Carbohydrate Polymers 97 (2013) 143–151

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

The study of plasma's modification effects in viscose used as an absorbent for wound-relevant fluids

Zdenka Peršin[a,e,*,1], Miha Devetak[a], Irena Drevenšek-Olenik[b,c], Alenka Vesel[a,d], Miran Mozetič[a,d], Karin Stana-Kleinschek[a,e,1]

[a] Centre of Excellence for Polymer Materials and Technologies, Tehnoloski Park 24, SI-1000 Ljubljana, Slovenia
[b] Jožef Stefan Institute, Department for Complex Matter, Jamova 39, 1000 Ljubljana, Slovenia
[c] University of Ljubljana, Faculty of Mathematics and Physics, Jadranska 19, SI-1000 Ljubljana, Slovenia
[d] Jožef Stefan Institute, Department of Surface Engineering and Optoelectronics, Plasma Laboratory, Jamova 39, 1000 Ljubljana, Slovenia
[e] University of Maribor, Faculty of Mechanical Engineering, Laboratory for Characterisation and Processing of Polymers, Smetanova 17, SI-2000 Maribor, Slovenia

ARTICLE INFO

Article history:
Received 27 November 2012
Received in revised form 25 March 2013
Accepted 12 April 2013
Available online 25 April 2013

Keywords:
Viscose
Oxygen plasma
Wound fluids absorption
Ageing
Storage atmosphere

ABSTRACT

Extreme non-equilibrium oxygen plasma was used for the deep functionalisation of viscose materials used for the healing of chronic wounds. Those thermal effects, which usually appear during plasma treatment due to the influence of charged particles, were avoided effectively by using electrode-less discharge at a very low power density of 25 W/l volume. A huge flux of neutrally reactive atoms at room temperature of 3×10^{23} $\mathrm{m}^{-2}\,\mathrm{s}^{-1}$, allowed for the effective diffusion of O-atoms into inter-fibril space and thus the activation of fibrils throughout the non-woven materials. Apart from the standard Wilhelmy balance and pedant drop method for determining the absorption dynamics on a macroscopic scale, optical polarisation microscopy was applied for studying the microscopic effects. The sorption characteristics were determined for saline solution, exudate, and blood and the results showed a dramatic improvement. Focusing on hydrophobic recovery prevention, the modified samples were stored for 10 days in air, nitrogen, and argon atmospheres. Some ageing effects occurred, whilst the absorption properties were independent of the storage atmosphere.

1. Introduction

Wounds are considered as the major cause of morbidity and impaired quality of life, especially by patients suffering from diabetes. It has been estimated that in 2010 over 1% of the world's population suffered from serious complications causing chronic ulcer wounds. The average cost of a treatment cycle is estimated to be about €6600 for leg ulcers and €10,000 for foot ulcers (Eucamed Medical Technology, 2011).

Wound dressings are regarded as the medical means of cleaning and protecting wounds in order to facilitate and accelerate the healing process. Although the healing process of wounds is a natural process, the speed of healing and fluid loss is still one of the major challenges. Significant improvements in developing wound dressing products have been recorded since the earliest century, but the properties of those materials currently used are still far from challenging the characteristics that chronic wounds exhibit.

Cellulose in the form of a cotton fabric is technically still one of more important composite components applied on wound dressings as an absorbent. However, it is rarely used in its 100% form because it sticks to the wound, as well as due to its rather low purity and high production costs. Viscose in the form of woven or non-woven textiles is more commonly used. Although the absorbency of viscose is much higher compared to similar materials (e.g. modal and lyocell), the capacities and rates are still insufficient when considering absorbent applications. In addition, the absorbency rate of viscose is definitely below the capacity of alginate (Rowe, Sheskey, & Quinn, 2009) whilst, on the other hand, there is no evidence suggesting that alginate wound dressings are more effective for healing diabetic foot ulcers than other types of dressings (Dumville, O'Meara, Deshpande, & Speak, 2012).

Several techniques have been developed for modifying viscose materials in order to improve their absorption properties (Durso, 1978; Fengel & Wegener, 1984; Freytag & Donzé, 1983; Lewin, 1984). Amongst them, treatment by gaseous plasma is of particular interest (Canal, Erra, Molina, & Bertran, 2007; Canal, Gaboriau, Villeger, Cvelbar, & Ricard, 2009; Gorensek, Gorjanc, Bukosek,

---

* Corresponding author at: University of Maribor, Faculty of Mechanical Engineering, Laboratory for Characterisation and Processing of Polymers, Smetanova 17, SI-2000 Maribor, Slovenia. Tel.: +386 2 220 7886; fax: +386 2 220 7990.
E-mail address: zdenka.persin@um.si (Z. Peršin).

[1] Member of the European Polysaccharide Network of Excellence.

0144-8617/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carbpol.2013.04.045

Kovac, Petrovic, et al., 2010; Gorensek, Gorjanc, Bukosek, Kovac, Jovacic, et al., 2010; Gorjanc, Bukosek, Gorensek, & Vesel, 2010; Mihailovic et al., 2010; Radetic, Jovancic, Puac, & Petrovic, 2005; Ristic, Jovancic, Canal, & Jocic, 2009; Vesel et al., 2010) due to quality procedural standards regarding efficiency and homogeneity, harmlessness of bulk properties, and the environmental impact. It is well-known that plasma created in air or oxygen causes the functionalisation of polymers with surface functional groups (Chan, Ko, & Hiraoka, 1996; Guimond, Hanselman, Amberg, & Hegemann, 2010; Junkar, Cvelbar, Vesel, Hauptman, & Mozetic, 2009; Vesel, 2008), which in turn causes a dramatic improvement of the surface-wetting characteristic, as one amongst the more important factors affecting the absorbency rate and the capacity (Canal et al., 2007; Ferrero, 2003; Hossain, Herrmann, & Hegemann, 2006; Morent et al., 2008; Pandiyaraj & Selvarajan, 2008).

For many industrial applications (e.g. paper, food, ceramics, agriculture, etc.) water, as a substance to be absorbed, is used adequately for determining a material's absorbing properties, whilst it cannot be applied for assessing wounds. Assessing a wound comprehensively requires not only the classifications of colour, depth, shape, size, exudate amount, and wound location, but also an understanding of wound dressings' absorption behaviour regarding exuding fluids. This phenomenon is addressed in this paper; and the results are presented as systematic studies on micro and macro scales.

It is well-known that plasma-treated surfaces undergo ageing, known as hydrophobic recovery or surface recovery (Arpagaus, Rossi, & von Rohr, 2005; Hegemann, Brunner, & Oehr, 2003; Hirotsu, Ketelaars, & Nakayama, 2000). Several methods have been explored for regressing the ageing, including optimisation of plasma treatment parametres (Kim, Kim, Park, & Ryu, 2002; Lawton, Price, Runge, Doherty, & Saavedra, 2005; Occhiello, Morra, Cinquina, & Garbassi, 1992), cross-linking to limit the mobilities of surface functional groups (Behnisch, Hollander, Zimmermann, 1993; Kim et al., 2002; Lawton et al., 2005; Nakamatsu, Delgado-Aparicio, & Da Silva, 1999; Occhiello et al., 1992), and various ageing environments (Brennan, Feast, Munro, & Walker, 1991; Canal, Molina, Bertran, & Erra, 2004; Kim, Kim, Cho, & Park, 2001; Kim et al., 2002; Lawton et al., 2005; Morra et al., 1990; Nakamatsu et al., 1999; Occhiello et al., 1992; Takke, Behary, Perwuelz, & Campagne, 2009). During some shelf-life investigations, nitrogen and argon atmospheres were used to study the storage lives of fruits and vegetables (Jamie & Saltveit, 2002; Klieber, Bagnato, Barrett, & Sedgley, 2002). Within the context of medical dressings used for wound-healing, it is important to establish the ageing characteristics of the materials during the period from plasma treatment to application. Thus, the objective of this investigation was not only to report the surface modification of viscose non-woven by oxygen plasma immediately after plasma treatment, but also ageing within air, argon, and nitrogen atmospheres over time periods of up to 10 days.

