

Sheila Shahidi,
*Mahmood Ghoranneviss,
**Jakub Wiener,
*Bahareh Moazzenchi,
*Hamideh Mortazavi

Effect of Hexamethyldisiloxane (HMDSO)/Nitrogen Plasma Polymerisation on the Anti Felting and Dyeability of Wool Fabric

Department of Textile,
Faculty of Engineering,
Islamic Azad University,
Arak Branch, Arak, Iran
E-mail: sh-shahidi@iau-arak.ac.ir,

*Plasma Physics Research Center,
Science and Research Branch,
Islamic Azad University,
Tehran, Iran

**Department of Textile Chemistry,
Faculty of Textile,
Technical University of Liberec,
Liberec, Czech Republic

Abstract

This work is focused on the characterisation of the physical and surface properties of plasma coated wool fabric. A thin film was deposited on wool fabric samples by means of the plasma polymerisation of hexamethyldisiloxane (HMDSO) and differences between such plasma-treated and untreated fabrics were evaluated. The films deposited were characterised by means of Fourier transform infrared (FTIR) spectroscopy. Also the surface morphology of samples was studied using a scanning electron microscope (SEM). Hydrophobic properties of the samples were tested using the water drop test. The results show that by plasma polymerisation, hydrophobic properties of the wool surface change to super hydrophobic. The main aim of the HMDSO/N₂ plasma polymerisation of wool fabrics is to improve anti felting properties and dyeing behaviour.

Key words: plasma, wool fabric, hexamethyldisiloxane, dyeability.

Introduction

Keratin fibres, like wool or human hair, can be considered as natural composite materials, where keratinous protein is the main basic constituent. Wool is a high-quality protein fibre and is widely used as a high quality textile material.

The morphology of wool is highly complex, which is not confined to the fibre stem but extends to the surface as well. Cuticle cells overlap each other to influence a directional frictional coefficient. Moreover the surface is highly hydrophobic, as a consequence of which in aqueous medium, because of the hydrophobic effect, fibres aggregate and under mechanical action exclusively move to their root end. This is the reason for felting and shrinkage.

The surface characteristics of textiles play an important role in their performance, and their modification by chemical/ physical processes permits to modify some properties such as dyeability, wettability, permeability and pilling performance [1 - 4].

Plasma treatment is an effective technique for homogeneously modifying the surface properties of wool fabrics, with gases producing different types of modification. This method significantly reduces process costs in terms of water and chemicals, and moreover the process is simple, clean and safe [5 - 7].

Several investigations concerning the effect of LTP (low temperature plasma) treatment on wool fibres, have shown that it can improve processing and per-

formance properties such as anti-felting, wettability, adhesiveness of the polymer to the surface, and dyeability [1, 5].

One of the siloxanes most commonly used is hexamethyldisiloxane (HMDSO), a monomer that cannot be polymerised following conventional polymerisation methodologies in liquid phase, while it can be polymerised during plasma treatments by rearranging the radicals produced by its dissociation. Using this pure monomer in plasma processes gives the possibility to obtain stable hydrophobic surfaces because of the high retention of methyl groups [9 - 11].

Hexamethyldisiloxane, a silicon containing organic monomer, has been extensively employed for plasma polymer layer deposition in rather different fields, but relatively little attention has been given to the application of HMDSO plasma-deposited films in the textile field [1].

The plasma polymerisation of hexamethyldisiloxane as an alternative ecological finishing process for improving the pilling performance of knitted wool fabrics was investigated [1, 6, 8, 12, 13].

In this research work, the effect of HMDSO plasma polymerisation on the felting, hydrophobicity and dyeability of wool fabrics is investigated. The results are presented graphically and discussed.

Experimental part

Materials and plasma treatment

The wool used in this work was produced by Iran Merinos Co., Iran.

