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Influence of the nanotechnological process of chemical modification on the antimicrobial activity and biodegradability of textile fibres

Vpliv nanotehnološkega postopka kemijske modifikacije na protimikrobno aktivnost in biorazgradljivost tekstilnih vlaken

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Abstract

The aim of this research was to study the possibility of introducing a three-stage procedure for chemical modification of textile fibres to achieve antimicrobial properties as well as to determine the influence of the procedure on chemical, morphological and functional properties of fibres and their degree of biodegradation. The procedure was applied to 100% cotton (CO) and 100% polyester (PES) fabrics and a CO/PES fabric blend with a ratio of 50%/50%. The procedure of chemical modification included (i) pre-treatment of fibres with oxygen plasma, (ii) application of organofunctional trialkoxysilane for the creation of a silica matrix, and (iii) in situ synthesis of silver chloride. For comparison, a silica matrix with incorporated silver nanoparticles was also created on the samples without plasma treatment. Untreated and chemically modified samples were buried in soil for a defined period of time, and biodegradation of the fibres was conducted. Chemical and morphological changes after chemical modification and biodegradation were determined by microscopic and spectroscopic analyses, thin-layer wicking, and colour measurements. The results show that chemical modification did not cause significant morphological changes to the fibres. Treatment with oxygen plasma increased the fibre hydrophilicity, which resulted in an increased concentration of adsorbed silver. The presence of silver on the CO and CO/PES fabrics significantly decreased the degree of biodegradation compared to the untreated samples. Plasma treatment increased the degree of fibre biodegradation irrespective of the silver concentration present on the fibres. The low degree of biodegradation of the PES fabric was more due to the high hydrophobicity and crystallinity of the fibres than to the presence of silver. Keywords: textile fibres, chemical modification, plasma treatment, absorptivity for silver, biodegradation

Izvleček

Namen raziskave je bil proučiti možnost vpeljave tristopenjskega postopka kemijske modifikacije tekstilnih vlaken za dosego protimikrobnih lastnosti ter določiti vpliv postopka na kemijske, morfološke in funkcionalne lastnosti vlaken in stopnjo njihove biorazgradnje. Uporabljene so bile 100-odstotna bombažna (CO) tkanina, tkanina iz mešanice bombaža in poliestra v razmerju 50 %/50 % (CO/PES) ter 100-odstotna poliestrska (PES) tkanina. Postopek kemijske modifikacije je vključeval: (i) predhodno obdelavo vlaken s plazmo kisika, (ii) nanos organofunkcionalnega trialkoksisilana za oblikovanje silicijeve oksidne matrice in (iii) nanos srebrovega klorida s sintezo in-situ. Primerjalno je bila silicijeva oksidna matrica z vključenimi nanodelci srebra oblikovana tudi na vzorcih, ki pred tem niso bili obdelani s plazmo. Neobdelani in kemijsko modificirani vzorci so bili za določen čas zakopani v humusno ilovico, kjer je potekla njihova biorazgradnja. Kemijske in morfološke spremembe vlaken pred kemijsko modifikacijo in po njej ter po biorazgradnji so bile določene z mikroskopskimi in spektroskopskimi analizami, metodo tankoplastnega pronicanja in barvnometrično analizo. Iz rezultatov raziskave je razvidno, da kemijska modifikacija ni povzročila večjih morfološki spremembe

Corresponding Author/Korespondenčna avtorica: **Prof DrSc Barbara Simončič** E-mail: barbara.simoncic@ntf.uni-lj.si Tekstilec, 2017, **60**(1), 14-24 DOI: 10.14502/Tekstilec2017.60.14-24 vlaken. Obdelava s plazmo kisika je povečala hidrofilnost vlaken, kar je posledično vplivalo na večjo koncentracijo absorbiranega srebra. Prisotnost srebra na vzorcih tkanin CO in CO/PES je pomembno znižala stopnjo biorazgradnje vlaken v primerjavi z neobdelanimi vzorci. Plazemska obdelava vlaken je povišala njihovo stopnjo biorazgradnje ne glede na koncentracijo prisotnega srebra. Na nizko stopnjo biorazgradnje vzorca PES-tkanine sta bolj kot prisotnost srebra vplivali visoka hidrofobnost in kristalinost polietilentereftalatnih vlaken.