2. Experimental

2.1. Materials

Cellulose material was used as a regenerated cellulose fibre in its non-woven form, as kindly provided by KEMEX, The Netherlands. The specific surface mass of the material was 175 g m^{-2} (SIST ISO 3801). The air permeability at room temperature was 650 L m^{-2} s^{-1} (SIST EN ISO 9237). The thickness of this material under normal conditions was about 1.7 mm (SIST EN ISO 5084). The samples were dried within a vacuum oven type VS-50SC (Kambič) under a constant pressure of 100 mbar and at a temperature of 20 °C for 24 h before plasma treatment. They were cut into pieces having dimensions of 22 cm × 22 cm for performing the plasma treatment. Systematic studies of the absorption properties were performed on macroscopic and microscopic scales.

2.2. Liquids for absorption measurements

The absorption properties of the cellulose material were tested with three different liquids: (1) saline solution, (2) synthetic blood and (3) synthetic exudate. These liquids are often used during routine quality control procedures by producers of wound dressings and other related products such as surgical gauzes, and tampons. The composition and physical properties of the used liquids are presented in Table 1. The physical properties of the used liquids were determined at 20 °C, i.e. density was determined using a hydrometer (ASTM 100) and viscosity by a Rheolab MC 100 Viscometer, Physica, Germany. The liquids 'surface tensions (γ_l) were measured using a Wilhelmy balance (Tensiometer Krűss K12; ASTM D1331) and the pedant-drop method (OCA 35 DataPhysic; ASTM D3825-09).

2.3. Plasma treatment

The samples were exposed to oxygen plasma created within a vacuum system pumped by a two-stage oil rotary pump with a nominal pumping speed of 60 m^3 h^{-1} and ultimate pressure <1 Pa. The discharge chamber was a 30 cm long glass cylinder with an inner diametre of 27 cm capped by aluminium side-plates. The plasma was excited in pure oxygen leaked into the system during continuous pumping by a radio frequency (RF) generator operating at the standard industrial frequency of 27.12 MHz, and a nominal power of 5 kW. A matching network was mounted between the generator and the induction coil, thus allowing for adjustment of the useful power according to the specific needs of the particular experiment, i.e. the output power was fixed at about 500 W. Such a discharge created almost perfectly-uniform plasma for the entire volume of the discharge chamber. The plasma parameters were estimated using electrical and catalytic probes. At a pressure of 75 Pa, as was used in the current experiments, the density of the charged-particles was of the order of 10^{15} m^{-3} whilst the neutral atom density, which depends slightly on the distance from the side-plates, was about 2×10^{21} m^{-3} in the centre of the discharge tube. A sample holder placed at the centre of the tube in order to fix cellulose samples was made of glass in order to prevent substantial drainage of O-atoms by heterogeneous surface recombination. The flux (j) of neutral O-atoms on the surface was homogenous over the entire sample's surface and was calculated from the measured O-atom density using the standard equation:

$$j = \frac{1}{4} n\upsilon \qquad (1)$$

where n are the measured densities of the neutral O-atoms and υ is their average thermal velocity at room temperature.

2.4. Capillary rise technique

The absorbency rate and absorbent capacity are the two more important performance parameters to be considered for the absorbent application of non-woven. The absorbency rate is governed by the balance between the forces exerted by the capillaries and the frictional drag offered by the fibre surfaces. The absorbent capacity is mainly determined by the interstitial spaces between the fibres, the absorbing and swelling characteristics of the material, and the resiliency of the web in the wet state. The absorbency rate is given by the slope of the weight gained due to liquid penetration, as a function of time, whilst the absorbent capacity is determined by the volume/mass of fluid absorbed at equilibrium divided by the dry mass of the test specimen.

Table 1
Composition and physical properties of liquids used in absorption measurements.

	Saline solution	Synthetic blood[a]	Synthetic exudate
Composition	9 g/L NaCl (99.5%; Merck KgaA, Germany)	70 g Tylose H 20p (regular grade; SE Tylose® GmbH & Co. KG, Wiesbaden, Germany) 50 g NaCl (99.5%; Merck KgaA, Germany) 20 g NaHCO3 (99.5%; Merck KgaA, Germany) 5 g Ca24 (Biochema Schwaben, Memmingen) 5 g dye Brilliant ponceau 4RC 70E (Simon & Werner GmbH, Flörsheim am Man, Germany) 500 g glycerine (Pharmaceutical quality, Merck KgaA, Germany)	0.37 g/L $CaCl_2H_2O$ (97%; Sigma–Aldrich, Germany) 8.3 g/L NaCl (99.5%; Merck KgaA, Germany)
Density (g/cm^3)	1.01	1.03	1.01
Viscosity (mPas)	1.75	7.93	7.45
pH	7	7	7
γ_l (mN/m)	69.56 ± 2.71 (WBT) 67.14 ± 2.27 (PDT)	48.13 ± 0.17 (WBT) 45.07 ± 1.93 (PDT)	66.49 ± 2.10 (WBT) 66.25 ± 1.82 (PDT)

WBT: Wilhelmy balance technique; PDT: pedant drop technique.

[a] Hy-Tec composition 5/94; Hy-Tec Hygene Technologie GmbH, Ratingen

The modified Washburn (Washburn, 1921) or capillary-rise technique (Jakobasch, Grundke, Mäder, Freitag, & Panzer, 2003), performed on a Krűss K12 Tensiometer device, was used to study the absorption properties of the cellulose material on a macroscopic scale. The cellulose samples were cut into spherical discs of 2.5 cm diametre and hung up on the sample holder in the Tensiometer apparatus. The sample mass was monitored as a function of time during the absorption experiment. The results are presented as wetting rise curves (m^2/t), where m is the mass increase and t is the time, and as the amount of liquid uptake (g fluid/g) in equilibrium.

2.5. *Optical polarisation microscopy*

Absorption kinetics on a microscopic scale for a single cellulose fibre was investigated by optical polarisation microscopy (Nikon Polarising Microscope Optiphot 2-pol). High resolution video recordings of the absorption process were made within a cross-polarisation regime. The fibres were pulled from non-woven cellulose and placed between two glass plates. Drops of liquid were placed along edge of the fibre and started to wet the fibre. The change in the intensity of polarised light travelling through the fibre is linked to the kinetics of the fluid absorption (Devetak et al., 2012) Video recordings were decomposed into frames and numerical data analysis was performed using Matlab software. The characteristic times of the transmitted intensity modification were determined by fitting the exponential saturation function (Karoglou, Moropoulou, Giakoumaki, & Krokida, 2005).

3. Results and discussion

3.1. *Absorption vs. plasma modification*

The absorption properties on the macroscopic and microscopic scales were monitored for all three liquids and the results obtained for the non-treated material were compared with the oxygen plasma modified materials. At least 10 measurements were performed for each sample and each liquid, in order to obtain statistically-significant results.

The macroscopic results are presented in Fig. 1 as the wetting rise curves for the plasma treated sample, as obtained by repeatedly monitoring the penetration flow of the synthetic blood.

Each wetting rise curve obtained for a single synthetic blood penetration measurement of the plasma treated sample differed slightly from the other measured curves. Similar results in terms of reproducibility were also obtained for the other two liquids used, as well as for the non-treated sample, and these results are not presented here. The wetting curves, representing the absorbency rate (see Fig. 1), were statistically processed (Karoglou et al., 2005) and were taken into account as average curves for further analysis.

Fig. 2 shows the effect of oxygen plasma treatment on the capability of the viscose non-woven sample to up-take the liquid. The results are presented as average wetting rise curves as obtained for all the test liquids used.

The results shown in Fig. 2 demonstrate a dramatic increase in the absorbency rate by oxygen plasma treated cellulose material as compared to the non-treated sample. The wetting rise curves for the saline solution and synthetic exudate increased by more than an order of magnitude, whilst the increase for synthetic blood was not as significant, but nevertheless noteworthy.

The plasma gained absorbent capacity, as the amount of test liquid up-take in equilibrium, is presented in Table 2.

