to multiple microorganisms. Nanosilica modified on the surface with copper particles exhibited antibacterial properties, and was used to remove the odour of mercaptans and sulfur compounds from petroleum [40].

Mesoporous copper-doped silica xerogels of a large specific surface area (463 m^2/g) and pore size of 2 nm, exhibiting antibacterial properties depending on the concentration of copper, were also obtained in the sol-gel process [41].

In the copper silicate $CuO\text{-}SiO_2$ antibacterial and antifungal properties of the copper oxide as well as virucidal activity are connected to the biocompatibility, nontoxicity and a variety of silica surfaces. Copper silicate is used in medicine and

biology, for instance, in the controlled release of drugs and thermal treatment of tumours. An additional advantage of copper silicate CuO-SiO_2 is the possibility to modify its surface and properties using hydrophobic substances, simple chemical processes and organofunctional compounds [42]. Cotton textiles impregnated with silica sol containing 0.5 - 2% by weight of copper nanoparticles exhibited excellent antibacterial properties against both gram-negative and gram-positive bacteria. In order to block hydroxyl groups of silica, some samples were subjected to modification in a reaction with hexadecyl(trimethoxy)silane [43].

SiO_2 core-shell nanoparticles containing approximately 0.1 μg of Cu (in the form of insoluble copper hydroxide) possessed significantly better antibacterial properties against *Escherichia coli* and *Bacillus subtilis* bacteria than those observed for $Cu(OH)_2$ alone [44]. In the case of core-shell $CuSiO_3$ structures the minimum concentration inhibiting the growth of these bacteria was 2.4 μg Cu/mL. However, it is known that silica nano-composites with copper compounds of different valencies, especially enhanced by adding compounds Cu(0) and Cu(I), exhibited a higher antibacterial efficacy than Cu (II) compounds against *Xanthomonas alfalfae* and *Escherichia coli* bacteria. Phytotoxicity studies performed (in *Vinca sp. and Hamlin orange*) under greenhouse conditions showed that these nanocomposites are safe for plants and can be used as biocides in agriculture [45].

Very good antimicrobial properties of Cu/SiO_2 nanocomposites obtained in the form of thin layers using the Chemical Vapour Deposition method (CVD) method were observed against multiple hospital pathogens (*Acinetobacter baumannii, Klebsiella pneumoniae, Stenotrophomonas maltophilia, Enterococcus faecium, Staphylococcus aureus* and *Pseudomonas aeruginosa*). The SEM method confirmed the nanostructure of Cu particles in the silica matrix. The shells of nanocomposites Cu/SiO_2 tested can also be used for the microbial protection of metal and ceramic surfaces [46].

Copper alginates and zinc alginates and their silica composites exhibit stronger antimicrobial activity than regular Cu and Zn saline solutions against *Enterococcus faecalis* strains, despite the fact that they were used in a lower concentration [47]. In addition, these hybrid materials showed to be biocompatible and did not cause cytotoxic effects against eukaryotic cells. They can therefore be useful in gradual drug release and tissue engineering while preserving a high microbial activity over a long period of time.

Copper nanoparticles deposited on the surface of sodium montmorillonite (MMT) or intercalated inside its layered structure exhibited high stability in air (more than 3 months) and excellent microbiological activity against multiple bacterial colonies: *Escherichia coli*, *Staphylococcus aureus*, *Pseudomonas aeruginosa & Enterococcus faecalis*, causing a loss of > 90% in bacteria after 12 h [5].

Cytotoxicity tests revealed the minimal adverse effect of this nanocomposite on human cells when the minimum concentration inhibiting the growth of micro-organisms (MBC) was too high. In spite of that the prospects of employing nanocomposite MMT-Cu for therapeutic purposes is promising. Strong antibacterial properties of monodisperse copper nanoparticles of 2 - 5 nm deposited on magnesium silicate [$Mg_8Si_{12}O_{30}(OH)_4 \cdot (H_2O)_4 \cdot 8H_2O$] (sepiolite) were observed against *Staphylococcus aureus* and *Escherichia coli* bacteria. Their effectiveness proved to be comparable with the biological activity of triclosan [48].

