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Physical and Absorptive Changes in Plasma Treated Viscose Fibres

Abstract
Chemical modification of the fibres was successful in improving their different properties, but there are environmental concerns related to the disposal of chemicals after treatment. Taking into account the advantages related to the technology of plasma treatment and the differentiated changes of the fibre matter processed, is plasma treatment, increasingly replacing chemical applications in finishing and pre-treatment of textiles products. For industrial uses, regenerated cellulose fibres are used to replace traditional materials, for example, nonwovens, like hygiene and medical products. The most important characteristics for hygiene and medical products are absorption ability and capability of water retention. The main aspect of our research was to analyse the physical and absorptive characteristics of viscose fibres, treated with plasma. The study revealed that plasma surface treatment modifies the absorptive structure, tensile and other physical properties of viscose fibres.

Key words: *viscose fibres, low pressure plasma treatment, physical properties, absorptive properties, hygiene products.*

Introduction

Plasma treatment is a fast solvent free technique. The operation procedure is simple and well controlled. It is also easy to create any ambiance of oxidative for reductive or inactive reasons by changing the feed gas [1]. Today, with increasing awareness of environmental concerns, a significant amount of ecological legislation has been introduced regarding fibre treatments that use huge amounts of chemicals and water.

Plasma surface treatment does not include chemicals and it is regarded as an environmentally friendly process. It causes changes to a limited depth, modifies the uppermost atomic layers of a material surface and leaves the bulk characteristics unaffected, even in the most delicate materials [2]. Dehydrogenation and consequent by unsaturated bond formation, trapped stable free radical formation and generation of polar groups through post plasma reaction are included in plasma treatment. The generation of increased polar groups resulting from plasma treatment has a significant influence on overall surface changes and water absorption [3]. The process of plasma modification is characterised by an interaction between the plasma and thin outer layer of the fibres [4].

It is expected that this kind of treatment can be applied to improve the wettability of different fibres, among them viscose fibres. Laboratory size plasma treatment is far from being an industry forward procedure. A better solution would be to combine the plasma process with pre or post plasma treatment. With laboratory plasma treatment it can be proven that it changes the surface, chemical and physical properties of the fibres. Future progress and different techniques can be a solution for plasma scaling problems. Plasma treatment can batch processes with limited, more sophisticated, advanced material. The main disadvantage of this technique is that it requires a vacuum system, which increases the cost of operation [5]. There are much higher expenses in the chemical modification of fibres and they exceed plasma treatment.

Regular viscose fibres have many different structures, which lead to different applications and properties. Since the mid-1970s significantly more effort has been spent on developing new applications for regenerated cellulose fibres in nonwovens than in conventional textiles [6]. In recent years, various fibres based on viscose have been specially developed to have high absorbencies for application in textile products, where a high uptake of aqueous fluids is part of the essential performance requirements, for example, in medical and sanitary products: surgical "wools", wadding, swabs and dressings, babies' napkins and tampons [7]. It is well known that there has been a great increase in the use of natural as well as synthetic fibres in the manufacturing of various medical products.

Major features of viscose fibres are different morphology, physical properties, softness, good processing characteristics, adequate liquid transport properties and good mechanical properties. The amount of water vapour absorbed at a certain temperature and the relative humidity are two of the important criteria for describing the properties of regenerated cellulose fibres [8]. The most important characteristics for hygeine and medical products are absorption ability and capability of water retention. The main aspect of our research was to determine the effects of plasma treated fibres and different analysis of the physical and absorptive properties.

Experimental

The regenerated cellulose fibres used in our study were regular viscose fibres obtained from Lenzing® AG, Lenzing Viscose CF®. The fibres were washed with 2 g/l of non-ionic detergent for 60 minutes at 60 °C to remove finishes and surface contaminants. After washing and drying, the fibres were treated with low pressure radio-frequency plasma and an argon gas was used.

The source of radio-frequency power was an IEVT VGK 200/1 high frequency generator operating at 27 MHz and at 300 W maximum power. Power dissipation in the plasma reactor was measured by a Zetagi HP 201 SWR through-line wattmeter. Experiments were carried out in a bell jar type Pyrex reactor with 150 mm o.d. and 200 mm in length. The Reactor was connected on one side by an inlet tube to a gas cylinder with flow regulator, and on the other side to a cold trap held at 77 K, which was evacuated by a diffusion pump. The plasma was inductively coupled through a coil, which consisted of seven turns of 3 mm o.d. copper tubing. The pressure in the reactor was measured by an MKS Baratron pressure meter (0-1000 Pa) and by an in-house Alpert gauge high vacuum meter. The power dissipation in the reactor was 25 W. Argon gas was supplied to the reactor from the gas cylinder and the flow was controlled

by MKS 1359 CJ Mass Flow Controllers. Prior to introducing the viscose fibres samples into the reactor, the system was pumped down to 10^{-3} Pa. After the introduction of viscose fibre samples into the reactor the system was evacuated to a pressure level of 100 Pa. The flow rate of argon was adjusted to 10 cm^3min^{-1} ,and the system was allowed to flush with argon. After flushing for 2.5 minute the pressure stabilised and the plasma was initiated. Samples were treated for 5 minutes at an argon flow rate of 10 cm^3min^{-1}, followed by treatment at an argon flow rate of 50 cm^3min^{-1} for 5, 10 and 15 minutes, respectively (Table 1).