The fabrics were woven with 22 dtex warp and weft yarns composed of 36 filaments. For sample preparation, size residues and contaminations on the fabrics were removed by conventional scouring processes; the fabrics were washed in 0.5 g l⁻¹ sodium carbonate and 0.5 g l⁻¹ anionic detergent solution (dilution ratio to water = 1:10) at 80 °C for 80 min and then washing was conducted twice with distilled water at 80 °C for 20 min and once at ambient temperature for 10 min. Hexamethyldisiloxane (HMDSO) was obtained from Merck, Germany (99.5%).

The plasma processing chamber consisted of a pyrex tube with a diameter of 15 cm and height of 12 cm and was equipped with a DC generator. Two aluminum parallel plates were inside the chamber, with the upper one connected to high voltage and operating as a cathode, and the lower one grounded and operating as an anode (**Figure 1**).

The plasma chamber was pumped down to 0.1 Pa using a turbo pump^P, and then

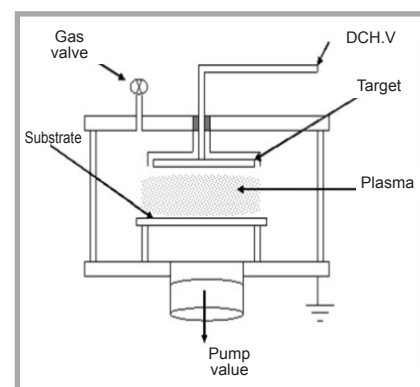


Figure 1. Schematic view of the low pressure DC Plasma generator.

HMDSO/N₂ was admitted into it up to a pressure of 0.07 Pa. The HMDSO/N₂ ratio was fixed at 80% - 20%. High voltage was applied and plasma generated between two electrodes. A fabric specimen was fixed to the lower electrode, allowing homogeneous plasma irradiation on the surface area; the distance between electrodes was 50 mm. The discharge power was 30 W and the deposition time varied between 0 to 8 minutes. After treatment, the power supply was switched off and the system returned to atmospheric pressure by introducing air into the plasma chamber.

Characterisation tests

Functional groups on the surface of samples were examined using an FTIR spectrometer (Bomem MB-100, made in Canada). The morphology of the fabrics was observed using a scanning electron microscope (SEM; LEO 440I, made in England). All of the samples were gold coated before examination.

After plasma polymerisation, fabrics were analysed by the water drop test. The quality of the repellent effect was evaluated by putting water drops on the fabric surface. Obviously this evaluation depends also on the nature of the fabric. Drops of controlled size were placed at a constant rate upon the fabric surface. The duration of time required for the water drop to penetrate through the fabric was measured, representing the water-repellency of the fabric.

For the dyeing process, aqueous solutions containing 1.0 wt.% of acid dye (C.I. Acid Red 57) were employed for dyeing wool fabrics. The bath ratio was 1:40 (1 g of fabric in 40 ml of dye solution). The following dyeing condition was adopted: initial temperature 40 °C, followed by a temperature increase of 3 °Cmin⁻¹ up to 80 °C, holding for 30 min at 80 °C. 2 g/l of sulfuric acid for pH adjustment was added for the anionic dyeing processes. After dyeing, the fabrics were rinsed with cold-hot-cold water and then dried at room temperature.

The reflection factor (R) and colour intensities of the fabrics were investigated using a UV VIS-NIR reflective spectrophotometer (Cary 500, Varian) over the range of 300 - 800 nm. The relative color strength (K/S value) was then established according to the following Kubelka-Munk equation, where K and S stand for

the absorption and scattering coefficient, respectively [4, 14].

$$K/S = (1 - R)^2 / (2R) \quad (1)$$

Dimensional changes of the wool fabrics treated were tested according to AATCC Test Method 99-1993 [14]. Due to the limited size of the plasma reaction chamber, the dimension of the fabric sample used was 65×35 mm², with 60×30 mm² marked inside the fabric. The fabric was conditioned before measurement. A measurement was then conducted to assess the shrinkage in length of both the warp and weft direction, and finally the area shrinkage was calculated. The degree of shrinkage in length and area change was calculated (expressed in %) according to *Equations 2* and *3*, respectively.

$$\text{Length change} = [(l_f - l_o) / l_o] \times 100 \quad (2)$$

$$\text{Area change} = [(A - O) / O] \times 100 \quad (3)$$

where:

l_f - final length after treatment, mm,
 l_o - original length before treatment, mm,
 A - final area after treatment, mm²,
 O - original area before treatment, mm².