It was noticed that Cu^{2+} ions incorporated into the structure of layers of calcium silicate $CaSiO_3$ deposited by electrophoresis on the surface of titanium were gradually released from such a coating and exhibited good antibacterial activity against strains of *Escherichia coli & Staphylococcus aureus* while showing higher corrosion resistance against pure titanium. However, $CaSiO_3$ does not have antibacterial properties on its own [49].

Strong antibacterial activity against *Escherichia coli* and *Staphylococcus aureus* were exhibited by both spherical copper and silver nanocomposites with mullite ($3Al_2O_3 \cdot 2SiO_2$). However, the microbial activity of the copper nanocomposite with mullite was higher than that of the silver nanocomposite with mullite, which was likely due to the smaller particle size of the latter. Both nanocomposites exhibited good cytocompatibility at a concentration of 1 mg/ml (MBC) and showed therapeutic properties in the treatment of wounds in mice [50].

Most often silver and its compounds have been used as antimicrobial additives in textile materials [51, 52]. Biodegradable polylactide (PLA) fiber materials containing Al_2O_3-Ag nanopowder were prepared by the electrospinning method, and displayed strong antimicrobial activities against *Escherichia coli* and *Sarcina lutea* [53]. Polypropylene and polyester needled and melt-blown nonwovens were good antimicrobial properties were prepared by spraying or dipping in a bath with diluted solutions (0.6 - 6 wt.%) of tetraalkylammonium salt *Sanitized® T 99-19* (Clariant International Ltd., Switzerland) and tested against different microorganisms (bacteria, moulds and yeast). The application of 2 wt.% of this commercial agent was sufficient for obtaining high biological activity against a wide spectrum of microorganisms. These bioactive nonwovens were recommended for such applications as respiratory protective equipment [54]. The PLA nonwovens were fabricated and modified by the melt-blown technique with quaternary ammonium salts as the biocidal agent, and supported on perlite, which contained plasticizing additives (monoethanoloamine, ethylene glycol, glycerol, and water). These composites exhibited good bioactivity against the bacteria studied (*Pseudomonas aeruginosa* and *Staphylococcus aureus)* and can be used as high-efficient respiratory protection filters [55].

The main goal of our research was a method for the biofunctionalization of textile materials using hydrated copper silicate premixed with a polymer component and plasticizer; then the mixture was heated until the polymer melted, and the molten composition was extruded and blown in a stream of hot air. Copper silicate hydrate [42], which is an inexpensive antimicrobial agent, was used in an amount of 0.1 - 4 wt.%.

Materials

Polypropylene (PP), polylactide (PLA), polyethylene (PE) and a PP/PE mixture were used as polymer components. PP (produced by Borealis, Austria type HL612 FB, MFR = 1200 g/10 min) and PLA (from NatureWorks LLC, USA), type Ingeo™ Biopolymer 3251D, MFR = 30 - 40 g/10 min (190 °C/2.16 kg), T_m = 160 - 170 °C)

in the form of granulates were used for fabrication of nonwoven samples. Powdered copper silicate hydrate (having the following chemical composition: 35.23 wt.% CuO, 62.16 wt.% SiO_2, 18.52 wt.% H_2O, 0.02 wt.% Na_2O and 0.01 wt.% K_2O) was prepared from sodium silicate [filtered, technical grade, made by Vitrosilicon S.A., Poland, 8.50 wt.% Na_2O, 27.18 wt.% SiO_2, density 1.39 g/cm^3, and silicate modulus (molar ratio) SiO_2 : Na_2O = 3.3) and a 5% solution of copper nitrate (p.a., made by Chempur, Poland) [42]. Polikol 600 (MW ~ 600 g/mol, freezing temperature: ~20 °C) was purchased from PCC Exol S.A. (Brzeg Dolny, Poland).