For the non-treated sample, the equilibrium by saline solution and synthetic exudate uptake was established within 300 s and the sample was able to absorb between 1.1 g and 1.3 g of liquid.

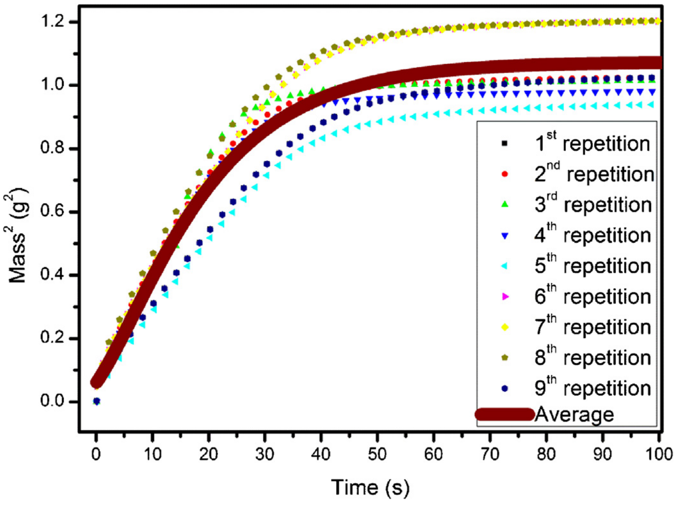

Fig. 1. Wetting rise curves obtained with repeated monitoring of synthetic blood sorption by plasma treated samples. Each curve represents the absorption measurements from one sample. The average curve is also presented.

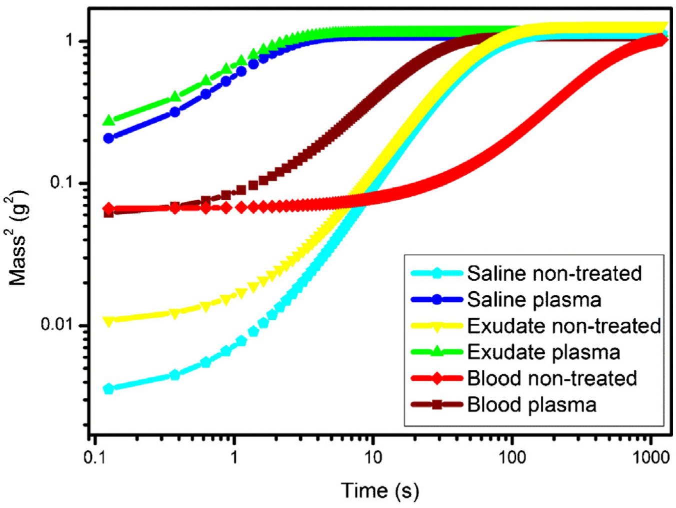

Fig. 2. Average wetting rise curves for non-treated and plasma treated non-woven viscose for three different liquids.

Table 2
Amount of liquid up-take in equilibrium for non-treated and oxygen plasma treated viscose non-woven.

Sample	Amount of liquid up-take (g liquid/g)		
	Saline solution	Synthetic blood	Synthetic exudate
Non-treated	1.1 ± 0.1	1.0 ± 0.1	1.3 ± 0.1
Oxygen plasma treated	1.1 ± 0.0	1.0 ± 0.1	1.1 ± 0.0

In the case of synthetic blood penetration, the equilibrium for the non-treated sample was established no sooner than within 1200 s, whilst the final absorbed uptake amounted to 1 g. It is worth mentioning that within 300 s, the non-treated sample was able to absorb only half of the final amount of the synthetic blood. The plasma treated sample was able to obtain the equilibrium uptake quicker, i.e. for saline solution and synthetic exudate it was established within 20 s, whilst for the synthetic blood it took 60 s. The final amount for all the absorbed liquid was 1 g.

Polarisation optical microscopy was used to monitor the absorption properties for a single cellulose fibre on the microscopic scale. Fig. 3 shows the relative modifications of the transmitted intensity, measured on 10 plasma treated fibres during the soaking of the synthetic exudate.

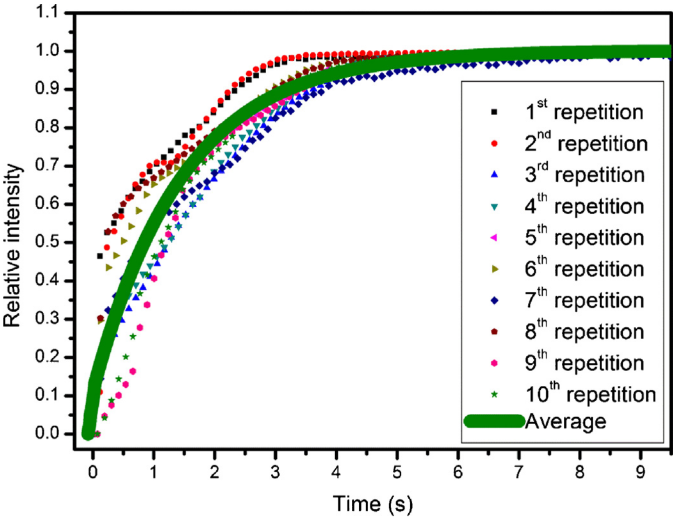

Fig. 3. Reproducibility of characteristic intensity change time measurements for plasma treated samples soaked with exudate.

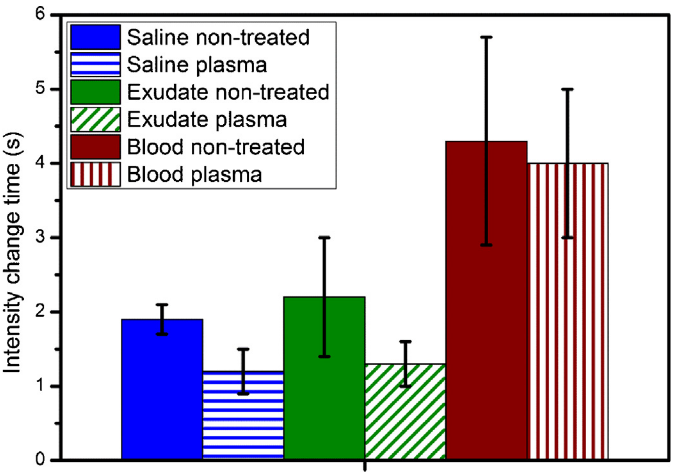

Fig. 4. Typical characteristic intensity change time expressed as a bar chart, calculated for non-treated and plasma treated materials for three different liquids.

It can be seen from Fig. 3, that the reproducibility of the results was good. Similarly good reproducibility was obtained for the other two liquids. The average intensity curves were fitted by the exponential saturation function. The characteristic microscopic absorption times were deduced. The results are presented as a bar chart in Fig. 4.

Plasma treatment reduced the absorption times for all liquids on the microscopic scale. This indicated a significant increase in the kinetics of the absorption process on the microscopic level for saline solution and synthetic exudate, whilst synthetic blood exhibited only a minor change.

It is evident, that low-pressure plasma was proven to be very efficient for textile fabric treatment. The low-pressure plasma ensured a more intense high electron energy-tail, and consequently a more efficient gas phase molecular fragmentation. From the results obtained for freshly plasma treated samples it could be suggested that plasma oxidation might induce different effects, i.e. (i) cleaning, (ii) functionalisation, and (iii) etching. In our previous study (Persin, Vesel, Stana Kleinschek, & Mozetic, 2012), the XPS survey spectra results for the oxygen plasma treated sample indicated a decrease in carbon concentration (by 5 at%) and the C1 peak (by 26%) in relation to surface cleaning. The surface functionalisation was illustrated by an increase in oxygen concentration (by 5.7 at%) and the formation of oxygen-containing functional groups, as deduced from the C3 and C4 peaks. As a result, a huge increase in polar components and, consequently, an increase in surface energy were observed (Persin, Stenius, & Stana-Kleinschek, 2011). Besides the aforementioned, there was also an increase in the sample's surface area (Vesel, Junkar, Cvelbar, Kovac, & Mozetic, 2008) resulting from etching and this had an influence on hydrophilicity.