Ključne besede: tekstilna vlakna, kemijska modifikacija, obdelava s plazmo, adsorptivnost za srebro, biorazgradljivost

1 Introduction

The introduction of nanotechnological processes, such as plasma treatment [1, 2], sol-gel technology [3, 4] and the application of nanoparticles [5, 6], has enabled breakthroughs in the production of textile products with unique properties and high added value. The processes can be performed separately or in combination. The combined processes are very complex and therefore represent great challenges for researchers in the field of textile finishing.

Plasma treatment directly influences chemical and morphological properties of the fibre surface. Using plasma treatment, the surface of fibres could be activated by bond breaking and the creation of novel reactive sites, the cleavage of functional groups, etching, surface cleaning and the deposition of new layers on the substrate [1, 2, 7–9]. While the inclusion of functional groups changes the reactivity of the substrate, etching of the surface causes an increase in the nano- or microroughness of the surface and the modification of its topography. The formation of a nanostructured surface that is characterized by a large specific surface area can contribute to new and improved fibre properties, including an increase in the adsorption capacity for nanoparticles.

In the process of chemical modification of textile fibres, organofunctional trialkoxysilanes that are the representatives of inorganic-organic hybrid (IOH) sol-gel precursors with a general formula R²-Si(OR)₃ are of great importance [3, 10, 11]. Whereas the structure of the organic group that is marked as R' is significant for the functional properties of the precursor, the inorganic part of the molecule designated Si(OR)₃ preserves the precursor's reactivity. The latter hydrolyses under appropriate conditions, forming silanol groups that in the reaction of condensation bind to each other with a siloxane bond Si-O-Si [12]. When applied to textile fibres, IOHs could polymerize into a three-dimensional network that is oriented with the silsesquioxane chain towards the fibre surface and with the pendant organic groups away from it. Because of its three-dimensional structure, the polymer network could also act as a silica matrix for the incorporation of different functional particles and biopolymers [10, 13, 14].

Among nanoparticles that are commonly used for chemical modification of textile fibres, silver and silver-based compounds are among the most prominent because of their excellent antimicrobial properties [15-18]. The antimicrobial activity of silver compounds is dependent on their controlled release mechanism. Silver cations and silver nanoparticles leach from fibres to their surroundings, where they act as a poison for a broad spectrum of microorganisms. The antimicrobial activity of silver nanoparticles is directly influenced by their particle size. Namely, because of their larger specific area, smaller particles have a greater reactivity than larger ones. To decrease the particle size as well as to increase the uniformity of their distribution, particles were incorporated into different matrixes, among them a sol-gel matrix [13, 14]. To this end, different application processes were used, with in situ synthesis recognized as the most ecologically acceptable [19, 20]. The advantages of nanotechnological processes encouraged us to introduce a three-stage procedure for chemical modification of textile fibres to achieve their antimicrobial activity. In the first stage of the procedure, the fibres were treated by oxygen plasma, followed by the creation of a silica matrix with organofunctional trialkoxysilane in the second stage, and nanoparticles of silver chloride were incorporated by in situ synthesis in the third stage. Important objectives of this research were to investigate the influence of the fibres' chemical and morphological properties on the efficiency of chemical modification and the influence of individual stages of the procedure on the sorption capacity of the fibres as well as biodegradability of the chemically modified fibres. Whereas the first two objectives can provide insight into the effectiveness of the process of fibre functionalisation, the third will produce information about the sustainability of the introduced procedure of chemical modification.

Fabric code	Fibres composition	Construction	Weight [g/m ²]	Density [threads/cm]	
				warp	weft
СО	100% cotton	plain-weave	115	48	29
CO/PES	50% cotton, 50% polyester	plain-weave	170	29	22
PES	100% polyester	plain-weave	50	25	24

Table 1: Fabric codes, fibres compositions and construction parameters

2 Experimental part

2.1 Materials and reagents

Three woven fabrics were used in the experiment, i.e., 100% cotton (CO) and 100% polyester (PES) fabrics and a CO/PES fabric blend with a ratio of 50%/50%. The fabric characteristics and fabric codes are presented in Table 1. Before use, the fabrics were washed with water, neutralized with acetic acid, extensively rinsed under tap water and dried at ambient temperature.

