Journal of Central European Agriculture, 2016, 17(2), p.315-324 DOI: 10.5513/JCEA01/17.2.1708

The uptake and release of humidity by wool irradiated with electron beam

Príjem a uvoľňovanie vlhkosti vlnou ožiarenou elektrónovým lúčom

Zuzana HANZLÍKOVÁ[1*], Jana BRANIŠA[1], Ján ONDRUŠKA[2] and Mária PORUBSKÁ[1]

[1] Department of Chemistry, Faculty of Natural Sciences, Constantine the Philosopher University, Tr. A. Hlinku 1, 949 74 Nitra, Slovak Republic, *correspondence: zuzana.hanzlikova@ukf.sk

[2] Department of Physics, Faculty of Natural Sciences, Constantine the Philosopher University, Tr. A. Hlinku 1, 949 74 Nitra, Slovak Republic

Abstract

In this work, wool samples a) degreased and stored in desiccator (WD), b) degreased and stored freely (WF), c) cleaned in water and stored freely (WW) were irradiated by accelerated electron beam with doses within the range (0-400) kGy in air. Content of S-sulphonate as primary oxidation product was determined in WD using FTIR spectra inverted in the second-order derivative spectra. The uptake of humidity by all the samples at room temperature and 97% relative humidity was examined gravimetrically. As expected, the highest humidity uptake was observed for WD and the smallest one for WW. Development of the humidity uptake showed some fluctuation for all samples and, for WD the fluctuation corresponded with generated S-sulphonate, presumably due to formation of numerous H-bonds. The increasing uptake of humidity for WD and WW was observed up to 40 kGy dose while for WF, the uptake decreased below the initial level already from 16 kGy. Surface tension was measured using sink-float method combining stalagmometry. The initial surface tension of WW was higher than for WD and WF but, grew equally for all samples from 25 kGy. From 100 kGy dose the surface tension showed stabilized level. The humidity release by WD was measured using thermogravimetry. Variation of the rate humidity release around 100 °C, adequate for desorption of weakly bound water, and the mass residue of the heated wool for 120 °C corresponding to release of total water, showed an inverse dependence. It was concluded that content of S-sulphonate is responsible for variability of the sorption properties. The more S-sulphonate formed, the higher uptake of humidity and the lower rate of humidity release that can be observed. It is suggested that, within a certain range, a properly chosen dose can affect humidity uptake.

Keywords: electron beam irradiation, humidity uptake, release, surface tension, wool

Abstrakt

V tejto práci vzorky vlny a) odmastenej a uloženej v exsikátore (WD), b) odmastenej a uloženej voľne (WF), c) čistenej vo vode a uloženej voľne (WW), boli ožiarené na vzduchu urýchleným elektrónovým lúčom s dávkami v rozsahu (0-400) kGy. Obsah S-sulfonátu ako primárneho oxidačného produktu bol stanovený vo WD pomocou druhej derivácie FTIR. Príjem vlhkosti všetkých vzoriek bol skúmaný gravimetricky pri laboratórnej teplote a relatívnej vlhkosti 97%. Ako sa dalo očakávať, najvyšší príjem vlhkosti bol pozorovaný pre WD, najnižší pre WW. Ukázalo sa, že príjem vlhkosti kolísal vo všetkých vzorkách, pre WD kolísanie korelovalo s vygenerovaným S-sulfonátom, pravdepodobne v dôsledku vzniku početných H-väzieb. Stúpajúci príjem vlhkosti pre WD a WW bol pozorovaný do dávky 40 kGy, zatiaľ čo pre WF príjem klesol pod pôvodnú úroveň už pri dávke 16 kGy. Povrchové napätie bolo merané flotačnou metódou kombinovanou so stalagmometriou. Počiatočné povrchové napätie WW bolo vyššie ako u WD a WF, avšak rástlo rovnako pre všetky vzorky od dávky 25 kGy. Od dávky 100 kGy sa povrchové napätie ustálilo. Uvoľňovanie vlhkosti vo WD bolo merané termogravimetricky. Zmeny rýchlosti uvoľňovania vlhkosti pri teplote okolo 100 °C, adekvátnej desorpcii slabo viazanej vody a hmotnosť zvyšku zahrievanej vlny pri 120 °C zodpovedajúcemu uvoľňovaniu celkovej vody, poskytli inverznú závislosť. Dospeli sme k záveru, že za variabilitu sorpčných vlastností je zodpovedný obsah S-sulfonátu. Čím viac S-sulfonátu sa vytvorilo, tým vyšší nárast vlhkosti a nižšia rýchlosť uvoľňovania vlhkosti bola pozorovaná. Predpokladá sa, že v rámci určitého rozmedzia a pri vhodne zvolenej dávke je možné ovplyvniť príjem vlhkosti.