Methods

Nonwovens were fabricated by the melt-blown technique using a one-screw laboratory extruder (Axon product, Germany) with a head (with 30 holes of 0.35 mm diameter each), compressed air heater and collecting drum.

The microbial activity of resulting nonwoven fabrics was tested against a colony of gram-negative bacteria *Escherchia coli* (ATCC 25922), gram-positive bacteria *Staphylococcus aureus* (ATCC 6538), and *Candida albicans* fungus (ATCC 10321).

DSC analyses were carried out using DSC 6200 Exstar SII Nano Technology apparatus (Seiko product, Japan); samples *(ca*. 5 mg) were heated in a nitrogen atmosphere to 200 °C and then cooled to 25 °C; the scanning speed was 10 °C/min.

Scanning electron microscopy (SEM) pictures were done with apparatus Zeiss VO 40 (Germany).

Results and discussion

Biofunctionalized nonwowen fabrics were prepared by the melt-blown technique. The equipment for manufacturing bioactive textile materials contained the following: a one screw extruder, a melt-blowing head, compressed air heater, and a receiving device in the form of a moving drum. Processing parameters for fabrication of PP and PLA nonwovens are presented in ***Table 1***. Polymer yields were dependent on the screw rotation speed (see data in ***Table 2***). After setting the parameters specified above for PP processing, all the ingredients were thoroughly mixed and transferred to the hopper of the screw extruder. Then the process of extrusion of the composite polymer non-woven fabric was initiated using the melt-blown method.

The content of copper silicate hydrate in the fabric manufactured was 0.1 - 4 wt.%

Table 1. *Processing parameters applied for preparation of PP and PLA composite nonwovens by melt-blown technique.*

Processing parameters	PP	PLA
Temperature of the extruder in zone 1, °C	240	195
Temperature of the extruder in zone 2, °C	280	245
Temperature of the extruder in zone 3, °C	285	260
Head temperature, °C	240	260
Air heater temperature, °C	260 - 280	270 - 290
Air flow rate, m3/h	6.3 - 9.0	3.2 - 7.0
Polymer yields, g/min (values of screw rotation speed are given in brackets)	3.0 (40 r.p.m.)	5.0 (40 r.p.m.)
	3.4 (50 r.p.m.)	5.4 (50 r.p.m.)
	4.0 (60 r.p.m.)	6.6 (72 r.p.m.)

Table 2. *Chemical compositions of composite non-woven fabrics (with PP or PLA) containing PEG Polikol 600 (or PCL-diol or other plasticizers) and hydrous copper silicate $CuSiO_3 \cdot xH_2O$, and the results of their microbiological tests.* ***Description****: phr - parts by weight per 100 parts of polymer weight, R - growth reduction factor R for bacteria, L - growth reduction factor L for bacteria, * - polycaprolactone diol PCL Capa™2054 (Perstorp) was used, a - a mixture of PP (HL 512 FB) and PLA (Ingeo 32510) in a weight ratio of 1:1 was used, b - a mixture of PP and polyethylene (with an average Mw = 35,000 g/mol and Mn = 7,000 g/mol, Aldrich) at a weight ratio of 9 : 1 was used, c - paraffin oil was used, d - [(R)-3-hydroxybutanoate] Biomer (r) P209F was used as PHA, e - PEG Polikol 400 was used.*