2.2 Chemical modification of fabric samples 2.2.1 Plasma treatment

The studied fabric samples were treated with weakly ionized oxygen plasma. The discharge chamber was a borosilicate glass cylinder. The plasma was created with an inductively coupled radiofrequency (RF) generator operating at a frequency of 27.12 MHz and an output power of 400 W. The pressure was fixed at 75 Pa. For each fabric, eight samples were placed into the discharge chamber and treated in oxygen plasma for 10 seconds at a current of 0.5 A.

2.2.2 Application of silica matrix

A mixture of 15 g/l organic-inorganic crosslinking agent iSys MTX (CHT, Switzerland) and 1 g/l antifoaming agent Kollasol CDO (CHT, Switzerland) was applied to the untreated and plasma-treated fabric samples by a pad-dry-cure process that included the immersion of the samples into a finishing bath at room temperature, squeezing to an 80% up-take, drying at 120 °C for 5 minutes and curing at 150 °C for one minute. After impregnation, the samples were left for 7 days under standard conditions (relative humidity of $65 \pm 2\%$, temperature of 20 ± 1 °C) to complete the network formation of the applied iSys MTX.

2.2.3 Application of silver nanoparticles by in situ synthesis

Silver nanoparticles were applied to the silica matrix previously created on the fabric samples in a Starlet-2 apparatus (DaeLim Starlet Co., Korea). Solutions of 0.5 mM silver nitrate (AgNO₃) and sodium chloride (NaCl) were prepared separately in metal containers with liquor to goods ratio of 50:1. Each sample was immersed into the AgNO₃ solution for 10 minutes at room temperature with constant stirring to allow the fibres to absorb the solution. Afterwards, the samples were transferred into the NaCl solution and treated under the same conditions. The immersion procedure was repeated twice for each sample, followed by sample squeezing in a two-roll padder at a 100% up-take and airdrying at room temperature. The sample codes according to the fabric codes and the procedure of chemical modification are presented in Table 2.

2.3 Biodegradation of samples

Biodegradation of the samples was performed by a soil burial test according to the ISO 11721:2003 standard [21]. Samples were buried in soil that was rich in microorganisms for periods of 3, 6, 9 and 12 days. During the experiment, soil contained a constant water content equal to $60 \pm 5\%$ of its maximum moisture retention capacity, which was maintained by spraying with water. After the specified time of burial (3, 6, 9, 12 days), the samples were removed from soil, rinsed under tap water, immersed in 70% ethanol for 30 minutes and air-dried.

2.4 Analytical methods

2.4.1 Scanning electron microscopy (SEM) with energy–dispersive X–ray spectroscopy (EDS)

Morphological properties of the samples before and after chemical modification were examined using a Joel JSM-6060 LV microscope (Joel, Japan). Prior to the measurements, a thin layer of gold was applied to the samples. Atomic concentrations of elements in the samples were determined using a Jeol JSM 5610 microscope, equipped with EDS system. In this case, a thin layer of carbon of a thickness of about 10 nm was previously applied to the samples.

Sample code	Procedure of chemical modification	
CO(N)	no treatment	
CO(P)	plasma treatment	
CO(Si-Ag)	application of silica matrix followed by the application of silver nanoparticles by the <i>in situ</i> synthesis	
CO(P-Si-Ag)	plasma treatment followed by the application of silica matrix followed by the <i>in situ</i> synthesis of silver nanoparticles	
CO/PES(N)	O/PES(N) no treatment	
CO/PES(P)	(P) plasma treatment	
CO/PES(Si-Ag)	application of silica matrix followed by the application of silver nanoparticles by the <i>in situ</i> synthesis	
CO/PES(P-Si-Ag)	plasma treatment followed by the application of silica matrix followed by the <i>in situ</i> synthesis of silver nanoparticles	
PES(N)	N) no treatment	
PES(P)	plasma treatment	
PES(Si-Ag)	application of silica matrix followed by the application of silver nanoparticles by the <i>in situ</i> synthesis	
PES(P-Si-Ag)	plasma treatment followed by the application of silica matrix followed by the <i>in situ</i> synthesis of silver nanoparticles	

Table 2: Sample codes and the procedure of chemical modification

2.4.2 Fourier transform infrared spectroscopy (FTIR)

Chemical changes of the fabric samples before and after chemical modification were examined by the FTIR analysis. The spectra of the samples were recorded with the ATR cell spectrometer Spectrum GX (Perkin Elmer, United Kingdom) in the spectral range from 4000 to 600 cm⁻¹. The average of thirty-two spectra was presented for each sample. Before measurements, the samples were dried for 30 minutes at a temperature of 100 °C.