Kľúčové slová: ožarovanie elektrónovým lúčom, povrchové napätie, príjem vlhkosti, uvoľňovanie, vlna

Introduction

Adsorption technologies based on polymeric materials are used to remove toxic substances from air and wastewater streams. Keratin protein found abundantly in sheep's wool is an interesting and potentially useful renewable biopolymer. It contains a variety of functional groups on the backbone and side chains of the proteins, and is an ideal component to fabricate a range of novel adsorbent systems for separation of toxic pollutants via physisorption or chemisorption mechanisms (Ghosh and Collie, 2014). Sheep wool fibre is a highly organized structure with a very complex fibre surface, which is responsible for the majority of wool properties, such as water repellence, resistance to chemical attack and felting behaviour (Thomas, 2007).

Many authors have dealt with dyeing wool as well as removing dyes from wastewater. It was found that increase in temperature of effluent results in substantial increase in adsorption. It was also established that pH of the effluent leads to decrease in the removal efficiency of the adsorbents (Kagbu et al., 2001).

The mechanisms of removing pollutants from a solution or atmosphere by keratin materials are based on a combination of physisorption and chemisorption (Kar and

Misra, 2004). Physisorption refers to trapping of pollutants in a porous network or on the surface of keratin materials. Chemisorption occurs at chemical functionalities present on keratin proteins. Particularly, the main functional groups including peptide bonds and side chains of amino acid residues offer active chemical sites for removal of metal ions and organic volatiles (Aluigi et al., 2009, 2011). Some radiation technologies are used to improve the physical-chemical properties of sheep wool as plasma application, corona charges, microwave, UV radiation, etc. However, the mentioned treatments modify the wool surface only. On the other hand, accelerated electron beam can penetrate the whole volume of the fibres and affect all parts of the fibre substructures (Porubská et al., 2015). Applying a physico-chemical treatment, the originally hydrophobic fibre becomes hydrophilic and is also capable of binding other substances (Kan et al., 2013). The aim of this study was to examine a variation of the humidity uptake and humidity release as well as the effect of electron beam irradiation on the surface tension of wool.

Material and methods

Material

In this work industrially scoured wool with fibre thickness of 22-27 μm was used in the form of wool combed sliver, supplied by the company Pradiareň vlny JK, Nové Mesto nad Váhom, Slovakia.
Surfactants Lansurf OA7 and Lansurf AE107 supplied by Lankem Ltd, Dukinfield, Cheshire, England were used to measure surface tension of wool fibres.
Dichloromethane p.a. supplied by company Centralchem, Bratislava, was used in wool degreasing.

Sample preparation

The individual samples of wool were prepared as follows: a) WD wool samples were extracted with dichloromethane in Soxhlet using 9 flow-off, then rinsed 2x in distilled water, first dried freely and finally dried in a laboratory oven at 60 °C for 4 h. Such wool being still warm was put into zip PE pockets, closed and saved in a dessicator till irradiation, b) WF wool samples were extracted and rinsed as above and dried freely, then put into open PE pockets, c) WW wool samples were cleaned 4x in warm water, then rinsed 1x in distilled water and dried freely, then put into open PE pockets.