The penetration of the fragmented gas particles into the voluminous textile is also influenced by the textile geometry, i.e. the distances between fibres in the textile. The non-woven sample consists of a high amount of disorderly gathered-together fibres, which also form the spaces between the fibres. At low-pressure, the mean free path (the distance travelled by a molecule or atom between successive collisions) during the gas phase are higher than the textile distances, and the collision of gas molecules with the fibre surface is enhanced as compared to gas-gas collision, thus favouring a good penetration of plasma species into the textile. Specifically, the obtained absorptivity of the looser structured non-woven had improved significantly. In addition, surface roughness on a larger scale, i.e. fine rough surface made of fibres, can also enhance the macroscopically hydrophilic nature (Ren, Cheng, Wang, & Li, 2010).

In addition, the absorbency rate and capacity also depend on the liquids' physical properties, e.g. viscosity and surface tension. The saline solution had the lowest viscosity, whilst the synthetic blood and exudate had the same and above all, higher values, respectively. The faster absorbency rate obtained by the saline solution can be attributed to its lower viscosity, meaning less resistance of the liquid to penetration. Surprisingly, the absorbency rate for synthetic blood was lower compared to synthetic exudate, although both had the same viscosity. These indicate that the viscosity was influenced by several factors, i.e. the compositions, sizes, and shapes of the molecules, inter-molecular forces, and the temperature. The composition of synthetic blood (see Table 1) consisted of a number of particles that differed in molecular size and shape. Since the synthetic exudate consisted of a more liquid phase (only two components were present) it could move more smoothly through the sample, and therefore a higher absorbency rate was observed. In practice, these factors were more pronounced. Namely, the blood consisted of plasma and particles such as red blood cells. Blood plasma is considered as a Newtonian liquid, whilst red blood cells are not. On the other hand, with increased temperature, the viscosity of the blood decreased. At 37 °C the viscosity of blood is normally around 3–4 mPas, whilst at 20 °C it is around 10 mPas. The results, as presented in Table 1, also indicate high values and could therefore explain the lower absorbency rate by the synthetic blood. Exudate is a serious liquid in a wound bed and is considered as a part of normal healing in wounds. As fluid passes through the inflamed vessel walls it may be seen that the wound exudate is, in essence, modified serum and will therefore contain similar solutes, i.e. mostly water and a small amount of albumin, electrolytes, and hormones. Since the synthetic exudate is also considered to be a thin and watery solution, the obtained absorbency rate could well fit into the real management of wound exudate.

Surface tension is also one of the causes of penetration action. The results in Table 1 show that the surface tensions obtained by the Wilhelmy balance technique (WBT) were slightly higher compared to the pendant drop (PDT) results. Careful consideration of the listed results seems to indicate that surface tension could be influenced by the techniques used to obtain it. Namely, the liquid surface tension is time-dependent and sensitive to exposed air, particularly by blood (Harkins & Harkins, 1929). When using a PDT method the great disadvantage is to hold the bubble at its maximum pressure for the time necessary to establish the equilibrium between the interior of the blood sample, and its surface. Since the WBT method requires the liquid sample to be placed in a vessel within the apparatus, and the time needed to carry out the experiment takes a few minutes, the obtained higher value could be explained. However, the surface tension results for synthetic blood obtained by both methods agreed well with the values of human blood found by other authors (Morgan & Woodward, 1913; Harkins & Harkins, 1929; Krishnan, Wilson, Sturgeon, Siedlecki, & Vogler, 2005). The results in Table 1 show that the saline solution had the highest surface tension, followed by synthetic exudate and synthetic blood, regardless of the used experimental technique. All the used liquids consisted of a certain amount of NaCl, that caused a lowering of surface tension regarding the water ($\gamma_{\text{water}} = 72.8$ mN/m; Gebhardt, 1982). Therefore the less surface tension thus caused the decreased penetration action. The synthetic exudate contained a similar amount of NaCl as the saline solution, but also $CaCl_2$ that in addition lowered the surface tension resulting in the slowest absorption rate. Since the synthetic blood contained the highest amount of NaCl, the lowest measured surface tension was reasonable and thus the lowest absorption rate.

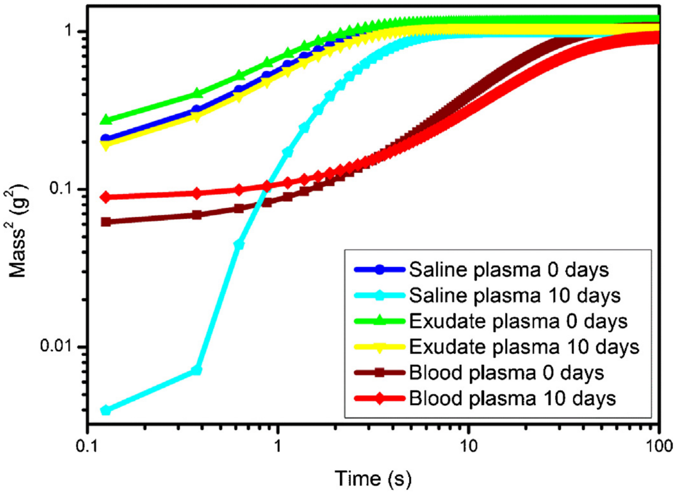

Fig. 5. Wetting rise curves for plasma treated samples immediately after treatment and ageing in air for 10 days; both axes have a logarithmic scale.

3.2. Absorption vs. ageing

An adequate study of absorption properties regarding any material modified by non-equilibrium plasma treatment should include the ageing effects. As has been shown by numerous authors (Van der Mei, Stokroos, Schakenraad, & Busscher, 1991; Morra, Occhiello, & Garbassi, 1993; Nakamatsu et al., 1999; Canal et al., 2004; Yun et al., 2004) the highly polar functional groups generated on the surface of organic materials are not stable, but tend to spontaneously decay. The ageing is particularly pronounced for intrinsically-hydrophobic polymers that have been activated by oxygen plasma treatment (Williams, Wilson, & Rhodes, 2004; Yun et al., 2004). In order to study the ageing effect of oxygen plasma treatment regarding absorption properties, the samples were stored for 10 days within an acclimatised chamber at a temperature of 20 ± 2 °C, and 65 ± 2% of relative humidity. Subsequently, systematic measurements on macro and micro scales were performed and the results are summarised in Figs. 5 and 6.

In Fig. 5 a logarithmic rather than a linear scale was used on the axes in order to emphasise changes between aged and non-aged samples. As with the freshly obtained results, the aged samples had the same trend for wetting rise curves obtained from amongst the liquids. Additionally, the aged sample reached the equilibrium of all

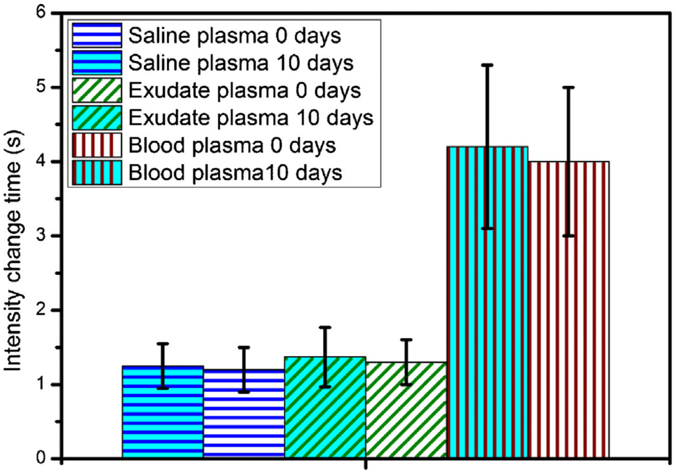

Fig. 6. Characteristic intensity change time for plasma treated samples immediately after treatment and ageing in air for 10 days.

Table 3
Amount of liquid up-take in equilibrium for 10 days plasma aged viscose non-woven as a function of storage atmosphere.

