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Wettability of the surface of bacterial cellulose film modified with the ion implantation

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Abstract: *Wettability of the surface of bacterial cellulose film modified with low energy ion implantation*
The paper presents the preliminary results of the modification on the water wettability of cellulose, using ion implantation method. Two kinds ions of the noble gases, i.e. helium and argon were implanted with fluences of 1e15 nand 1e16 cm^{-2}, and with the ion energy of 60 keV. The measurements of the contact angle values show the different influence of both types ions on the hydrophobicity of the modified cellulose, but the hydrophobicity of implanted cellulose increases in all cases. The real investigations were supplemented with the modelling results of the depth profiles of the implanted ions and the main parameters of the modelled peaks.

Keywords: bacterial cellulose, wettability, surface modification, ion implantation

INTRODUCTION

Cellulose is one of the most abundant organic polymers found in the world. It is a significant structural component of the primary cell wall of green plants, various forms of algae and oomycets. Since it is a non-toxic, biodegradable polymer with low density, high tensile, compressive strength, high stiffness and specific strength values closer to that of glass fibres, it is widely used in various fields such as nanotechnology, pharmaceutical, food, cosmetic, textile, paper, automotive industries, etc. Cellulose fibre-reinforced composites are using e.g. in packaging, construction, panelling, sporting equipment (Leveneur et al. 2018).

Sometimes, the basic properties, like a hydrophobicity of cellulose are insufficient. There are few methods of the modification of the properties, which can be used to the property improvement of cellulose.

The using continuous or pulse beams of electrons, ions or plasma is the non-conventional and non-popular way of the cellulose treatment.

The authors of Ref. (Barlak et al. 2017) presented the studies electron-irradiated beech wood. It has been shown that the roughness and water wettability change depends on the number and energy density of electron pulses.

Leveneur et al. modified the chemical and mechanical properties of cellulose fibers using the ion implantation of 15 keV Ar^+, 10 keV O^+ and 10 keV N^+, with fluencies (doses) above 1e14 cm^{-2}. The chemical and structural analysis showed that all cases resulted in molecular and microscopic damage similar to pyrolysis at ~250-300°C, while the estimated temperature during the ion implantation was below 80°C (Leveneur et al. 2018).

Similarly, the change of the microstructure and crystallinity of cellulose, implanted by 10 keV energy nitrogen ions were observed by Zhang et al. Cellulose relative degree of crystallinity reduced gradually with the increase of the implantation fluences. When the implantation fluences increased to 1e17 cm^{-2}, this parameter decreased 6.84% than the control sample (Zhang et al. 2011).

Abitoye et al. presented the results of ion implantation of the polyamide and cellulose acetate nanofiltration membranes to increase their effective surface charge, because the presence of a permanent charge in the membrane matrix allows for increased electrostatic repulsive forces throughout the entire pH range. Fluoride ions F^-, (from BF_3) were implanted with fluence of 1e10 and 5e10 cm^{-2} and with the ion energy of 10 keV (Abitoye et al. 2005).

This present paper shows the results of the preliminary investigation of the wettability change of bacterial cellulose, implanted with two different types of ions. Helium with the atomic mass of 4.002602 u and the the diameter of the atom of about 62 pm and argon with atomic mass of 39.948 u and the diameter of the atom of about 360 pm, are noble gases, which don't react chemically with the atoms of the implanted materials. Their influence on modified material has rather physical character, but they can induce the chemical reactions between elements of the modified materials, due to the introduction large dose of their kinetic energy. The both elements were used to the modification of cellulose in the ion implantation processes.

MATERIALS AND METHODS

Bacterial cellulose samples

Bacterial cellulose was obtained from the culture of microorganisms that make up the ecosystem called SCOBY. The cultivation of the microorganisms was carried out on a medium containing 10% edible sucrose and 0.03% peptone for a period of 14 days in a heat incubator (J.P. Selecta Laboratory Equipment Manufacturer, Barcelona, Spain). The temperature and humidity conditions of the cultivation were 26 ± 2ºC and 66 ± 2%. The gel film produced on the surface of the culture was washed several times in distilled water and then dried at 24 ± 2 ° C in a laboratory dryer (J.P. Selecta Laboratory Equipment Manufacturer, Barcelona, Spain) until constant weight was obtained. The dried bacterial cellulose was in the form of a thin film with a thickness of 0.13 ± 0.02 mm.

The density of the investigated cellulose was determined from the mass and the volume of the used samples. The atomic concentration of carbon, hydrogen and oxygen, i.e. main components of the material, was determined based on the determined value of the degree of cellulose polymerization (Betlej et al. 2022). The calculation error is 5% because the calculation did not take into account 5% of the impurities.