Sample irradiation

All of the wool samples were irradiated by accelerated electron beam with doses 0-16-25-40-63-100-156-250-400 kGy repeating 100 kGy cycles plus needed supplementing dose, if necessary. Between individual irradiation cycles, the samples were allowed to cool down for 30 min to maintain the temperature below 50 °C. For each irradiation dose, the samples of about 12 g in mass put in PE pockets were placed into carton boxes grouped according to selected absorbed doses. The exposure in air was conducted at the University Centre of Electron Accelerators in Trenčín in linear electron accelerator UELR-5-1S (manufacturer FGUP “NIIEFA”, Petersburg, Russia) with 5 MeV of installed energy, an electron beam (hereafter, EB) intensity of 200 mA, mean power of 1 kW and mean dose rate of 750 kGy*h^{-1}.

FTIR spectral analysis

FTIR spectral analysis was performed on WD as a representative model. For the measurement, the fine-cut wool sample was blended with KBr in a small grinder and pressed into disc in a pellet press. The moulded disc was kept in the dessicator till spectral measurement. Infrared spectrum was scanned using AVATAR 330 Thermo Nicolet FTIR Spectrometer (manufacturer Thermo Nicolet Corporation, Madison, USA) in the range of 400 – 4000 cm^{-1} at 4 cm^{-1} resolution and 3 scan repetitions per analysis. The FTIR spectrum was inverted in the second-order derivative spectrum. The signal for S-sulphonate (Bunte salt) was read at 1022 cm^{-1} and divided by the signal for reference Amide III at 1232 cm^{-1}. This absorbance ratio was relative to the corresponding ratio of the non-irradiated sample thus representing development of the sulphonate with absorbed dose (Kan and Yuen, 2006).

The uptake of humidity

Amount about 0,5 g of wool sample dried for 8 hours at 90 °C and put into a small glass cup was placed in a dessicator over K_2SO_4 solution saturated at 25 °C corresponding to (97.30 ± 0.45) % relative humidity (Greenspan, 1977). The sample was kept in the dessicator for 12 days and, after removing weighed immediately. Based on the mass growth, the uptake of humidity was calculated using relation:

$$\text{Percentage of mass growth} = \frac{m_1 - m_2}{m_1} \cdot 100\% \tag{1}$$

where m_1 is initial mass of dried sample (g), m_2 is mass of moist sample (g).

Measurement of surface tension

Surface tension of wool fibres was determined using flotation method (Bateup et al., 1976). A wool snip was put into surfactant solution of variable surface energy. Surface tension of the solution with the floating snip was measured by stalagmometer and identified with the fibre surface tension.

The humidity release and rate of mass loss

Thermogravimetric analysis in air atmosphere (TGA/dTGA) Mettler Toledo TGA/SDTA851e equipment was used for humidity release and rate of mass loss of wool in the samples prepared according to paragraphs Sample preparation and Sample irradiation. The wool fibres in amount of around 15 mg were placed into a corundum crucible 100 µl in volume. The heating rate was 20 °C*min^{-1} within the interval from 25 °C to 250 °C with 3 repetitions per analysis. Thermal parameters (mass change and rate of mass loss) were read from the first run. The residual mass for 120 °C was read from the responding curve directly and the rate of mass loss was estimated as slope of curve decreasing in inflection point within (98-105) °C. Both parameters were recalculated into percentage regarding mass data.

Results and discussion

FTIR analysis and humidity uptake

Among other things, the irradiation of wool with electron beam in air leads to the splitting disulphide bridges in keratin molecule and following oxidation gave S-sulphonate:

$$R-S-S-R \xrightarrow{e^-} R-S-S^{\cdot} - \xrightarrow{O_2} R-S-SO_3^- \qquad (2)$$

Introducing polar oxygenic group modifies some properties of wool. The wool gets an altered affinity for other polar substances, which could potentially be exploitable for some purposes. They were examined sorption behaviour of the irradiated wool samples towards humidity as a simple example.