Results and discussion

Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) was used to examine functional

groups of the untreated and plasma polymerized samples. The results are shown in *Figure 2*.

The polymerised sample exhibited a broad band between 1000 cm⁻¹ and 1100 cm⁻¹ and a narrow band around 1260 cm⁻¹. The band observed at around 1025 cm⁻¹ was due to asymmetric Si-O stretching vibration in the Si-O-Si bond, while that at 1260 cm⁻¹ was attributed to the asymmetric deformation vibration of CH₃ groups in the molecule Si-(CH₃)_x [1, 5]. The absorption band at around 1400 cm⁻¹ is due to the asymmetric deformation vibration of CH₃ groups in the molecule Si-(CH₃)_x, and bands at around 2960 and 2900 cm⁻¹ are, respectively, due to the asymmetric and symmetric stretching of the C-H bond in methyl groups. The broad band at 3400 cm⁻¹ is assigned to NH stretching vibration. A peak at 1530 cm⁻¹ appears owing to the presence of NH₂ and NH deformations.

As is seen, the bands attributed to NH groups are sharper on the HMDSO/N₂ treated sample as compared with untreated wool, which is due to using nitrogen as fed gas in the plasma polymerisation system.

It should be mentioned that the results related to polymerised samples were the same, thus just one of them is shown in *Figure 2* and compared with untreated wool.

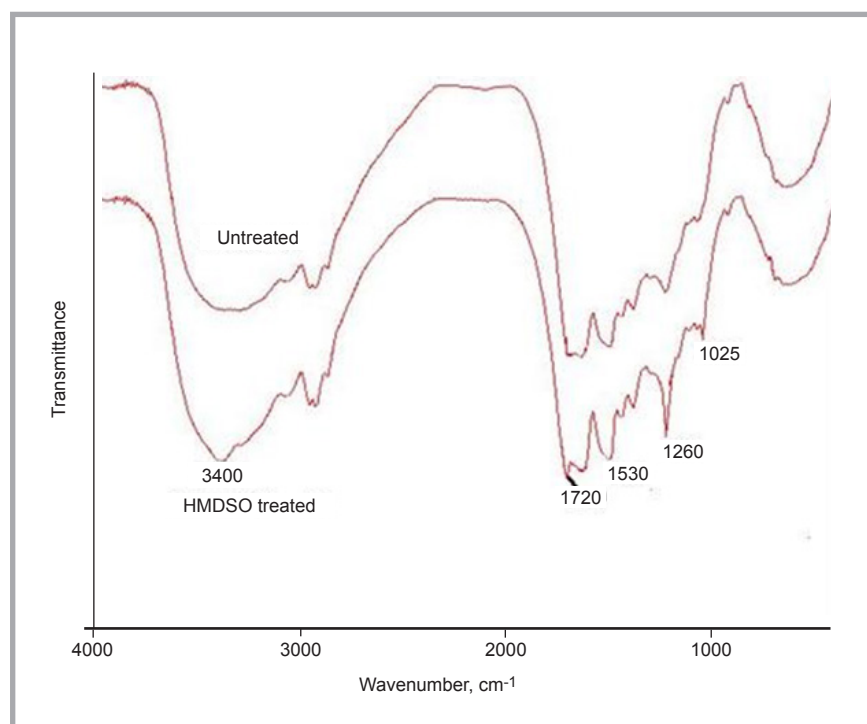


Figure 2. FTIR spectra of untreated and HMDSO treated samples.