Storage atmosphere	Amount of liquid up-take (g liquid/g)		
	Saline solution	Synthetic blood	Synthetic exudate
Air	0.99 ± 0.0	0.86 ± 0.0	1.0 ± 0.0
Nitrogen	0.95 ± 0.0	0.90 ± 0.1	1.0 ± 0.0
Argon	1.0 ± 0.1	0.93 ± 0.1	1.0 ± 0.1

the liquids' uptakes during the same time as the non-aged sample, although the shapes of the curves indicated a lower rate. Similarly, there were no significant differences in the uptake amount by aged samples (i.e. 1 g of saline and synthetic exudate solution and 0.9 g of synthetic blood) compared to the fresh one.

It is apparent from Fig. 6 that on the microscopic scale there was an ageing component whilst the plasma treated viscose material was stored in air. However, the ageing, in terms of intensity change time, was not a dominating factor.

The X-ray photoelectron spectroscopy measurements (XPS), as obtained in our previous study (Persin et al., in press) indicated the same amounts of the polar groups still present within the modified region of the air stored samples, whilst the wetting rise curves (see Fig. 5) suggest otherwise, although the hydrophobic recovery was insignificant. This apparent anomaly could be explained by the relative surface sensitivities of the two techniques. By using the XPS technique, elemental information was obtained from a depth of about 3 nm. However, the absorption results suggest that the surface sensitivity was of the order of 1 nm and that a depletion in surface concentration of the polar groups occurred following storage in air. Furthermore, the polar groups could be located deeper inside the polymer due to their migration from the surface into the bulk. This mechanism could explain the loss of wettability, thus demonstrating the lower absorption rate attributed to the reorientation of very near-surface functional groups. In addition, another mechanism could explain the loss of adsorption properties when stored in air, i.e. reorganisation of those free radicals that were created during plasma oxidation, and/or their reactions with unsaturated hydrocarbon molecules. It is also worth mentioning that auto-oxidation, due to the contact of trapped radical sites within the sample surface with oxygen or water molecules from the ambient air, could also have occurred. The latter could be considered as a minor phenomenon compared to plasma oxidation.

Another explanation for minor hydrophobic recovery could exist in the non-woven structure. Namely, in looser- structured fabrics, long-living radicals and energetic particles assuredly move into the inter-fibre spaces, that is to say that plasma species bombardment with a higher surface area caused higher penetration into the textiles (Hossain et al., 2006). This resulted in the desired modification in bulk ensuring a minor loss of gained absorptivity.

3.3. *Adsorption ageing vs. storage atmosphere*

With the intention of seeking for better conditions that could improve or even prevent ageing of the oxygen plasma treated samples; the samples were stored for 10 days within different atmospheres, i.e. air, argon, and nitrogen. The absorption properties of 10 day plasma aged samples for all three liquids, as a function of storage atmospheres, were evaluated on macro and micro scales. The macro results, presented as wetting rise curves, are shown in Figs. 7–9, and the liquid uptake amount is shown in Table 3. In Fig. 7 the results obtained for saline solution, in Fig. 8 the results as monitored for synthetic exudate absorption, and in Fig. 9 the absorption of synthetic blood, are presented. The characteristic microscopic results for plasma aged samples, as a function of liquid absorption and storage atmospheres, are presented in Fig. 10.

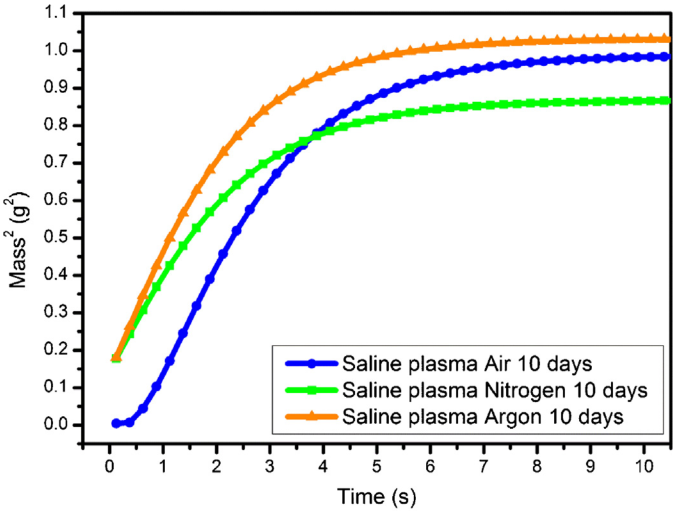

Fig. 7. Wetting rise curves for 10 days plasma aged samples obtained during absorption of the saline solution as a function of atmospheric storage.

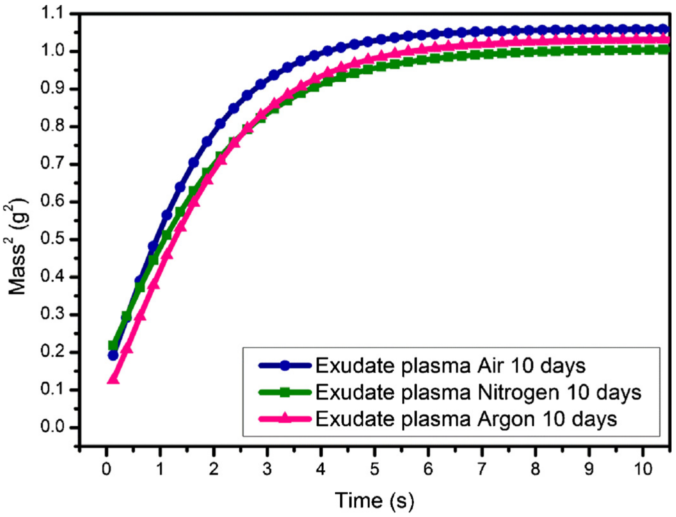

Fig. 8. Wetting rise curves for 10 days plasma aged samples obtained during the absorption of synthetic exudate as a function of atmospheric storage.

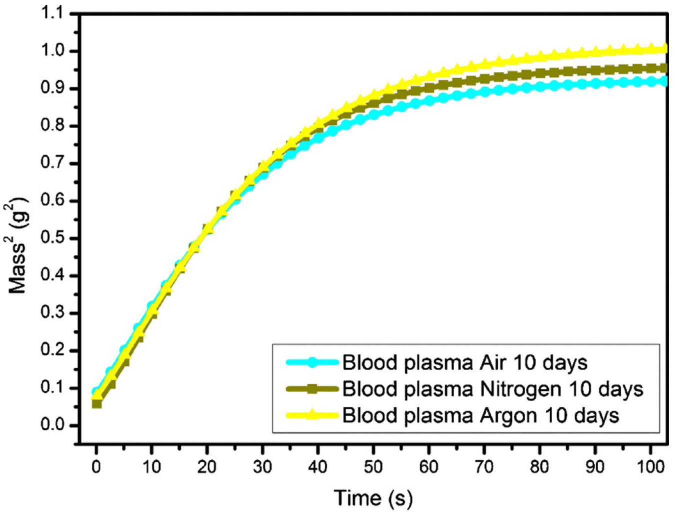

Fig. 9. Wetting rise curves for 10 days plasma aged samples obtained during the absorption of synthetic blood as a function of atmospheric storage.

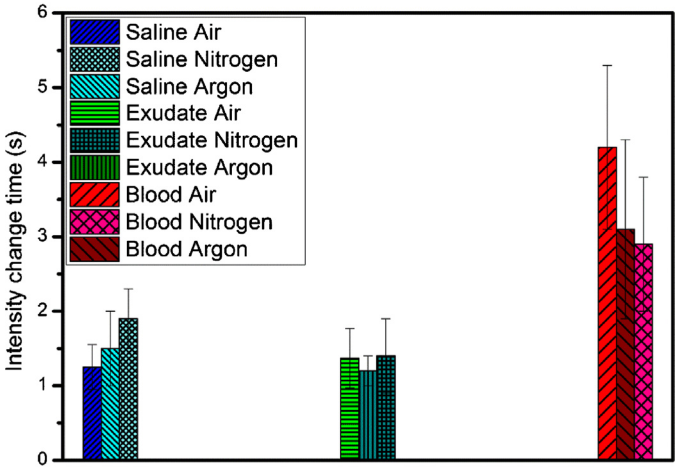

Fig. 10. Characteristic intensity change time for 10 days plasma aged samples as a function of liquid absorption and storage atmospheres.