Modelling and modification

The ion implantation processes were preceded by Monte Carlo simulations of the main parameters of the depth profiles of the implanted elements (like peak volume dopant concentration N_{max}, projected range R_p, range straggling ΔR_p, kurtosis and skewness) (Barlak et al. 2019), using freeware type code SRIM-2013.00 (The Stopping and Range of Ions in Matter) (SRIM). The simulation was performed for 100 000 implanted ions of helium and argon, perpendicular to the implanted target (the angle of the ion incidence was defined as 0°). The theoretical values of the sputtering yield *Y* were additionally calculated, using commonly known freeware-type quick ion implantation calculator SUSPRE (SUSPRE), from the energy deposited in the surface region of the material using the Sigmund formula.

The modelled substrate material C-H-O (modelling codes treat the sample as a set of atoms that do not form chemical compounds) had a composition: 44.5% of carbon, 6.2% of hydrogen and 49.3% of oxygen in atomic percentages. The substrate material density, adopted for the simulation was 1.583 g/cm^3. All above values were determined for the real material.

In all cases, the simulations/calculations were performed for room temperature and for the total implanted fluences of 1e15 and 1e16 cm^{-2}. The value of the acceleration voltage was taken of 60 keV. The energy of the implanted ions was 60 keV, due to the homogeneous ion beams of He^+ and Ar^+.

The modelling did not account for the phenomenon of substrate sputtering by the implanted ions, substrate damages and the chemical reactions between the implanted ions and/or the substrate components.

The ion implantation processes were performed using semi-industrial implanter of gaseous ions, with non-mass separated beam, described in detail elsewhere (Barlak et al. 2022). Helium and argon of 5N purity were used as the source of the implanted ions. The beam current was at a level of 100 μA for the cross-sectional area of the ion beam of about 30 cm^2. The beam current density was at a level of about 3 $\mu A/cm^2$.

The implanted cellulose samples in the sample holders (Fig. 1) were clamped onto a stainless steel plate to avoid overheating effects, so the estimated value of temperature of the implanted pieces did not exceed 50°C. The working pressure in the vacuum chamber was at a level from 2 to 5e-3 Pa.

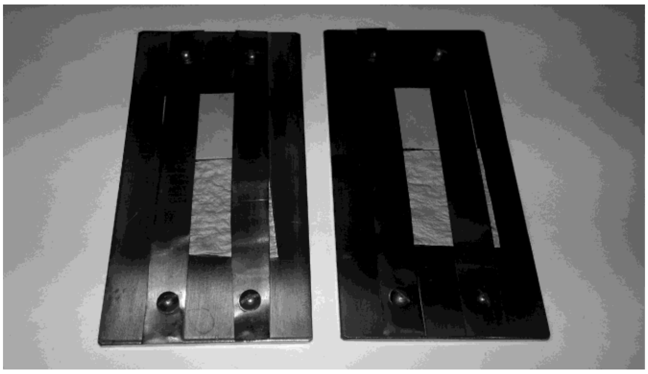

Figure 1. The implanted cellulose in steel sample holders

Determination of the contact angle

Virgin (non-modified, non-implanted) and implanted cellulose samples were tested for the wettability. The contact angle measurement was performed with a Haas Phoenix 300 goniometer (Surface Electro Optics, Suwon City, Korea) based on the sessile drop method. Using an image analysis system (Image XP, Surface Electro Optics, version 5.8, Suwon City, Korea), the angle between the tangent to the drop contour and the straight line passing through its base was determined. The measurement of wetting for a water droplet was performed after 5, 20, 40, and 60 s from the moment of depositing the water drop on the cellulose surface.

RESULTS AND DISCUSSION

Fig. 2 and Table 1 present the results of the computer simulations of the main parameters and the depth profiles of ions implanted without mass separation to C-H-O material. The results obtained for helium and argon were presented at this same graph for the better comparison. Additionally, the main process parameters of the ion implantation were introduced to the table.

The presented in the table unit "($atoms/cm^3$)/($atoms/cm^2$)" is a special unit of plot ordinate used in SRIM code results. With these units, by multiplying by the ion fluence (in $atoms/cm^2$) the ordinate values convert directly into a density distribution with the unit of $atoms/cm^3$.