Table 1. Parameters of plasma treated viscose fibres.

Sample	Time of treatment, min	Argon flow rate / time	
1	5	10 cm^3min^{-1} / 2.5 min	50 cm^3min^{-1} / 2.5 min
2	10	10 cm^3min^{-1} / 5 min	50 cm^3min^{-1} / 5 min
3	15	10 cm^3min^{-1} / 5 min	50 cm^3min^{-1} / 10 min

The reactivity and absorption abilities were analysed using various standard methods determining water absorption (capability of water retention (ASTM D 2402-90 [9]), liquid absorptive capacity, liquid absorbency time).

Moisture content of the fibres was determined according to standard SIST EN 20139:1999 [10].

Capability of water retention was determined according to standard ASTM D 2402-90 [9]. The standard method determines the ratio between the mass of water retained in the fibres after soaking (for 2 hours), and centrifuging (for 20 minutes), and the mass of dried fibres (temperature 105 °C, 4 hours).

The molecular and supramolecular structures (degree of polymerisation-DP, crystallinity, molecular orientation) were also investigated. Other properties of the treated fibres such as tenacity, elongation at break and work of rapture were evaluated with an Instron 6022 tensile testing machine. To determine the effects of the plasma treatment of viscose fibres, density, birefringence and temperature of the beginning of degradation were also evaluated.

Results and discussion

Pressure, power, plasma gas flow rate, reactor conditions like the temperature and moisture of the fibres, have different effects on the gas phase and condensed phase mechanisms. Plasma used in our study was a low pressure, partly ionised, gas.

Differences in molecular and fine structure cause different reactivity, absorption and tensile properties. Reactivity and absorption abilities were analysed using various methods for determining water absorption like moisture content, capability of water retentionand liquid absorptive capacity. Liquid absorptive capacity and liquid absorbency time were determined as the time required for the basked filled with 5 g of fibres to sink below the surface of the water. After the sample was removed from the water and drained for 30 seconds, the weight gave the absorptive capacity. As seen from data given in Figure 1, liquid absorbency time increases with the time of treatment.

Figure 1 shows absorption abilities before and after plasma treatment. As seen in the graph, the water retention value is higher in plasma treated fibres and increases with the time of treatment. Untreated and plasma treated fibres have a water retention value of over 60%, which is suitable for use in hygiene and medical products. The liquid absorbency time and absorptive capacity are highest in plasma fibres treated for 15 minutes. The lowest values are in untreated fibres with a liquid absorptive capacity of 13,68 g/g and water retention value of 62,80 %.

Some structural characteristics which influences the absorption and mechanical properties of fibres could be also obtained from the birefringence and temperature at the beginning of degradation. The temperature at the beginning of degradation decreases with the time of treatment, the highest being in untreated viscose fibres with 329.0 °C (Figure 2).

The molecular and supramolecular structures were determined with a degree of polymerisation-DP, crystallinity and temperature at the beginning of degradation. As seen in Figure 2, the degree of polymerisation, temperature at the beginning of degradation and crystallinity decrease with the time of treatment. The lowest values are in samples treated with plasma for 15 minutes.

Structure analysis of the researched fibres show that important structure character-

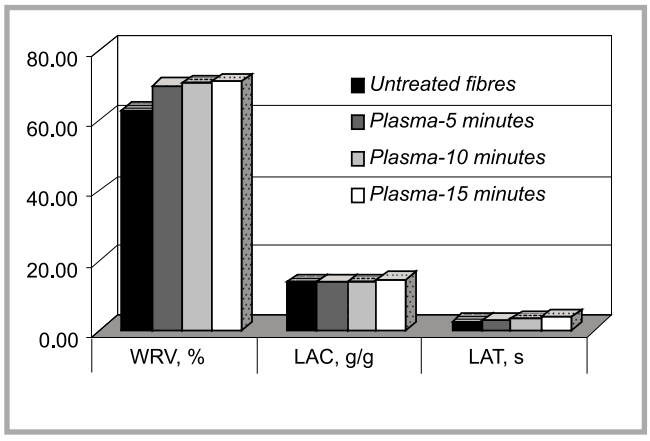

Figure 1. Water retention value (WRV), liquid absorptive capacity (LAC) and liquid absorbency time (LAT) of untreated and plasma treated fibres for 5, 10 and 15 minutes.