The macroscopic results for the plasma aged samples indicated no significant differences in wetting curves as a function of storage atmospheres for synthetic blood and exudate (see Figs. 8 and 9). The slight influences of atmospheres are evident for aged samples from the absorption of saline solution (see Fig. 7). As well the aged samples stored in nitrogen and argon atmospheres obtained the equilibrium liquids uptake within the same time as those samples stored in air. The results presented in Table 3 indicate that storage atmosphere had no influence on the amount of the liquid's up-take.

Fig. 10 displays that storage within the different atmospheres modified the kinetic properties of the absorption process to some extent. The absorption kinetics for different fluids had altered differently. The exudate absorption kinetics was the least influenced by the storage atmosphere whilst the blood absorption kinetics displayed a stronger discrepancy between air and the other two storage atmospheric gasses. This could have been related to the lowest surface tension obtained by synthetic blood compared to the other two liquids. Since the surface tension was directly connected to the cohesive energy, it would appear that the ageing effect and atmosphere storage affected the kinetics of the blood adhesion to the fibre surface on the microscopic scale.

The macroscopic (Figs. 7–9) and microscopic (Fig. 10) results for the plasma aged samples indicated no significant differences in the absorption properties amongst the different atmospheres used for storage. This could be explained by two hypotheses, i.e. saturation, which is one of the important parametres resulting in a reduction of the ageing effect after plasma treatment, and the influence of atmospheric gas. Saturation may occur on a sufficiently thick surface, as well as deep inside the material. This phenomenon can be explained by the rather low penetration depth of reactive plasma particles capable of surface reactions with cellulose material, leading to the formation of highly polar functional groups. The penetration depth depends on the stabilities of the reactive gaseous particles during the gas phase, as well as on the surfaces. The major mechanism of the loss of particles, such as positively charged ions, neutral atoms, and metastable atoms and molecules, which are rather stable at low pressures, is heterogeneous surface recombination, neutralisation or relaxation. The neutralisation of oppositely charged particles occurs at any surface with a high probability, so they cannot penetrate into porous materials as long as the electric field across the material is negligible. A high electric field across the porous samples, on the other hand, often causes extensive exothermic reactions leading to the thermal degradation of cellulose. In order to avoid such effects it is better to use other reactive particles for the functionalisation of porous materials. The more suitable of such particles are neutral atoms in the ground state, the relativities of which at room temperature are small (Hody et al., 2006), as is the recombination coefficient on organic materials (Aleksandrova, Grinevich, & Chesnokova, 1997; Junkar et al., 2009). Neutral oxygen atoms abound in the experimental reactor due to the choice of materials used for construction of the discharge chamber. In this experimental work, the chamber was made from Pyrex glass with a recombination coefficient in the order of 10^{-4} (Wickramanayaka, Hosokawa, & Hatanaka, 1991). The side-plates were made from polished and subsequently oxidised aluminium with a similar inertness as neutral O atoms. The atoms are therefore unlikely to be lost by surface recombination, and since the pressure was low enough so that gas phase recombination by three-body collisions was unlikely, and the dissociation fraction of oxygen molecules was large, notwithstanding the small specific discharge power. The volume of the plasma chamber was about 20 l, the power was approximately 500 W, and therefore the specific power was only 25 W/l volume. Such a low power was very appropriate in order to prevent thermal degradation of the cellulose during plasma treatment. The flux of O atoms onto the sample surface was about $3 \times 10^{23}\ \mathrm{m^{-2}\ s^{-1}}$. The surface density of the atoms in a solid material was of the order of $10^{19}\ \mathrm{m^{-2}}$. If the reaction probability was only 10^{-4}, the surface would be saturated with surface functional groups in less than 1 s. In this study, however, the treatment time lasted for 10 min. Such a long treatment time was necessary to allow for the diffusion of neutral oxygen atoms throughout the cellulose material. The atoms were lost by surface functionalisation as well as heterogeneous recombination, and therefore the densities of the atoms inside the porous material decreased. Following this, surface saturation with functional groups deep inside the material can occur only at treatment times much greater than the time needed for saturation of the samples' surfaces, which is less than 1 s. In more powerful reactors this time might be decreased significantly but one has to use the applied discharge power carefully since the thermal effects may degrade the cellulose material before achieving bulk functionalisation.

Atmospheres, rich in argon, are known to have diffusivity characteristic that might influence the diffusion of O_2 from air (Burg & Burg, 1965). The latter research work, carried-out on fruits, indicated that a nitrogen atmosphere might reduce the gas diffusion and increase the concentration gradient of O_2 between the inside and outside of the material. Based on this mention, the obtained absorption results for the aged samples, which were shown to be practically independent of the storage atmosphere, could be explained. In the light of the gained results, one can conclude that the oxygen plasma treated cellulose sample could be stored in air. Furthermore, no additional costs and supplementary equipment would be needed to provide adequate conditions in order to maintain the plasma-induced absorbency within 10 days.

3.4. *Comparison between the macroscopic and microscopic absorption results*

Since the dry sample in the form of fabric exhibits three stages of transport behaviour when responding to an external liquid environment, the comparison between the macro and micro absorption results were reasonable. The macroscopic results (Figs. 2,5,7–9) revealed more significant changes in the absorption properties compared to the microscopic ones (Figs. 3, 4, 6 and 10) after plasma treatment, as also for the aged samples, as well the same trend also shown for those aged samples stored within different atmospheres. The liquid diffusion into interfibrilar voids took place during the first stage of the liquid transfer process. In addition the fibres' surfaces were also covered rapidly with liquid. The second stage was a relatively slow procedure where the sorption of liquid into the fibres took place. The third stage was reached as a final steady-state where all the stages of the transport became steady. The differences between the macro and micro scale results could be due to the fact that the fibre itself had a limited absorption capacity compared to the fabric. The fabric represented a container of capillaries that is made of interconnected pores formed of fibres. Based on this and the fact that diffusion was determined by liquid surface tension, the virtual discrepancy between the macro and micro results could be explained.

4. Conclusions

Cellulose material in its non-woven form was treated with rather mild oxygen plasma in order to improve absorption properties. Instead of water, which is commonly-used for determining the absorbency, three wound-relevant fluids, i.e. saline solution, synthetic blood, and exudate were used. In order to obtain insight into the absorption mechanism, two complementary methods were applied. Ageing studies were also performed in order to examine the absorption durability of modified surfaces as function of different storage atmospheres.

Both the macro and micro scale methods based on systematic measurements demonstrated a good reproducibility of results. Plasma treatment had a significant effect on the macroscopic results and demonstrated an increase in the absorbency rate and the capacity, more pronounced for saline and exudate solutions. The same trend was also observed for the kinetics of the absorption process on the micro scale level, although the changes were less outstanding. The ageing effect was observed, but it was less pronounced and was indicated as being independent of the storage atmospheres. The discrepancy between the macroscopic and microscopic measurements led to the conclusion that the heterogeneous complex structure and the liquid's surface tension caused the differences in the penetration action amongst the used test liquids.

Nevertheless, plasma as a uniquely effective surface engineering tool, streaming from its unparalleled physical, chemical and thermal ranges, and its dry and environmentally-friendly nature, offers substrate material suitable for application in wound dressing practice. The gained knowledge from this research study and an understanding of wound-relevant fluids' absorption behaviour combined with knowledge of the properties of non-woven material, could contribute to an assessment of the healing process leading to successful wound management.

Acknowledgements

The authors acknowledge the financial support from the Ministry of Higher Education, Science and Technology of the Republic of Slovenia through the contract No. 3211-10-000057 (Centre of Excellence Polymer Materials and Technologies).