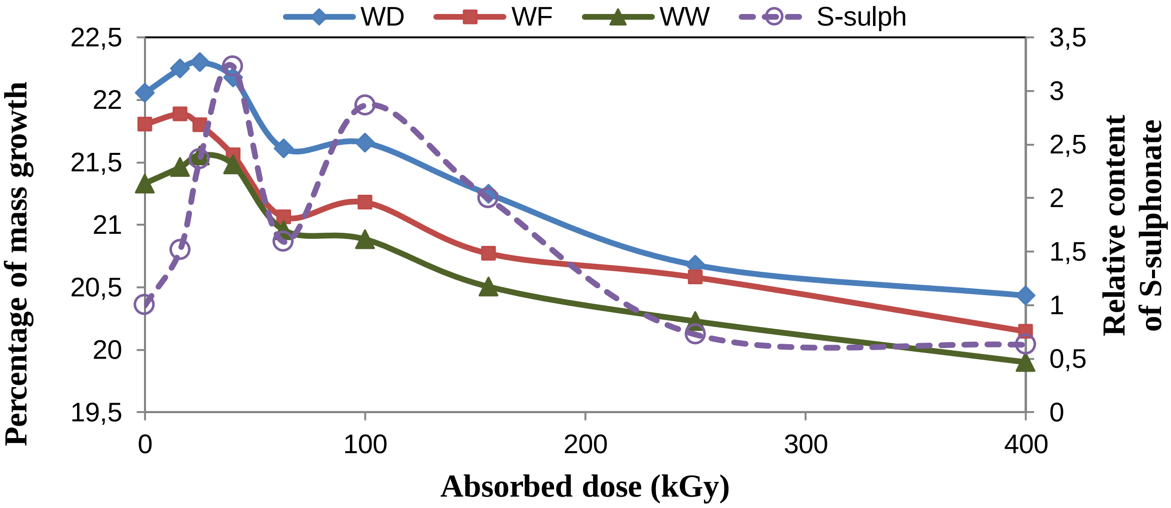

Figure 1. Comparison of humidity uptake for all wool samples depending on absorbed dose and related to content of S-sulphonate in the degreased dry wool (WD)

Obrázok 1. Porovnanie príjmu vlhkosti všetkých vzoriek vlny v závislosti od absorbovanej dávky a obsahu S-sulfonátu v odmastenej suchej vlne (WD)

As seen in Figure 1, course of humidity uptake with absorbed dose shows fluctuation for all wool samples. Regarding a scatter of experimental data, maximal wettability is observed within (16-40) kGy dose. The following decrease occurs for 63 kGy and the humidity uptake is under the initial level for all samples eventually. It was found (Porubská et al., 2015) that 63 kGy dose corresponds to minimal portion of α-helical and maximal β-sheet conformation of secondary structure due to peptide denaturalization. Moreover the second growth of the humidity uptake for 100 kGy dose follows a subsequent smaller increase of α-helical conformation (Porubská et al., 2015). These fluctuations are consistently observable also for S-sulphonate also in this work. It was supposed that the higher content of S-sulphonate the better conditions to create H-bonds between molecules H_2O and polar S-sulphonate groups. It can be said that the humidity uptake traces the generation of S-sulphonate content. In whole range of absorbed dose the order of the humidity uptake is as follows: WD > WF > WW. That is expected since WD is grease-free and kept in desiccator for a long time, while WF, also grease-free, was kept freely at ambient conditions. Both sample WD and WF showed more wettability than WW. The last sample containing some residual grease on the surface is more hydrophobic and access for humidity into the bulk is more hindered.

Beyond 100 kGy dose, decreasing wettability as well as S-sulphonate content is observable. Also in this dose range the S-sulphonate content traces the wettability of the samples. Considering previous results of Porubská et al. (2015), S-sulphonate level and composition of secondary structure are connected mutually and S-sulphonate generation is supported by the α-helical conformation. However beyond 63 kGy, the β-sheet conformation prevails restraining the humidity uptake. So that it can be concluded that the humidity uptake by the irradiated wool increases over initial level only for non-denatured wool containing S-sulphonate. Accordingly the falling humidity uptake under level of the irradiated and corresponding non-irradiated wool can be indicator of denaturation.