2.4.3 Thin-layer wicking

The thin-layer wicking test of wettability (TLW) was performed in the horizontal direction for the untreated and plasma-treated samples, according to Chibowski [22]. The fabric samples were cut into strips with a width of 1 cm and a length of 10 cm and dried for 30 minutes at a temperature of 100 °C. Each dry sample was inserted between two glass plates with a ruler and carefully contacted with deionized water in a Petri dish. Starting from when the water began to penetrate into the fabric sample, the time at which the water penetrated a certain distance in the fabric was measured. For each fabric sample, at least 10 measurements were

made, and the average value was presented as the result.

2.4.4 Inductively coupled plasma mass spectrometry (ICP-MS)

The concentration of silver on the chemically modified samples was determined by ICP-MS with the use of a Perkin Elmer SCIED Elan DRC spectrophotometer (Perkin Elmer, United Kingdom). Samples of the mass of 0.5 g were prepared in the Milestone microwave system by the acid decomposition with 65% HNO₃ and 30% H_2O_2 . For each fabric sample, three measurements were performed and a mean value was presented as a result.

2.4.5 Colour measurements

The lightness, L^* , of the samples before and after biodegradation was determined with a Spectraflash 600 PLUS-CT spectrophotometer (Datacolor, Switzerland) using a standard CIE D65 light source, 6.6mm aperture and CIE 1964 10° observation. Before measurements, the samples were conditioned at $65 \pm 2\%$ relative humidity and 20 ± 1 °C for 24 hours. For each fabric sample, 10 measurements were taken, and the mean value was presented as the result.

3 Results and discussion

3.1 The influence of chemical modification on the morphological and chemical properties of the fibres

SEM images of the untreated and chemically modified fabric samples (Figure 1) show that chemical modification did not cause visible changes to their surfaces. SEM/EDS analysis also revealed bright spots on the samples treated in the solutions of $AgNO_3$ and NaCl, which prove the formation of silver chloride (AgCl) particles in the *in situ* synthesis (Figure 2). The presence of AgCl on the fibres was also confirmed by EDS analysis (Table 3). Due to the silicon matrix present on the fibres, silicon and titanium were also detected by EDS analysis.



Figure 1: SEM images of untreated and finished samples

Tekstilec, 2017, **60**(1), 14-24



Figure 2: SEM/BSE images of fabric samples treated with the solutions of AgNO, and NaCl

 Table 3: Elemental compositions of the fabric samples determined by EDS analysis

Comula codo	Atomic concentration of element [%]					
Sample code	С-Ка	O-Ka	Si–Ka	Ag–La	Cl–Ka	Ti–Ka
CO(P-Si-Ag)	63.273	35.911	0.397	0.175	0.090	0.155
CO/PES(P-Si-Ag)	68.136	30.879	0.256	0.197	0.138	0.393
PES(P-Si-Ag)	75.329	24.296	0.007	0.006	0.280	0.089

3.2 The influence of the plasma treatment on the fibres' absorption capacity

The results of the TLW measurements (Figure 3) show that the rate of thin-layer wicking of water into the PES(N) sample (maximum slope of the line) was much slower than that into the CO/ PES(N) and CO(N) samples. This indicates that the



Figure 3: Rate (x^2/t) of thin-layer wicking of water into untreated and plasma-treated samples: \circ CO(N), \bullet CO(P), \Box CO/PES(N), \bullet CO/PES(P), \triangle PES(N), \blacklozenge PES(P)

wettability of the samples is directly related to the chemical structure of the fibres. This was also expected, because in contrast to the highly hydrophilic cotton fibres, polyester fibres are very hydrophobic and therefore very difficult to be wetted. Plasma treatment substantially increased the wettability of all three fabrics, which resulted in the increase of the water penetration rate; it was 5 times greater in the case of the PES(P) sample than in the case of the PES(N) sample.