References

Aleksandrova, S. N., Grinevich, Y. I., & Chesnokova, T. A. (1997). Recombination probabilities for oxygen atoms on a polyethylene terephthalate surface. *Journal of Applied Spectroscopy*, *64*(6), 798–803. http://dx.doi.org/10.1007/BF02678863

Arpagaus, C., Rossi, A., & von Rohr, P. R. (2005). Short-time plasma surface modification of HDPE powder in a plasma downer reactor – process, wettability improvement and ageing effects. *Applied Surface Science*, *252*, 1581–1595. http://dx.doi.org/10.1016/j.apsusc.2005.02.099

Behnisch, J., Hollander, A., & Zimmermann, H. (1993). Factors influencing the hydrophobic recovery of oxygen plasma treated polyethylene. *Surface & Coatings Technology*, *59*, 356–358. http://dx.doi.org/10.1016/0257-8972(93)90112-2

Brennan, W. J., Feast, W. J., Munro, H. S., & Walker, S. A. (1991). Investigation of the ageing of plasma oxidized PEEK. *Polymer*, *32*(8), 1527–1530. http://dx.doi.org/10.1016/0032-3861(91)90436-M

Burg, S. P., & Burg, E. A. (1965). Gas exchange in fruits. *Plant Physiology*, *18*, 870–884.

Canal, C., Molina, R., Bertran, E., & Erra, P. (2004). Wettability, ageing and recovery process of plasma-treated polyamide 6. *Journal of Adhesion Science and Technology*, *18*(9), 1077–1089.

Canal, C., Erra, P., Molina, R., & Bertran, E. (2007). Regulation of surface hydrophilicity of plasma treated wool fabrics. *Textile Research Journal*, *77*(8), 559–564. http://dx.doi.org/10.1177/0040517507078062

Canal, C., Gaboriau, F., Villeger, S., Cvelbar, U., & Ricard, A. (2009). Studies on antibacterial dressings obtained by fluorinated post-discharge plasma. *International Journal of Pharmaceutics*, *367*(1–2), 155–161. http://dx.doi.org/10.1016/j.ijpharm.2008.09.038

Chan, C. M., Ko, T. M., & Hiraoka, H. (1996). Polymer surface modification by plasmas and photons. *Surface Science Reports*, *24*(1–2), 1–54. http://dx.doi.org/10.1016/0167-5729(96)80003-3

Devetak, M., Skoporc, N., Rigler, M., Persin, Z., Drevensek-Olenik, I., Copic, M., et al. (2012). Effects of plasma treatment on water sorption in viscose fibres. *Materials and Technology*, *46*(1), 69–73.

Dumville, J. C., O'Meara, S., Deshpande, S., & Speak, K. (2012). Alginate dressings for healing diabetic foot ulcers. *Cochrane Database of Systematic Reviews*, *2*(CD009110) http://dx.doi.org/10.1002/14651858.CD009110.pub2

Durso, D. F. (1978). Chemical modification of cellulose. In R. M. Rowell, & R. A. Young (Eds.), *A historical review ZDA: Modified cellulosics* (pp. 23–37). NY: Academic Press.

Eucamed Medical Technology (2011). http://www.eucomed.org/ (20.11.11).

Fengel, D., & Wegener, G. (1984). Wood, chemistry, ultrastructure reactions. In D. Fengel, & G. Wegener (Eds.), *Reactions in alkaline medium* (pp. 66–105). Berlin, New York: Walter de Gruyter.

Ferrero, F. (2003). Wettability measurements on plasma treated synthetic fabrics by capillary rise method. *Polymer Testing*, *22*(5), 571–578. http://dx.doi.org/10.1016/S0142-9418(02)00153-8

Freytag, R., & Donzé, J. J. (1983). Handbook of fiber science and technology: Volume I: Chemical processing of fibers and fabrics, fundamentals and preparation part A. In M. Lewin, & S. B. Sello (Eds.), *Alkali treatment of cellulose fibres* (pp. 91–121). New York and Basel: Marcel Deckker, Inc.

Gebhardt, K. F. (1982). *Grundlagen der physikalischen Chemie von Grenzflächen und Methoden zur Bestimmung grenzflächenenergeticscher Größen*. Stuttgart, Germany: Fraunhofer- Institut für Grenzflä chentechnik IGB.

Gorensek, M., Gorjanc, M., Bukosek, V., Kovac, J., Petrovic, Z., & Puac, Lj. N. (2010). Functionalization of polyester fabric by Ar/N_2 plasma and silver. *Textile Research Journal*, *80*, 1633–1642. http://dx.doi.org/10.1177/0040517510365951

Gorensek, M., Gorjanc, M., Bukosek, V., Kovac, J., Jovancic, P., & Mihailovic, D. (2010). Functionalization of PET fabrics by corona and nano silver. *Textile Research Journal*, *80*(3), 253–262. http://dx.doi.org/10.1177/0040517509105275

Gorjanc, M., Bukosek, V., Gorensek, M., & Vesel, A. (2010). The influence of water vapor plasma treatment on specific properties of bleached and mercerized cotton fabric. *Textile Research Journal*, *80*, 557–567. http://dx.doi.org/10.1177/0040517509348330

Guimond, S., Hanselman, B., Amberg, M., & Hegemann, D. (2010). Plasma functionalization of textiles: Specifics and possibilities. *Pure and Applied Chemistry*, *82*(6), 1239–1245.

Harkins, H. N., & Harkins, W. D. (1929). The surface tension of blood serum, and the determination of the surface tension of biological fluids. *Journal of Clinical Investigation*, *7*(2), 263–281.

Hegemann, D., Brunner, H., & Oehr, C. (2003). Plasma treatment of polymers for surface and adhesion improvement. *Nuclear Instruments & Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, *208*, 281–286. http://dx.doi.org/10.1016/S0168-583X(03)00644-X

Hirotsu, T., Ketelaars, A. A. J., & Nakayama, K. (2000). Plasma surface treatment of PCL/PC blend sheets. *Polymer Engineering and Science*, *40*, 2324–2331. http://dx.doi.org/10.1002/pen.11365

Hody, V., Belmonte, T., Pintassilgo, C. D., Poncin-Epaillard, F., Czerwiec, T., Henrion, G., et al. (2006). Modification of hexatriacontane by O_2–N_2 microwave post-discharges. *Plasma Chemistry and Plasma Processing*, *26*(3), 251–266. http://dx.doi.org/10.1007/s11090-006-9017-3

Hossain, M., Herrmann, A. S., & Hegemann, D. (2006). Plasma hydrophilization effect on different textile structures. *Plasma Processes and Polymers*, *3*(3), 299–307. http://dx.doi.org/10.1002/ppap.200500152

Jakobasch, H. J., Grundke, K., Mäder, E., Freitag, K. H., & Panzer, U. (2003). Contact angle wettability & adhesion. In K. L. Mittal (Ed.), *Application of the surface free energy concept in polymer processing* (pp. 921–936). The Netherlands: Zeist VSP BV.

Jamie, P., & Saltveit, M. E. (2002). Postharvest changes in broccoli and lettuce during storage in argon, helium, and nitrogen atmospheres containing 2% oxygen. *Postharvest Biology and Technology*, *26*, 113–116.

Junkar, I., Cvelbar, U., Vesel, A., Hauptman, N., & Mozetic, M. (2009). The role of crystallinity on polymer interaction with oxygen plasma. *Plasma Processes and Polymers*, *6*(10), 667–675. http://dx.doi.org/10.1002/ppap.200900034

Karoglou, M., Moropoulou, A., Giakoumaki, A., & Krokida, M. K. (2005). Capillary rise kinetics of some building materials. *Journal of Colloid and Interface Science*, *284*, 260–264.