Sample No.	Polymer	PEG (PCL-diol *)	$CuSiO_3 \cdot xH_2O$	R, % (L) Escherichia coli (ATCC 25922)	R, % (L) Staphylococcus aureus (ATCC 6538)	R, % (L) Candida albicans (ATCC 10321)
		phr	phr			
1	PP/PLA [a]	5	2	98.90 (1.9)	97.39 (1.6)	99.68 (2.3)
4	PP		1	73.76 (0.5)	82.24 (0.8)	97.80 (1.7)
5			2	98.70 (1.9)	97.16 (1.6)	99.54 (2.3)
15			3	>99.70 (>3.4)	98.20 (1.7)	80.40 (0.7)
7			4	>99.94 (>3.2)	99.98 (3.7)	99.82 (2.7)
8	PP/PE [b]	15 [c]	1	>99.92 (>3.2)	99.94 (3.6)	99.80 (2.6)
9	PHA [d]	5		>99,97 (>3,7)	99.80 (2.6)	>99.79 (1,2)
10	PLA			>99.94 (>3.2)	99.97 (3.6)	>99.74 (1.1)
11			2	>99.94 (>3.2)	99.98 (3.9)	>99.74 (1.1)
13		(5) *	1	>99.96 (>3.4)	99.60 (2.4)	84.7 (0.8)
16		5	0.50	>99.96 (>3.4)	93.01 (1.2)	51.0 (0.3)
17		(5) *		>99.98 (>3.7)	99.80 (2.6)	84.4 (0.8)
18		5	0.25	>99.98 (>3.7)	99.20 (2.6)	47.0 (0.3)
20		5	0.10	>99.98 (>3.6)	52.84 (0.3)	62.3 (0.4)
21		0	0	0 (-0.2)	10.26 (0.0)	0 (-0.1)
22		5		0 (-0.3)	16.58 (0.1)	0 (-0.1)
23		5 [e]	1.0	>99.98 (>3.7)	99.52 (2.3)	80 (0.7)
24		2.5	0.50	>99.98 (>3.7)	99.91 (3.0)	23.3 (0.1)
26		1.5		>99.98 (>3.7)	35.71 (0.2)	31.4 (0.2)

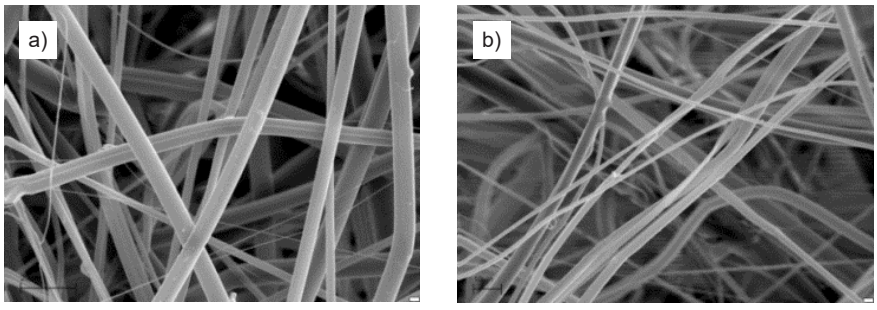

Figure 1. *SEM pictures of PP and PLA nonwovens modified with copper silicate: a) sample nr. 5 (PP), b) sample nr. 10 (PLA).*