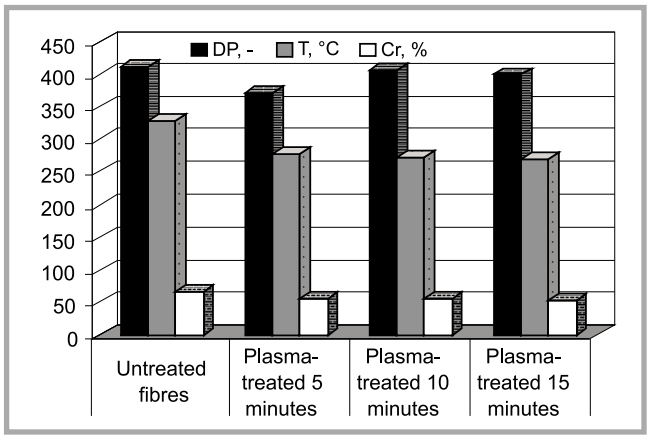

Figure 2. Degree of polymerisation (DP), temperature of beginning of degradation (T) and crystallinity (Cr) of untreated and plasma treated fibres for 5, 10 and 15 minutes.

istics (density, birefringence) decrease from untreated to plasma treated fibres (Table 2). A decrease in density is seen in viscose fibres treated with plasma for 15 minutes.

To describe the tensile behaviour of the fibres more completely, a continuous record of load versus elongation was made (Table 3). The tensile properties of the fibres such as specific stress, maximum load and breaking elongation were measured with an Instron 5567 tensile testing machine. Treated viscose fibres differ most in values obtained from tenacity, elongation and work of rapture. Tenacity decreases with the time of treatment, but elongation at break increases and is highest in the fibres treated with plasma for 15 minutes, as seen in Table 3. Work of rapture is lowest in untreated fibres with value 0.831 cN/cm.

Conclusion

The study revealed that plasma treatment modifies the structure and properties of viscose fibres. By applying a low pressure radio-frequency plasma to viscose fibres it showed that there were surface and deeper changes, which caused differences in the outer part of the fibres and changes in the polymer network.

The analysis showed that treated viscose fibres have smaller crystallinity, degree of polymerisation, lower tenacity, and temperature at the beginning of degradation, but a higher water retention value, liquid absorbency time, liquid absorptive capacity and are more extensible. As regards tenacity, it is higher in untreated samples, because of the higher orientation of the macromolecules. Degree of polymerisation – DP for treated viscose fibres decreases with the time of treatment, meaning that plasma treatment causes damage to fibres. Plasma treatment was found to improve the wettability and water retention of viscose fibres. The changes in morphology and the formation of polar groups on the substrate surfaces, caused by plasma treatment, are responsible for the improved properties. All the fibres tested had adequate tensile properties. Based on the results obtained it was found that five minutes plasma treatment is enough for effective modification of viscose fibres.

Table 2. *Density (ρ) and birefringence(Δn) of untreated and plasma treated fibres for 5, 10 and 15 minutes.*

Sample	Δn, -	ρ, g/cm³
Untreated fibres	0,0354	1,4241
Plasma-treated 5 minutes	0,0254	1,4317
Plasma-treated 10 minutes	0,0232	1,4284
Plasma-treated 15 minutes	0,0243	1,4254

Table 3. *Tensile properties - tenacity (σ), elongation at break (ε_b) and work of rapture (A) of untreated and plasma treated fibres for 5, 10 and 15 minutes.*

Sample	σ, cN/tex	ε_b, %	A, cN·cm
Untreated fibres	27,68	21,5	0,831
Plasma–treated 5 minutes	27,51	21,7	0,845
Plasma–treated 10 minutes	26,56	22,3	0,876
Plasma–treated 15 minutes	25,99	22,5	0,878

Acknowledgment

The research was financially supported by the Slovenian Research Agency.

References

1. *Huang H. C., Ye D., Huang B.; Nitrogen plasma modification of viscose-based activated carbon fibres. Surface and Coatings Technology, 2007.*
2. *Poll H. U., Schladitz U., SchreiterS.; Penetration of plasma effects into textile structures. Surface and Coatings Technology, 2001, pp. 489 - 493.*
3. *Liu Y. C., Xiong Y., LuD.; Surface characteristics and antistatic mechanism of plasma-treated acrylic fibres. Applied Surface Science, Vol. 252 (2006), pp. 2960-2966.*
4. *Biniaś D., Włochowicz A., Biniaś W.; Selected Properties of Wool Treated by Low – Temperature Plasma. Fibres & Textiles in Eastern Europe, Vol. 12 (2004), No. 2 (46), pp 58-62.*
5. *Chan C. M., Ko T. M., HiraokaH.; Polymer surface modification by plasmas and photons. Surface Science Reports 24, 1996.*
6. *Woodings C.; Application developments in cellulose fibres. In Cellulose fibres, edited by Woodings, C., Woodhead Publishing Ltd., ISBN 18557345, Cambridge, 2001, pp. 199-203.*
7. *Cumberbirch R. J. E.; High – absorbancy viscose fibres. Textiles, Vol. 13 (1985), No. 3, pp 58-62.*
8. *Klemm D., Philipp B., Heinze T., Heinze U., Wagenknecht W.; Comprehensive Cellulose Chemistry, Fundamentals and analytical Methods, 1998, Vol. 1.*
9. *ASTM D 2402-90: Standard Test Method for Water Retention of Textile Fibres (Centrifuge Procedure), 1990.*
10. *SIST EN 20139:1999: Standard Test Method for determination of the moisture content of fibres.*

Received 15.11.2007 Reviewed 15.01.2008