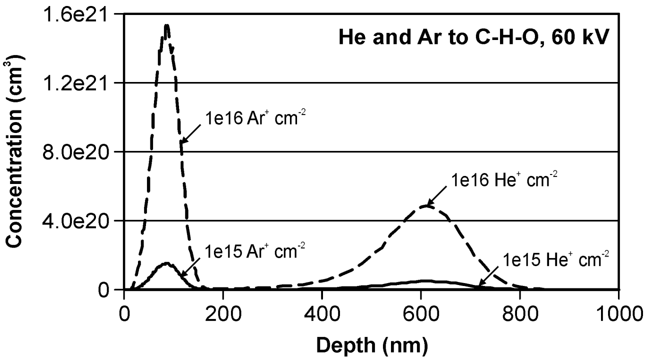

Figure 2. The modelled helium and argon depth profiles in C-H-O material

Table 1. The process parameters, peak parameters and sputtering yield values for all implanted cases

Implanted ions	He^+		Ar^+	
Acceleration voltage (kV)	60			
Ion energy (keV)	60			
Current beam (µA)	100			
Current beam density (µA/cm^2)	3			
Fluence (cm^{-2})	1e15	1e16	1e15	1e16
(atoms/cm^3)/(atoms/cm^2)	4.86e4		1.55e5	
Peak volume dopant concentration N_{max} (cm^{-3})	4.86e19	4.86e20	1.55e20	1.55e21
Projected range R_p (nm)	584.8		84.1	
Range straggling ΔR_p (nm)	196		50.2	
$R_p/\Delta R_p$	2.98		1.68	
Skewness	-0.9998		0.0571	
Kurtosis	5.4376		2.699	
Sputtering Yield Y (atoms/ion)	0.01		1.65	

The depth profile of helium is deeper, lower and wider in the comparison with the profile of argon (e.g. $R_p/\Delta R_p$ ratio is nearly two fold higher for He^+ and N_{max} values and the kurtosis value are more than three and two fold higher for Ar^+, respectively). The skewness value is negative for helium and positive for argon. It means the shift the peak maximum into the material in the first case and to the material surface in the second case.

There is a significant difference in the sputtering yield values. The sputtering practically don't exist in the case of He^+ implantation, while it is more than a hundred times greater in the case of Ar^+ implantation.

Fig. 3 shows the results of 60 s measurements of water contact angle of the virgin and He^+ and Ar^+ ion implanted cellulose samples. The results are presented in the pairs, i.e. for the treated and suitable non-treated material, due to observed large difference between different samples. The values on the axes are respectively the same for direct comparison of the results.

The experimental points were supplemented with trend lines, their equations and values of the R^2 determination coefficient values, determined using Microsoft Excel 2010 spreadsheet. The fit was made using a 2nd degree polynomial in all virgin cases and the fitting using linear trend lines was possible for all implanted samples. The determined values of R^2 coefficient are in the range from 0.8702 to 0.99.

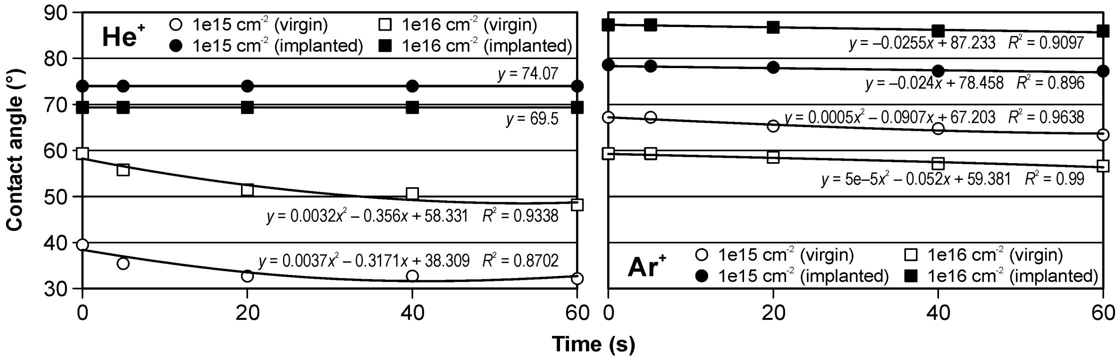

Figure 3. The change of the contact angle values in the time for the virgin and implanted samples

It can be observed that:
- there are a large differences of the contact angle values for the virgin material,
- the modification changes the character of the time dependence contact angle from 2nd degree polynomial to close to linear in all cases,
- the contact angle of the implanted samples changes in the time relatively little, especially, for the samples implanted with helium,
- the hydrophobicity of the implanted material increases in all investigated cases, regardless of the implanted element and its implanted fluence,
- the contact angle for materials implanted with helium is in the range from 69.5 to 74.07°, while the value range of this parameter is from 77.18 to 85.92° for argon; it may be related to the depth of implantation of elements, i.e. helium in the depth of the material, argon - closer to its surface,
- the contact angle is smaller for the larger dose of helium and vice versa - the larger for the larger dose of argon; the difference is about 5° for the first case and about 10° - for the second; the implanted elements give a different effect,
- the change of the contact angle is similar for both implanted elements, for the fluence of 1e15 cm^{-2}.