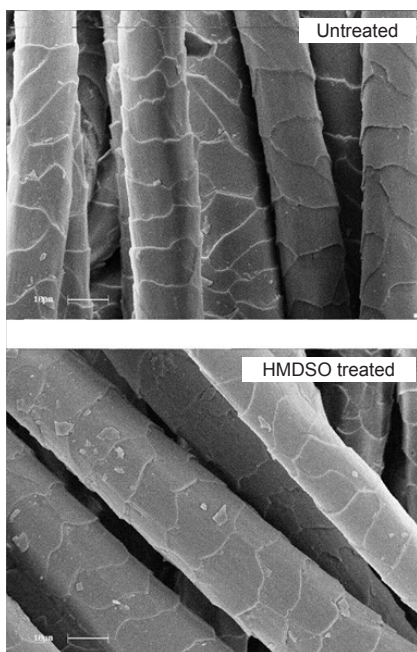


Figure 3. SEM images of untreated and HMDSO treated wool.

Morphological examination

Figure 3 shows SEM images of untreated and treated wool fibre surfaces. SEM analysis revealed no significant differences between surface morphologies of the polymerised and untreated wool fabrics. Minimal damage occurs to the scale structure as a result of the plasma treatment. No signs of the plasma polymer covering the surfaces were detected.

Water drop test

The quality of water repellency of the samples was evaluated by the water drop test, in which drops of controlled size were placed at a constant rate upon the fabric surface and the duration of the time required for them to penetrate the fabrics was measured. The results are

shown in **Table 1**, in which the absorption times were recorded for different treated samples. As we know, the presence of a microporous hydrophobic layer, called an epicuticle, makes the fibre surface difficult to get wet. As can be seen, after HMDSO polymerisation the water-absorption time increased to more than one hour. It is seen that water drops are absorbed on the surface of untreated wool after 3 minutes, after plasma polymerisation, the water repellent effect appears and drops remain on the fabric surfaces without any change in their structure and hydrophobic properties of the wool surface change to super hydrophobic.

Here we should mention that the water-absorption time increased for both sides of the fabrics. By increasing the time of polymerisation, no noticeable changes were observed for the water absorption time.

After dyeing, the water absorption time of samples was investigated, the results of which are shown in **Table 2**. As is seen, for untreated samples, the water absorption time decreased to 2 min after the dyeing process. The results show that after dyeing, the water repellent properties of polymerised wool were reduced.

Dyeability of wool samples

One of the most important concerns in the textile industry is the dyeability of finished fabrics. Hence in this research work, the dyeing property of polymerised fabrics was investigated. A reflective spectrophotometer was used for studying the colour intensity of the fabrics before and after plasma polymerisation, the results of which are shown in **Figure 4**.

Table 1. Absorption time of treated and untreated samples.

Samples	Absorption time
Untreated	3 min
2 min plasma polymerization	47 min
4 min plasma polymerization	>1 hr
6 min plasma polymerization	
8 min plasma polymerization	

Table 2. Absorption time of treated and untreated samples after dyeing.

Samples after dyeing	Absorption time
Untreated	2 min
2 min	6 min
4 min	8 min
6 min	
8 min	

As can be seen, the reflection factor of the dyed HMDSO treated sample is less than dyed untreated one. It should be mentioned that the reflection curve for all the HMDSO treated samples overlapped, hence just one of them is shown in **Figure 4**.

The results show that plasma treatment is effective in increasing the dye exhaustion of wool with acid dye. Furthermore the colours achieved much more brilliant shades with the plasma treatment. As can be seen, the K/S value of the plasma treated sample is more than the original one.

