Development of hydrophobic textile surfaces by polysiloxane films using PECVD technique

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ABSTRACT

Recently there has been much interest on the surface functionalization of textiles with reactive silicon or fluorocarbon compounds using the Plasma Enhanced Chemical Vapour Deposition (PECVD) technique. Plasma polymerization of silicon-based monomers on several types of fabrics have been studied to improve properties like: durable hydrophilic/hydrophobic character, enhanced abrasion resistance with a consequent reduction of pilling formation, barrier layers against chemical attack, and higher colour fastness, among others. In this work, hexamethyldisiloxane (HMDSO) and methoxy(dimethyl)octylsilane (MDMOS) films were deposited onto polyester, lyocell and their blends using PECVD technique under different operational conditions. The process consists of a first stage of activation of the textile fibre surface using plasmas of different gases (O_2, N_2, Air and Ar) followed by a second stage based on the deposition of the films onto previously activated textile fibre surfaces. Plasmas of the vapours of HMDSO, MDMOS, and their mixture were used in the study. Polymerization processes performed using vapours of HMDSO have been widely studied. However, to our knowledge this is the first work which uses PECVD of MDMOS onto textile substrates. Characterization of $Si:O_x:C_y:H_z$ coatings formed onto textile fibres has been done by FTIR-ATR spectroscopy using silicon-based coatings onto aluminium substrates as a reference. Modifications of wettability properties have been analyzed using wetting and wicking measurements. Abrasion resistance and yellowing index have been measured. Durability to washing and drying processes of the effects conferred to textiles by polysiloxane coatings was also analyzed. Surface topography of non-treated and plasma-treated samples has been observed by SEM technique. Furthermore, the chemical characterization of the coatings was done by DSC measurements.

Keywords: surface treatment, low-pressure plasma, PECVD, polysiloxane, hydrophobic character, abrasion resistance

1. Introduction

The possibility of selective surface modification using plasma, while keeping bulk characteristics unchanged, has greatly widened the application fields of polymers. The plasma gas is capable of modifying the surface of the substrates, generating new functional groups that increase the hydrophilicity of the fibres. This will also result in increased adhesion properties. On the other hand, the surface functionalization of polymers with reactive silicon (or fluorocarbon compounds) or with acrylate monomers by means of Plasma Enhanced Chemical Vapour Deposition (PECVD) technique can result in a hydrophobic or hydrophilic surface, respectively [1-3].

Due to the high barrier and hydrophobic properties of silicon oxide films, PECVD is considered as one of the best techniques allowing industrial-scale deposition of high-quality barrier coatings. In particular, hexamethyldisiloxane (HMDSO) is one of the most common monomer described in the literature concerning PECVD deposition [4-8]. The generation of high-density plasma is important for plasma assisted deposition, because high-density plasma can be used as an activation source for lowering the substrate temperature and enhancing the film quality [9].

The great potential for significant improvements in the properties of textiles by PECVD technique is highly promising. It is reported to produce changes in the surface topography, surface chemistry and surface wettability of PET nonwovens [10]. In another study, the water vapour permeability of PET films using PECVD of silicon oxide (SiOx) films showed an impressive enhancement, as compared to uncoated films [11]. Radio frequency plasma enhanced chemical vapour deposition (RF PECVD) of titanium oxide films for bactericidal applications is reported recently. The films were deposited on glass and cotton textile substrates [12]. In another study, plasma polymer films were deposited from HMDSO on PET surfaces under different operating conditions and the dense SiOx coatings exhibited high barrier properties [13].

Plasma polymerization of silicon-based monomers on textile fabrics can improve several properties like: durable hydrophilic/hydrophobic character, enhanced abrasion resistance with a consequent reduction of pilling formation, barrier layers against chemical attack, etc. In this work, hexamethyldisiloxane (HMDSO) and methoxy(dimethyl)octylsilane (MDMOS) films were deposited onto polyester, lyocell and their blends using PECVD technique under different operational conditions.

2. Experimental

2.1. Textiles

The textiles used are: polyester (100% PES) raw woven fabric, 150 g/m^2; lyocell (100% TENCEL®) raw woven fabric, 165 g/m^2 and 2/1 twill; and lyocell/polyester (50% TENCEL / 50% PES) raw woven fabric, 170 g/m^2.

2.2. Plasma treatments

We have treated textile samples (210 mm x 230 mm) with LP-plasma in a vacuum chamber of 34 L with four trays arranged symmetrically inside the chamber between five planar electrodes located at a constant distance and capacitively coupled through a matching network to a 40 kHz LF-generator (1.0 kW capacity) (TETRA 30

LF PC, Diener Electronic GmbH). The process consists of a first stage of activation of the textile fibre surface using plasma of a non-polymerizing gas followed by a second stage based on the deposition of the films onto previously activated textile fibre surfaces. For the activation stage, textile samples were subjected to low-pressure plasma of different gases (O_2, N_2, Air and Ar) at 600 W during 1, 5 and 10 minutes. Volumetric flow rate was kept constant at 10 cm^3 per minute (measured in normalised units). Immediately after activating the surface of textiles, the vapours of hexamethyldisiloxane (HMDSO) and/or methoxy(dimethyl)octylsilane (MDMOS) monomer has been introduced into the vacuum chamber at a pressure of 0.30 mbar. Power level was kept constant at 600 W. Time durations of 10, 20 and 30 minutes have been studied. At the end of low-pressure plasma treatments an air-flushing for 10 s followed by a venting of the vacuum chamber for 60 s have been done for each experiment.