Fig. 4 presents the time dependent values of the relative change (with regard to the virgin material) of the contact angle, to avoid the high influence heterogeneity of the virgin material.

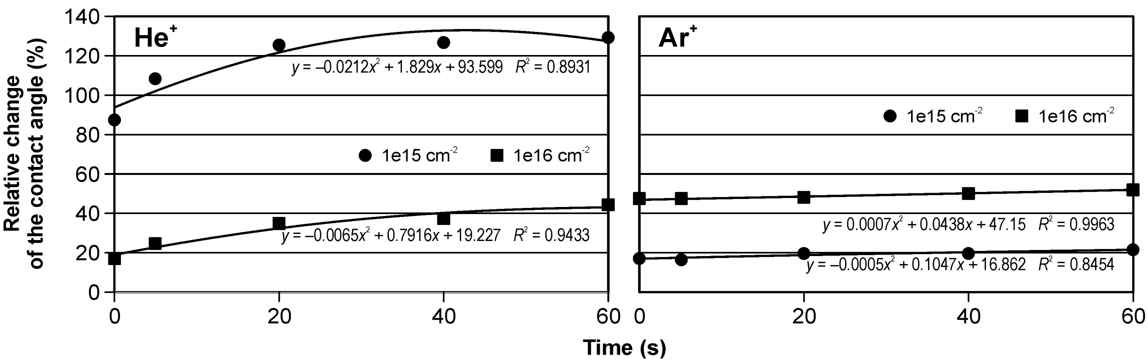

Figure 4. The change of the contact angle with respect to the virgin material

It is easy to see that:
- the time depended relative change of the contact angle for helium implantation is more parabolic, while the change of this relationship for argon implantation is more linear,
- the upward trend in the time is observed for all cases,
- the tendency is maintained that the values of the contact angle values for helium are higher for a lower dose, unlike for argon,

- the contact angle difference between the lower and higher fluence is about 80% for helium and about 30% for argon,
- the relative change of the contact angle is very similar for both implanted elements, for the fluence of 1e16 cm^{-2}.

The change of the contact angle with respect to the lower implanted fluence is presented in Fig. 5.

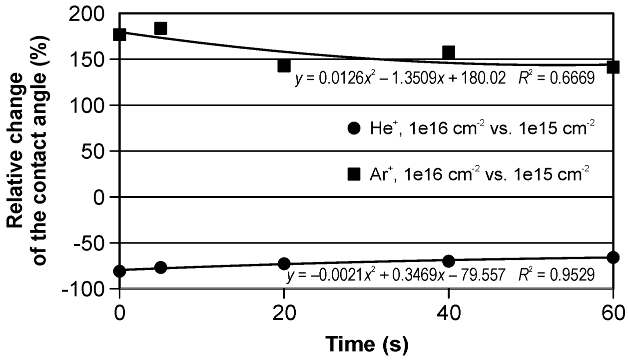

Figure 5. The change of the contact angle with respect to the lower implanted fluence

It is seen that:
- the relative change of the contact angle is smaller for the ion implantation of helium; the negative values shows the decreasing of the contact angle in the reference to the smaller fluence,
- opposite situation is for the ion implantation of argon; the positive values shows the increasing of the contact angle in the reference to the smaller fluence,
- the upward trend in the time is observed for helium implantation and the downward trend is observed for argon implantation.

CONCLUSIONS

The presented results shows that the possibility of the change of the hydrophobicity of cellulose implanted with helium or argon. These elements have the different influence, probably due to their possibilities of the different penetrating into the modified material. The values of the contact angle are higher for the lower dose of implanted helium and the higher for the higher dose of implanted argon. It should be noted that the hydrophobicity of implanted cellulose increases in all cases.

The presented investigation should be continued. The range of the energy of implanted ions should be extended to lower values. The range of the implanted fluencies it is also underused.

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Streszczenie: *Zwilżalność powierzchni celulozy bakteryjnej modyfikowanej metodą implantacji jonów*. Artykuł przedstawia wstępne wyniki modyfikacji na zwilżalność wodą implantowanej jonami celulozy. W badaniach wykorzystano dwa rodzaje gazów szlachetnych, tj. hel i argon. Implantowane dawki wynosiły 1e15 i 1e16 cm^{-2}, a energia jonów 60 keV. Pomiary kąta zwilżania pokazują różny wpływ obydwu typów jonów na hydrofobowość modyfikowanej celulozy, jednakże hydrofobowość wzrasta we wszystkich przypadkach. Badania zostały uzupełnione wynikami modelowania głębokosciowych profili implantowanych jonów i głównych parametrów modelowanych pików.

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