As was shown in FTIR and the water drop test, by HMDSO plasma polymerisation, Si-O-Si bonds were created on the surface of wool samples. The existence of silicon groups on the surface is the main reason for changing the hydrophobic properties of wool to super hydrophobic. According to these results achieved, it is expected that the dyeabil-

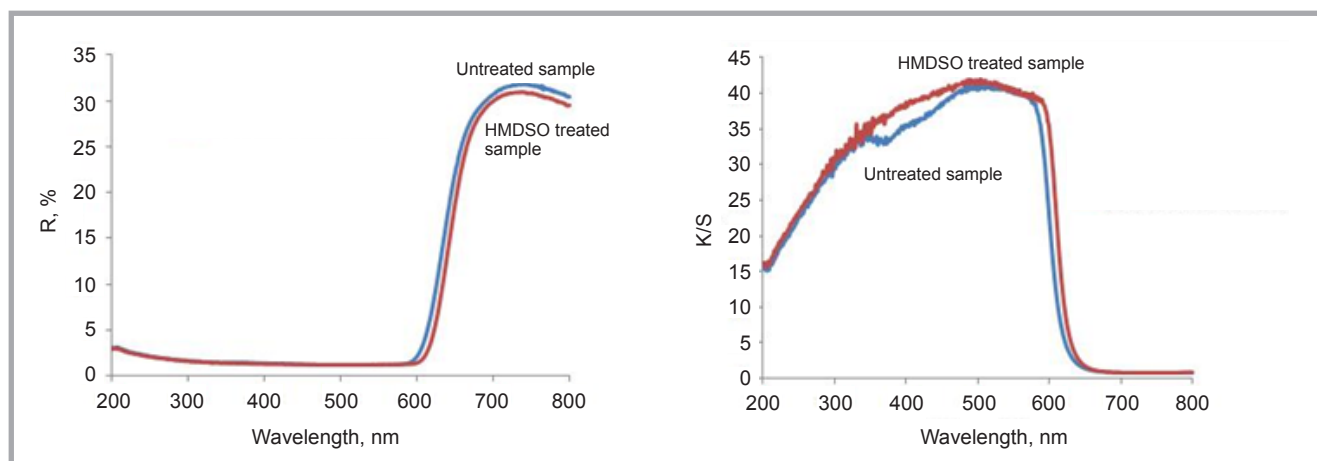


Figure 4. Reflection spectroscopy results of untreated and HMDSO treated samples.

Table 3. Influence of the HMDSO polymerization on the shrinkage behaviour of wool fabrics.

Samples	Dimensional change, %		Area felting shrinkage, %
	in warp direction	in weft direction	
untreated	20	5	24
2 min	5	0	5
4 min	0		0
6 min			
8 min			

Table 4. Influence of the HMDSO polymerization on the shrinkage behaviour of wool fabrics after dyeing.

Samples	Dimensional change, %		Area felting shrinkage, %
	in warp direction	in weft direction	
untreated	10.0	5.0	14.5
2 min	2.5	0	2.5
4 min	0		0
6 min			
8 min			

ity of wool after plasma polymerisation decreases noticeably, but as is seen, opposite results were achieved. The dyeability of polymerised wool is little improved, which is due to the creation of nitrogen containing groups on the surface after plasma treatment. As was mentioned in the experimental part, nitrogen was used as fed gas along with HMDSO in this study. By increasing the amount of NH groups on the surface of wool fibres, the dyeability of the fabric is improved; however, it is not significant.

It can be concluded that plasma polymerisation up to 8 minutes do not have any negative effect on dyeability of the fabrics.

Fabric shrinkage

In the shrinkage test of the fabrics, we observed that the dimensional change in the warp direction is greater than that in the weft direction. It was found that in all HMDSO polymerisation treatments, the fabrics have got only a slight change in their dimensions after the relaxation process (up to 5% in the warp direction). However, the shrinkage for untreated wool fabric, as shown in **Table 2**, was the greatest both in the warp and weft directions.

The felting dimensional change is an irreversible process which occurs in wool fabric when it is subjected to agitation in laundering [14 - 17].