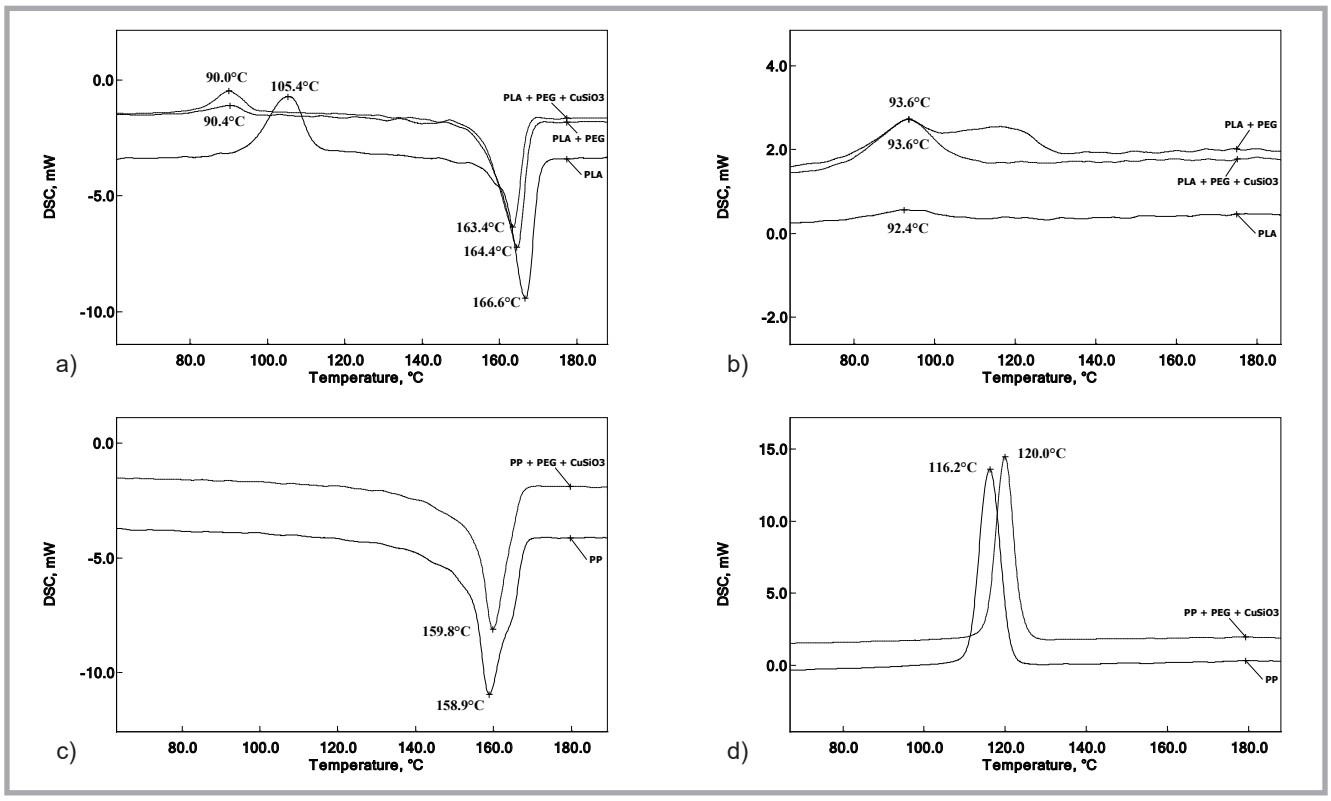

Figure 2. *DSC data: (a) PLA nonwoven heating thermogram, (b) PLA nonwoven cooling thermogram, (c) PP nonwoven heating thermogram, (d) PP nonwoven cooling thermogram.*

with respect to a selected polymer or polymer mixtures and the remaining ingredients. SEM images of hybrid PP and PLA composites (***Figure 1***) showed homogeneous distribution of copper silicate within polymer matrices.

As dispersants and wetting agents of $CuSiO_3$ and as plasticizers for polymers were used as different liquid additives: mostly oligomers of ethylene glycol (PEG) or propylene glycol, copolymers of ethylene glycol and propylene glycol, paraffin oil, dialkyl diesters of phthalic acid, polycarbonate diol, and poly(caprolactone) diol. Plasticizers were used in an amount of 1.5 - 15 wt.% with respect to the mass of polymer or polymer mixture, usually 5 wt.%.

The nonwovens prepared were subjected to microbial activity tests against a colony of gram-negative bacteria (*Escherchia coli*), gram-positive bacteria (*Staphylococcus aureus*), and the *Candida albicans* fungus. Results of these studies gave new textile materials which provide excellent antimicrobial protection against different microorganisms – for most samples biofunctionalized with $CuSiO_3$ the growth reduction factor R for bacteria exceeded 99% (see ***Table 2***). Sample no. 21 of unmodified PLA nonwoven showed weak antibacterial activity against *Staphylococcus aureus* (R = 10.3), probably due to the presence of lactic acid (LA), which could be formed from the hydrolysis of PLA in the phosphate buffer solution during the analytical microbiological test. The antibacterial properties of LA are commonly known [56]. Sample no. 22 of PLA nonwoven modified with 5 phr of PEG 600 exibited even slightly higher antibacterial activity against *Staphylococcus aureus* (R = 16.6), which could result from the synergistic effect of lactic acid and PEG. Sugar solution with PEG-400 did not have a lethal effect on microorganisms [57]. However, it is known from literature that solutions of concentrated polyethylene glycol (PEG 400) have significant antibacterial activity against various pathogenic bacteria, including *Klebsiella pneumoniae*, *Pseudomonas aeruginosa*, *Escherichia coli*, and *Staphylococcus aureus*. This effect was assigned to the lowering of water activity and the specific action of PEG-400 molecules on bacterial cells - clumping and morphological changes ini bacterial cells [58].