Surface tension

Surface tension is an important parameter connected with polarity of a sample. Exposure of wool fibres to electron beam affected not only surface of the fibres but the whole their volume as shown in study of Porubská et al. (2015). The authors found that the irradiation in air provokes oxidation of keratin S-groups generating more-less polar species. Since most of S-groups occur next to surface, the majority of oxidized species is situated there and affects surface energy mostly as revealed by results of surface tension measurements (Figure 2). The results indicate different values for the initial samples and 16 kGy doses. At the beginning only sample WW can be distinguished from the others presenting higher surface tension by 1.6 $mN*m^{-1}$ compared to WD and WF. It is considered that the difference is due to a different humidity content arising from the sample preparation when the WW fibres were washed in water and dried only freely. Therefore corresponding surface tension is rather higher while WD and WF samples show the same initial values. However, 16 kGy dose diminishes the difference to 0.4 $mN*m^{-1}$ (for WF) and 0.8 $mN*m^{-1}$ (for WD) suggesting that the oxidation process runs faster for WF than for WD due to a higher humidity content. Namely besides atmospheric oxygen, any humidity in irradiated fibre provides an oxygen source necessary for reaction with free radicals to create S-oxidized species. Following doses 25 and 40 kGy induced the same surface tension for all samples. It can indicate completion of a certain oxidation level of the fibre surfaces levelling the surface energy. In the next step at 63 kGy, further oxidation process is in progress up to a stable level from 100 kGy. As mentioned above, 63 kGy dose is connected with start of the keratin denaturation that is completed at higher doses. Even if oxidation continues inside wool structures, the surface layers are completed and related surface tension values are definitive as seen in Figure 2. In addition as presented by other authors (Kan and Yuen, 2006;

Douthwaite et al., 1993), cystine oxidation products in keratin including S-sulphonate are not stable and may progressively be converted to cysteic acid. However, all those intermediates are polar and regardless of type, they induce an equal surface tension on the fibre surface. That is why the dependency levels from 100 kGy.

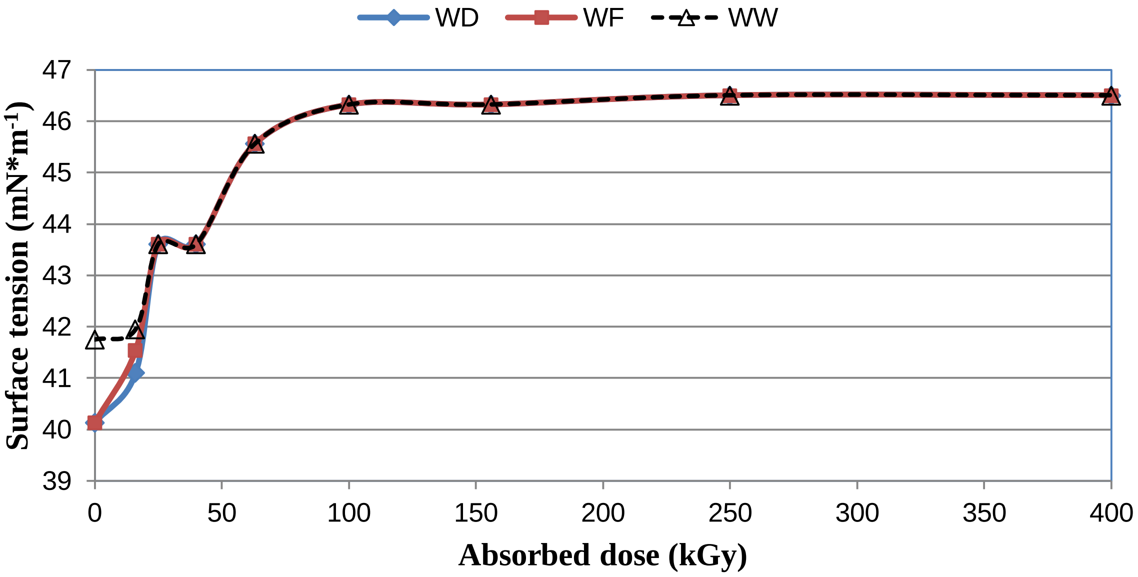

Figure 2. Variation of surface tension for the wool samples depending on absorbed dose

Obrázok 2. Zmeny povrchového napätia vzoriek vlny v závislosti od absorbovanej dávky

The humidity release and rate of mass loss

Additional information on the effect of irradiation on the wool characteristics was obtained by measuring variation of the fibre mass under heating depending on absorbed dose. The mass residue represents dry matter obtained from progressive heated wool after release of humidity bound either physically or chemically. Therefore a temperature of 120 °C was selected as representative supposing that both water types would be eliminated at this point, while dependence for rate of water loss within (98-105) °C could reflect rather a release of physically bound water. Such measurement was carried out with WD sample. The relative residual fibre mass responding to temperature of 120 °C as well as rate of water release within (98-105) °C are shown in Figure 3.