In addition to increasing the wettability of the fibres, plasma treatment increased the adsorptivity of the fibres for silver as well. It is evident from Table 4 that the amount of adsorbed silver was two times higher on the plasma-treated CO sample than on the untreated CO sample and 3 times higher on the plasma-treated PES sample than on the untreated PES sample. These results support the conclusion that the pre-activation of the fibre surface with oxygen plasma contributed substantially to the effectiveness of chemical modifications. Furthermore, very similar values for silver concentrations obtained on the plasma untreated samples CO(Si-Ag), CO/PES(Si-Ag) and PES(Si-Ag) proved that silver particles were bonded into the silica matrix previously created on the fibre surface and that the chemical structure of the fibres did not significantly influence the adsorptivity for silver.

Sample code	Concentration of silver [mg/kg]		
CO(Si-Ag)	54 ± 11		
CO(P-Si-Ag)	110 ± 22		
CO/PES(Si-Ag)	69 ± 14		
CO/PES(P-Si-Ag)	117 ± 63		
PES(Si-Ag)	46 ± 9		
PES(P-Si-Ag)	140 ± 28		

Table 4: Concentration of silver in the untreated andplasma-treated fabric samples

3.3 The influence of chemical modification on fibre biodegradation

Photographs of the fabric samples before and after soil burial (Figure 4) show that the microorganisms present in soil caused biodegradation of the fibres, as reflected in the darkening of the samples. Visible colour changes of the fibres after soil burial are the result of the fibres moulding and rotting, which was caused by the absorbed microorganisms. The fibre moulding and rotting caused dark grey-brown stains on some of the samples or even deterioration into small pieces when rotting was very intensive. The higher the rate of the sample biodegradation was, the more intensive was the darkening of the sample during burial. The rate of biodegradation of the samples in soil also represented a criterion for the effectiveness of the antimicrobial protection of the chemically modified fibres. The higher the antimicrobial protection, the lower the rate of fibre biodegradation.

The results in Figure 5 clearly show that the rate of the sample biodegradation and the consequent darkening of the samples characterized by the change in the lightness, ΔL^* , were directly affected by the chemical composition of the fabric and its chemical modification as well as the burial time. Accordingly, among the untreated samples, the CO(N) sample degraded to the greatest extent, followed by the CO/PES(N) sample, and the PES(N) sample degraded to the smallest extent under the same conditions (Figure 5a). These results prove that PES fibres are much more resistant to biodegradation than CO fibres and suggest that hydrophobic highly crystalline PES fibres provide much poorer conditions for the growth of microorganisms in comparison to hydrophilic CO fibres.

A comparison of the values of ΔL^* calculated as the difference between the sample lightness values before and after soil burial clearly indicates that plasma treatment of the samples increases the rate of their biodegradation, irrespective of the chemical composition of the fabric and the time of burial. This phenomenon can be explained that the treatment of the samples with oxygen plasma increased the hydrophilicity of the fibres (Figure 3), which had a favourable impact on the microorganisms' growth. In addition, plasma treatment generated new oxygen atoms on the fibre surface, which also improved the conditions for the microorganisms' growth.



Figure 4: Photographs of representative samples before (a) and after 18 days (b) of soil burial

Tekstilec, 2017, 60(1), 14-24



Figure 5: Differences in lightness, ΔL^* , between the unburied samples and samples after 6, 12 and 18 days of burial: a) untreated (N) and plasma-treated (P) CO, CO/PES and PES samples; b) without plasma (Si-Ag) and with plasma treatment (P-Si-Ag) chemically modified CO, CO/PES and PES samples

The presence of silver nanoparticles in the CO(Si-Ag), CO(P-Si-Ag), CO/PES(Si-Ag) and CO/PES/ (P-Si-Ag) samples significantly reduced the fibre biodegradation, as shown by the low ΔL^* values determined between the unburied and buried samples, which did not exceed the value of 8 even at the maximum days of burial (Figure 5b). The reason for this was attributed to the release of silver from the fibre surface into soil, where it destroyed the microorganisms in the fibres' surroundings. On the other hand, the higher values of ΔL^* obtained for the plasma-treated samples in comparison to the untreated ones confirmed once again that plasma treatment enhanced the fibre biodegradation, despite the fact that the concentration of silver is higher on the plasma-treated samples in comparison to the untreated ones (Table 3). These results suggest that the characteristics of the fibre surface significantly affect the fibre biodegradation process even in the presence of the antimicrobial agent. This is confirmed by the results obtained for the PES samples after 18 days of burial, for which it was found that the least damage was suffered by the PES(N) sample ($\Delta L^* = 0.86$) and that all chemical modifications of the PES fibres, including the application of silver, increased the rate of fibre biodegradation. Biodegradation was not inhibited even in the case of the PES(P-Si-Ag) sample with a high concentration of silver.