Poly(ethylene glycol) is the most common plasticizer of poly(lactic acid) (PLA) [59] and poly(hydroxyalkanoates) [60]. An addition (1 - 7 wt.%) of PEG200 (1 - 7 wt.%) to PLA caused a gradual reduction in the glass transition temperature of PLA-PEG200 blends from 62.85 °C to 48.54 °C, and in the presence of 10 wt.% of PEG200 T_g it reached 51.63 ºC. On the other hand, with an increase in PEG200 content the temperature resistance of mixtures of PLA-PEG200 gradually decreased [59]. On the basis of literature data [58] concerning thermal and DSC studies of PLA-PEG200 blends, we expected that the addition of PEG should decrease both the melting temperature and glass temperature of the hybrid composites studied. However, we were aware that the addition of $CuSiO_3$ could cause the opposite effect. Therefore we performed thermal testing for a few selected samples of PP and PLA hybrid nonwoven.

Three types of PLA nonwovens – pristine PLA, PLA with 5 wt.% of PEG, PLA with 5 wt.% of PEG and 2 wt.% of $CuSiO_3$ – were subjected to our DSC analyses.

Comparing the heating thermograms of these nonwovens, the shifting of peaks assigned to PLA melting to lower temperatures (from 166.6 °C to 163.4 °C) was observed after the addition of PEG and then $CuSiO_3$ (***Figure 2.a***). In the case of peaks corresponding to PLA

recrystallization the same tendency was observed (i.e. shifting from 105.4 °C to 90.0 °C); however, the recrystallization peaks were significantly decreased in their area, which means that the addition of PEG and $CuSiO_3$ resulted in a decrease in PLA recrystallization enthalpy (***Figure 2.a***).

Comparing the cooling thermograms of three types of PLA nonwovens, a slight shifting of PLA crystallization peaks to higher temperatures (from 92.4 to 93.6 °C) was observed, but the PLA crystallisation enthalpy increased distinctly, and in the case of PLA nonwoven containing 5 wt.% of PEG an additional crystallization peak/plateau appeared (***Figure 2.b***).

Apart from PLA nonwovens, two types of PP nonwovens – pristine PP, PP containing 5 wt.% of PEG and 2 wt.% of $CuSiO_3$ – were analysed by the DSC technique. In the case of PP nonwovens, PEG and $CuSiO_3$ addition caused the shifting of both PP melting and PP crystallization peaks to higher temperatures (from 158.9 to 159.8 °C on heating thermograms and from 116.2 to 120.0 °C on cooling thermograms) and did not affect the enthalpy of these processes (***Figures 2.c*** and ***2.d***).

The shifting of peaks to higher temperatures on the DSC thermograms after introducing additives to the nonwoven structure is rather rare. In the case of crystallization, shifting to higher temperatures was observed both for PLA and PP nonwovens, which could be explained by the nucleating effect of the additives.

Conclusions

The biofunctionalization of nonwovens prepared by the melt-blowing technique from polypropylene and biodegradable polylactide with the addition of inexpensive copper silicate as the antimicrobial agent (0.5 - 1 wt.%) and some plasticizers (mainly 5 wt.% of liquid PEG) provided new textile materials with very good and even excellent antimicrobial properties against colonies of gram-negative bacteria (*Escherichia coli*), gram-positive bacteria (*Staphylococcus aureus*) and a yeast fungus (*Candida albicans*). They can find many practical application for the production of sanitary materials, special socks and elements of shoes with antimicrobial properties, and also of bioactive filtration materials for air conditioning systems. The application of PLA and PHA gave biodegradable nonwoven fabrics.

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