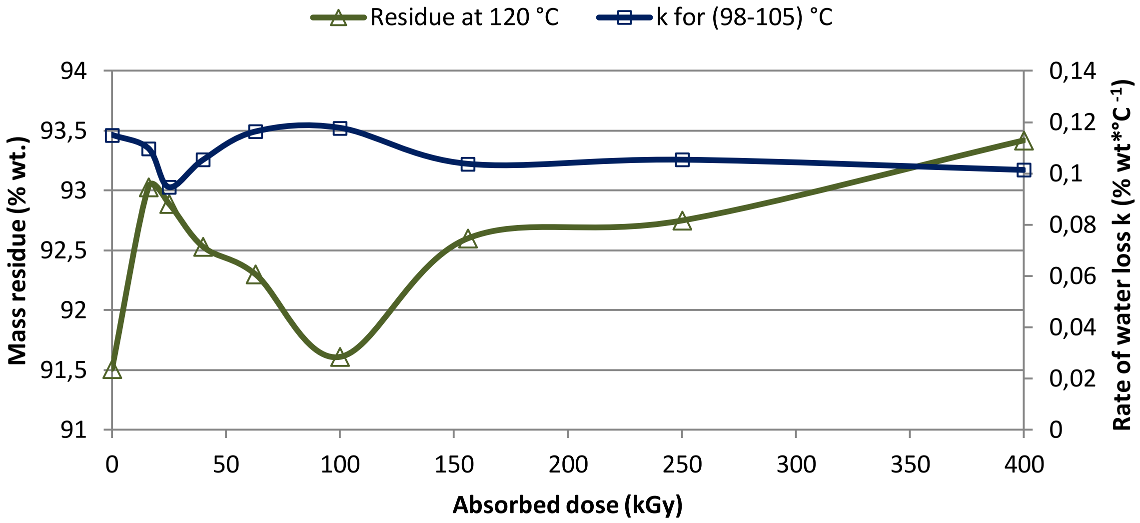

Figure 3. Dependence of residual mass at 120 °C and rate of water loss in degreased dry wool (WD) on absorbed dose within range of (98-105) °C

Obrázok 3. Závislosť zvyškovej hmotnosti pri 120 °C a rýchlosť straty vody v suchej odmastenej vlne (WD) v závislosti od absorbovanej dávky v rozsahu (98-105 °C)

As evident from the dependence of mass residue on absorbed dose, the weakest retention of water is for non-irradiated sample and the residual dry matter is of the lowest value. However for the next doses 16 and 25 kGy, the smallest loss of the humidity indicates the strongest retention of total water as well as the lowest rate for splitting off of physically bound water. Simultaneously around this dose range, the humidity uptake and S-sulphonate content attain the maximum and the surface tension increases. This confirms a strong attraction between polar S-sulphonate groups and water molecules. Also a favourable access of water molecules into α-helices has to play a role. Towards 100 kGy dose the residual mass decreases, the rate of loss for physically bound water growths indicating weakened binding both water types despite the second maximum for S-sulphonate content (Figure 1). This finding is also connected with denaturation of polypeptide skeleton and transformation of α-helical conformation into β-sheet one. From 150 kGy a stable course for the rate of loss for physically bound water is read and the residual mass at 120 °C increases. It can be assumed that releasing only chemically bounded water from denatured wool is in question and the lowest value of the retention corresponds to ultimate dose of 400 kGy when content of the S-sulphonate is under the initial level. As seen in Figure 1, also the humidity uptake is correspondingly the lowest.