The presence of microorganisms on the CO samples after the 18 days of burial was confirmed by the FTIR analysis. It is known from the literature that during their growth, microorganisms produce proteins that are characterized by two absorption bands, namely, at 1635 cm⁻¹, which belongs to amide I, and at 1530 cm⁻¹, which belongs to amide II [23]. The intensity of these absorption bands represents a measure of the rate of the microorganisms' growth and consequently a measure of the rate of the fibres' biodegradation. An inspection of the spectra in Figure 6 reveals the expected absorption bands in the 1500–900 cm⁻¹ region, which belong to the fingerprint of cellulose. Furthermore, the spectra show an absorption band at 1635 cm⁻¹, which is attributed to the HOH vibration of the adsorbed water molecules, absorption bands at 2918 cm⁻¹ and 2853 cm⁻¹ due to the CH and CH₂ vibrations in the macromolecules of cellulose, and an absorption band at 3340 cm⁻¹ due to the OH vibrations of the adsorbed water molecules. In the spectra of the CO(N) and CO(P) samples after 18 days of burial, an increase in the absorption band intensity at 1635 cm⁻¹ and the presence of an additional absorption band at 1530 cm⁻¹ confirm the growth of microorganisms on the untreated and plasma-treated cotton fibres during burial. Both spectra also show an additional absorption band of small intensity at 1725 cm⁻¹, which is characteristic of C=O vibrations and attributed to the aldehyde and carboxyl groups formed during the hydrolysis and the oxidative decomposition of the cellulose macromolecules in the process of biodegradation.



Figure 6: IR ATR spectra of untreated sample CO(N)before burial (a) and of untreated and chemically modified samples after 18 days of burial: b - CO(N), c - CO(P), d - CO(Si-Ag), e - CO(P-Si-Ag)

In contrast to the spectra of the CO samples, the absorption bands at 1635 cm⁻¹ and 1530 cm⁻¹, attributed to amide I and amide II, could not be observed in the spectra of the CO/PES (Figure 7) and PES (Figure 8) samples because these bands are blurred by the bands of the PES fingerprint. Namely, there are two characteristic absorption bands in the 1800–1500 cm⁻¹ region in the spectrum of the PES sample, i.e., an absorption band at 1720 cm⁻¹ due to the strong C=O symmetric vibrations of the carbonyl group in the ester bond and an absorption band at



Figure 7: IR ATR spectra of untreated sample CO/ PES(N) before burial (a) and of untreated and chemically modified samples after 18 days of burial: b – CO/PES(N), c – CO/PES(P), d – CO/PES(Si-Ag), e – CO/PES(P-Si-Ag)

1578 cm⁻¹ due to the asymmetric vibrations of the C-O bonds of the carboxylate anion. Therefore, to be able to determine the influence of the PES fibre biodegradation on the intensity of the bands at 1635 cm⁻¹ and 1530 cm⁻¹, the differential IR ATR spectra should be prepared and analysed.



Figure 8: IR ATR spectra of untreated sample PES(N) before burial (a) and of untreated and chemically modified samples after 18 days of burial: b - PES(N), c - PES(P), d - PES(Si-Ag), e - PES(P-Si-Ag)

4 Conclusion

In this study, a three-step nanotechnological process for chemical modification of textile fibres consisting of plasma treatment followed by silica matrix creation and in situ synthesis of silver nanoparticles was successfully introduced with the aim of increasing the fibres' antimicrobial activity. The treatment of all of the fabric samples with the oxygen plasma increased the wettability of the fibres and their sorption capacity for AgNO₃ and NaCl solutions, which resulted in a significant increase in the concentration of AgCl particles formed in the in situ synthesis. The presence of AgCl particles on the samples provided antimicrobial protection to the fibres and thereby reduced their rate of biodegradation during burial. Plasma treatment increased the biodegradability of the fibres, irrespective of their chemical composition. This was true even for the samples with the incorporated silver, in spite of the fact that the concentration of silver particles on these samples was greater than that on the samples that were not plasma-treated. These results confirm the importance of oxygen plasma treatment for both the efficiency of chemical modification as well as the fibre biodegradation.

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