The maximum value of felting dimensional changes in the untreated wool fabric was 20%, which was only a moderate change for untreated fabric. However,

when this value is compared with that of treated fabric (5%), it demonstrates that this treatment could impart significant shrink-resistance and anti-felting effects to wool fabric. **Table 3** shows that the area shrinkage significantly improved after the treatment.

After dyeing, the shrinkage properties of both untreated and treated samples were evaluated, the results of which are shown in **Table 4**. As can be seen, the shrinkage property of untreated fabric after dyeing is improved. Dimensional changes in the warp and weft directions reach 10 and 5%, respectively. Also the dyeing process does not have any negative effect on anti-felting properties of the polymerised samples.

Conclusion

In this research work, wool fabrics were polymerised using HMDSO as a precursor and nitrogen as fed gas in the plasma system. Different deposition times from 0 to 8 min were applied. The IR spectra of coated wool samples confirmed the presence of HMDSO thin film on the surface of fibres.

SEM analysis revealed no differences between the surface morphologies of the coated and untreated wool fabrics. Also it is demonstrated that HMDSO polymerisation could impart significant shrink-resistance and anti-felting effects to wool fabrics.

It is also shown that the dye ability of wool could be increased. The increase

in the dye ability of wool samples is attributed to the creation of Nitrogen containing groups due to plasma chemical modification. The results show that by plasma polymerisation, the hydrophobic properties of the wool surface changes to super hydrophobic. However, the water repellent properties of polymerised wool were reduced after dyeing.

References

- Rombaldoni F, Mossotti R, Montarsolo A, Songia MB, Innocenti R, Mazzuche G. *Fibers and Polymers* 2008; 9: 566.
- Mazrouei-Sebdani Z, Khoddami A, Malakpour S. *Colloid & Polymer Science* 2011; 289: 1035.
- Demir A, Ark B, Ozdogan E, Seventekin N. *Fibers and Polymers* 2010; 11: 989.
- Ghoranneviss M, Shahidi S, Anvari A, Motaghi Z, Wiener J, Slamborova I. *Progress in Organic Coatings* 2011; 70: 388.
- Mossotti R, Lopardo G, Innocenti R, Mazzuchetti G, Rombaldoni F, Montarsolo A. *Textile Research Journal* 2009; 79: 853.
- Kim BS, Chun BH, Lee WI, Hwang YS. *Journal of Thermoplastic Composite Materials* 2009; 22: 21.
- Rongon JA, Goruppa AA, Buravalla VR, Tomlinson GR, Jones FR. *Journal of Mechanical Engineering Science* 2004; 218: 669.
- Rombaldoni F, Mossotti R, Montarsolo A, Demichelis R, Innocenti R, Mazzuchetti G. *AUTEX Research Journal* 2008; 8: 77.
- Grimoldi E, Zanini S, Siliprandi RA, Riccardi C. *European Physical Journal* 2009; 54, 165.
- Sonnenfeld A, Tun TM, Zaj'ı'ckov'a L, Kozlov KV, Wagner HE, Behnke JF, Hippler R. *Plasmas and Polymers* 2001; 6: 237.
- Mortazavi SH, Ghoranneviss M, Sari AH. *Journal of Fusion Energy* 2011; 30; 83.
- H.cker H. *Pure and Applied Chemistry* 2002; 74: 423.
- Fracassi F, d'Agostino R, Fanelli F, Fornelli A, Palumbo F. *Plasmas and Polymers* 2003; 8: 259.
- Shahidi S, Rashidi A, Ghoranneviss M, Anvari A, Wiener J. *Surface & Coatings Technology* 2010; 205: S349.
- Pascual E, RJulia M. *Journal of Biotechnology* 2001; 89: 289.
- Roberts GAF, Wood FA. *Journal of Biotechnology* 2001; 89: 297.
- Jovancic P, Jovic D, Molina R, Juliá MR, Erra P. *Textile Research Journal* 2001; 71: 948.

Received 18.06.2013 Reviewed 19.11.2013