Conclusion

Irradiation of wool fibres with electron beam in the range of (0-400) kGy dose results in generation of S-sulphonate, variation of humidity uptake and its release and of surface tension. All parameters show some fluctuation depending on absorbed dose as well as on conformational composition of secondary structure of wool. The humidity uptake for the irradiated sample is higher than for the parent wool within

(16-40) kGy when content of S-sulphonate is high and simultaneously, a helical conformation prevails. Surface energy of the irradiated samples increases from starting doses and from 100 kGy levelling effect is observed. The non-irradiated wool shows the lowest retention of humidity and the highest rate of its release. Low doses give rise to retention but elevated doses lead to decrease with minimum for 100 kGy. Beyond this dose the retention increases again and from 150 kGy, the release mainly of strongly bound water occurs in accordance with responding low the humidity uptake being under value for the non-irradiated wool. The falling humidity uptake under level of identical but non-irradiated wool can be indicator of denaturation.

Acknowledgements

This work was sponsored by University Grant Agency of Faculty of Natural Sciences, Constantine Philosopher University in Nitra, under project VIII/8/2015. The authors thank Michael Lawson for spelling and grammar corrections.

References

Aluigi, A., Tonetti, C., Vineis, C., Tonin, C., Mazzuchetti, G. (2011) Adsorption of copper (II) ions by keratin/PA6 blend nanofibres. European Polymer Journal, 47 (9), 1756-1764. DOI: 10.1016/j.eurpolymj.2011.06.009

Aluigi, A., Vineis, C., Tonin, C., Tonetti, C., Varesano, A., Mazzuchetti, G. (2009) Wool keratin-based nanofibres for active filtration of air and water. Journal of Biobased Materials and Bioenergy, 3 (3), 311-319. DOI: 10.1166/jbmb.2009.1039

Bateup, B. O., Cook, J. R., Feldtman, H. D., Fleischfresser, B. E. (1976) Wettability of wool fibers. Textile Research Journal, 46 (10), 720-723. DOI: 10.1177/004051757604601005

Douthwaite, F. J., Lewis, D. M., Schumacher-Hamedat, U. (1993) Reaction of cystine residues in wool with peroxy compounds. Textile Research Journal, 63 (3), 177–183. DOI: 10.1177/004051759306300308

Ghosh, A., Collie, R. S. (2014) Keratinous Materials as Novel Absorbent Systems for Toxic Pollutants. Defence Science Journal, 64 (3), 209-221. DOI: 10.14429/dsj.64.7319

Greenspan, L. (1977) Humidity Fixed Points of Binary Saturated Aqueous Solutions. Journal of Research of the National Bureau of Standard-A, Physics and Chemistry, 81A, 89-96.

Kagbu, J. A., Amupitan, O. J., Oyedeji, O. J., Elaigwu, P. (2001) Evaluation of yankassa sheep wool as an adsorptive matrix for bleaching textile effluents. Journal of the Chemical Society of Nigeria, 26 (1), 14–17.

Kan, C. W., Tsoi, W. Y. I., Yuen, C. W. M., Choi, T. M., Tang, T. B. (2013) Achieving nano-scale surface structure on wool fabric by atmospheric pressure plasma treatment. In: M. Thomas, K. L. Mittal, eds. (2013) Atmospheric Pressure Plasma Treatment of Polymers: Relevance to Adhesion. Hoboken, NJ, USA: John Wiley & Sons, Inc. 157–173. DOI: 10.1002/9781118747308.ch5

Kan, C. W., Yuen, C. V. M. (2006) Surface characterisation of low temperature plasma-treated wool fibre. Journal of Materials Processing Technology, 178 (1-3), 52-60. DOI: 10.1016/j.jmatprotec.2005.11.018

Kar, P., Misra, M. (2004) Use of keratin fiber for separation of heavy metals from water. Journal of Chemical Technology and Biotechnology, 79 (11), 1313-1319. DOI: 10.1002/jctb.1132

Porubská, M., Hanzlíková, Z., Braniša, J., Kleinová, A., Hybler, P., Fülöp, M., Ondruška, J., Jomová, K. (2015) The effect of electron beam on sheep wool. Polymer Degradation and Stability, 111, 151-158. DOI: 10.1016/j.polymdegradstab.2014.11.009

Thomas, H. (2007) Plasma modification of wool. In: R. Shishoo, ed. (2007) Plasma Technologies for textiles. Woodhead Publishing Limited, 228–246. DOI: 10.1533/9781845692575.2.228