Kim, B. K., Kim, K. S., Cho, K., & Park, C. E. (2001). Retardation of the surface rearrangement of O_2 plasma-treated LDPE by a two-step temperature control. *Journal of Adhesion Science and Technology*, *15*(14), 1805–1816. http://dx.doi.org/10.1163/15685610152715791

Kim, B. K., Kim, K. S., Park, C. E., & Ryu, C. M. (2002). Improvement of wettability and reduction of aging effect by plasma treatment of low-density polyethylene with argon and oxygen mixtures. *Journal of Adhesion Science and Technology*, *16*(5), 509–521. http://dx.doi.org/10.1163/156856102760070349

Klieber, A., Bagnato, N., Barrett, R., & Sedgley, M. (2002). Effect of post-ripening nitrogen atmosphere storage on banana shelf life, visual appearance and aroma. *Postharvest Biology and Technology*, *25*, 15–24. http://dx.doi.org/10.1016/S0925-5214(01)00163-6

Krishnan, A., Wilson, A., Sturgeon, J., Siedlecki, C. A., & Vogler, E. A. (2005). Liquid–vapor interfacial tension of blood plasma, serum and purified protein constituents thereof. *Biomaterials*, *26*, 3445–3453. http://dx.doi.org/10.1016/j.biomaterials.2004.09.016

Lawton, R. A., Price, C. R., Runge, A. F., Doherty, I. I. I. W. J., & Saavedra, S. S. (2005). Air plasma treatment of submicron thick PDMS polymer films: effect of oxidation time and storage conditions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *253*, 213–215. http://dx.doi.org/10.1016/j.colsurfa.2004.11.010

Lewin, M. (1984). Handbook of fiber science and technology: Volume I: Chemical processing of fibers and fabrics, fundamentals and preparation part B. In M. Lewin, & S. B. Sello (Eds.), *Bleaching of cellulosic and synthetic fabrics* (pp. 91–243). New York and Basel: Marcel Deckker, Inc.

Mihailovic, D., Saponjic, Z., Molina, R., Puac, N., Jovancic, P., Nedeljkovic, J., et al. (2010). Improved properties of oxygen and argon RF plasma-activated polyester fabrics loaded with TiO_2 nanoparticles. *ACS Applied Materials & Interfaces*, *2*(6), 1700–1706. http://dx.doi.org/10.1021/am100209n

Morent, R., De Geyter, N., Verschuren, J., De Clerck, K., Kiekens, P., & Leys, C. (2008). Non-thermal plasma treatment of textiles. *Surface & Coatings Technology*, *202*(14), 3427–3449. http://dx.doi.org/10.1016/j.surfcoat.2007.12.027

Morgan, J. L. R., & Woodward, H. E. (1913). The weight of a falling drop and the laws of tate. *Journal of the American Chemical Society*, *35*, 1249–1262.

Morra, M., Occhiello, E., & Garbassi, F. (1993). The effect of plasma-deposited siloxane coatings on the barrier properties of HDPE. *Journal of Applied Polymer Science*, *48*(8), 1331–1340. http://dx.doi.org/10.1002/app.1993.070480803

Morra, M., Occhiello, E., Marola, R., Garbassi, F., Humphrey, P., & Johnson, D. (1990). On the aging of oxygen plasma-treated polydimethylsiloxane surfaces. *Journal of Colloid and Interface Science*, *137*(1), 11–24. http://dx.doi.org/10.1016/0021-9797(90)90038-P

Nakamatsu, J., Delgado-Aparicio, L. F., & Da Silva, R. (1999). Ageing of plasma-treated poly(tetrafluoroethylene) surfaces. *Journal of Adhesion Science and Technology*, *13*, 753–761.

Occhiello, E., Morra, M., Cinquina, P., & Garbassi, F. (1992). Hydrophobic recovery of oxygen-plasma-treated polystyrene. *Polymer*, *33*(14), 3007–3015. http://dx.doi.org/10.1016/0032-3861(92)90088-E

Pandiyaraj, K. N., & Selvarajan, V. (2008). Non-thermal plasma treatment for hydrophilicity improvement of grey cotton fabrics. *Journal of Materials Processing Technology*, *199*(1–3), 130–139. http://dx.doi.org/10.1016/j.jmatprotec.2007.07.046

Persin, Z., Stenius, P., & Stana-Kleinschek, K. (2011). Estimation of the surface energy of chemically and oxygen plasma-treated regenerated cellulosic fabrics using various calculation models. *Textile Research Journal*, *81*(16), 1673–1685. http://dx.doi.org/10.1177/0040517511410110

Persin, Z., Vesel, A., Stana Kleinschek, K., & Mozetic, M. (2012). Characterisation of surface properties of chemical and plasma treated regenerated cellulose fabric. *Textile Research Journal*, *82*(20), 2078–2089. http://dx.doi.org/10.1177/0040517512445338

Persin, Z., Mozetic, M., Vesel, V., Maver, T., Maver, U., & Stana Kleinschek, K. Cellulose/Book 2. In Theo G.M. Van De Ven (Ed.), Plasma induced hydrophilic cellulose wound dressing. InTech Publisher. (ISBN 980-953-307-487-5), in press.

Radetic, M., Jovancic, P., Puac, N., & Petrovic, Z. L. J. (2005). Environmental impact of plasma application to textiles. *Journal of Physics Conference Series*, *71*, 012017. http://dx.doi.org/10.1088/1742-6596/71/1/012017

Ren, W., Cheng, C., Wang, R., & Li, X. (2010). Effect of fiber surface morphology on the hydrophilicity modification of cold plasma-treated polypropylene nonwoven fabrics. *Journal of Applied Polymer Science*, *116*, 2480–2486. http://dx.doi.org/10.1002/app

Rowe, R. C., Sheskey, P. J., & Quinn, M. E. (2009). Handbook of pharmaceutical excipients. In R. C. Rowe (Ed.), *Alginic acid* (pp. 48–51). London, UK: Pharmaceutical Pr.

Ristic, N., Jovancic, P., Canal, C., & Jocic, D. (2009). One-bath one-dye class dyeing of PES/cotton blends after corona and chitosan treatment. *Fibers and Polymers*, *10*(4), 466–475. http://dx.doi.org/10.1007/s12221-009-0466-1

Takke, V., Behary, N., Perwuelz, A., & Campagne, C. (2009). Studies on the atmospheric air–plasma treatment of PET (Polyethylene Terephtalate) woven fabrics: Effect of process parameters and of aging. *Journal of Applied Polymer Science*, *114*, 348–357.

Van der Mei, H. C., Stokroos, I., Schakenraad, J. M., & Busscher, H. J. (1991). Ageing effects of repeatedly glow-discharged polyethylene: influence of contact angle, infrared absorption, elemental surface composition, and surface topography. *Journal of Adhesion and Science Technology*, *5*, 757–769.

Vesel, A. (2008). XPS study of surface modification of different polymer materials by oxygen plasma treatment. *Journal of Microelectronics Electronic Components and Materials*, *38*(4), 257–265.

Vesel, A., Junkar, I., Cvelbar, U., Kovac, J., & Mozetic, M. (2008). Surface modification of polyester by oxygen- and nitrogen-plasma treatment. *Surface and Interface Analysis*, *40*(11), 1444–1453. http://dx.doi.org/10.1002/sia.2923

Vesel, A., Mozetic, M., Strnad, S., Stana-Kleinschek, K., Hauptman, N., & Persin, Z. (2010). Plasma modification of viscose textile. *Vacuum*, *84*, 79–82. http://dx.doi.org/10.1016/j.vacuum.2009.04.028

Washburn, E. W. (1921). Dynamics of capillary flow. *Physical Review*, *17*, 273–283. http://dx.doi.org/10.1103/PhysRev.17.273

Wickramanayaka, S., Hosokawa, N., & Hatanaka, Y. (1991). Variation of the recombination coefficient of atomic oxygen on Pyrex glass with applied RF power. *Japanese Journal of Applied Physics*, *30*(11R), 2897–2900. http://dx.doi.org/10.1143/JJAP.30.2897

Williams, R. L., Wilson, D. J., & Rhodes, N. P. (2004). Stability of plasma-treated silicone rubber and its influence on the interfacial aspects of blood compatibility. *Biomaterials*, *25*, 4659–4673.

Yun, Y. I., Kim, K. S., Uhm, S. J., Khatua, B. B., Cho, K., Kim, J. K., et al. (2004). Aging behavior of oxygen plasma-treated polypropylene with different crystallinities. *Journal of Adhesion Science and Technology*, *18*(11), 1279–1291.