2.3. Wettability properties

Wettability properties have been analyzed using the drop test, wicking and contact angle measurements. Drop test have been carried out for each sample according to AATCC 39:1980. Wicking properties have been measured according to UNE-EN ISO 9073-6:2000. Dynamic contact angle measurements have been carried out using a Krüss K100 MK2 tensiometer. Wilhelmy method has been applied on 20 mm x 20 mm textile samples. An average value of contact angle using five replicates has been calculated for each sample. All measurements were determined at 65 ± 2 % of relative humidity and 20 ± 0.5 ºC (ISO 139:2005) 24 hours after the plasma treatments.

2.4. Surface and chemical analysis

Characterization of the coatings formed onto textile fibres has been done by FTIR-ATR spectroscopy (Nicolet 710 FTIR - Ge crystal, Pike®, Miracle™) and DSC measurements (Perkin Elmer DSC 7) using silicon-based coatings deposited onto aluminium substrates as a reference. Modifications of the surface topography of lyocell and polyester fibres and fabrics have been observed by SEM images (JEOL JSM 5610 SEM).

2.5. Physical and durability properties

Abrasion behaviour was measured on fabrics using a Nu-MARTINDALE Abrasion and Pilling Tester according to UNE-EN ISO 12947-2:1999.

Yellowness index have been measured using a Datacolor Spectraflash SF600 PLUS-CT spectrophotometer.

Durability to washing and drying processes of the effects conferred to textiles by silicon coatings has also been analyzed. Five washing cycles at 40ºC have been done using a WASCATOR FOM 71 MP-Lab washing machine according to EN ISO 6330:2001.

3. Results and discussion

3.1. Selection of the gas to activate the surface

Some preliminary plasma treatments have been carried out to select the most suitable gas to activate the surface before plasma polymerization stage. Low pressure plasmas of nitrogen, oxygen, air and argon gases during 1, 5 and 10 minutes on 100% polyester (PES), 100% Tencel and blends of 50/50 PES/Tencel fabrics have been used.

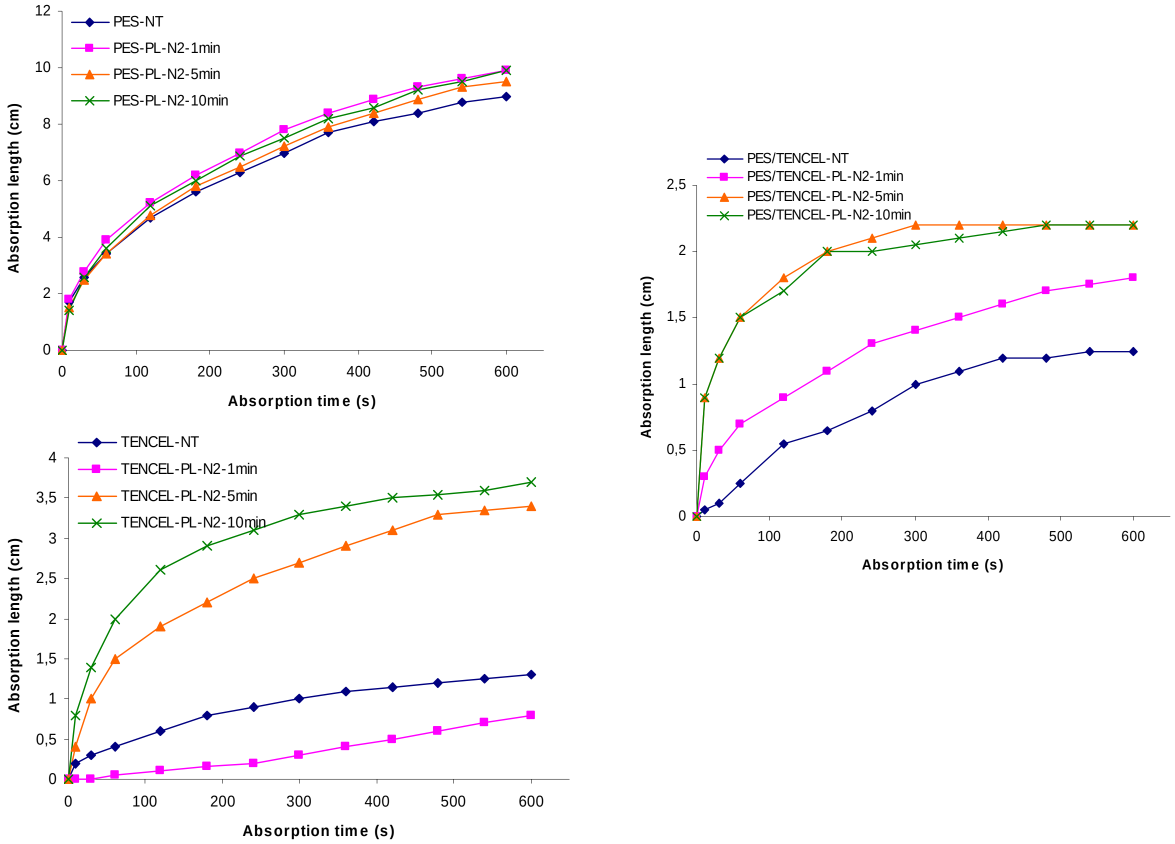

Fig. 1.- Wicking properties of non-treated (NT) and plasma-treated (PL) textiles using different times of treatment

The effect of nitrogen plasma-treatments on 100% Tencel is significantly higher than the one on polyester (Fig. 1). The improvements of wettability tend to be higher when time of treatment is increased. However, five minutes of treatment are enough to achieve a good wettability (Fig. 1).

When comparing the effect of several gases, the best wicking properties are achieved using plasma of air for all the textiles analyzed (Fig. 2). This is a surprising result that can be very interesting to probably develop a most economical industrial process in the near future.

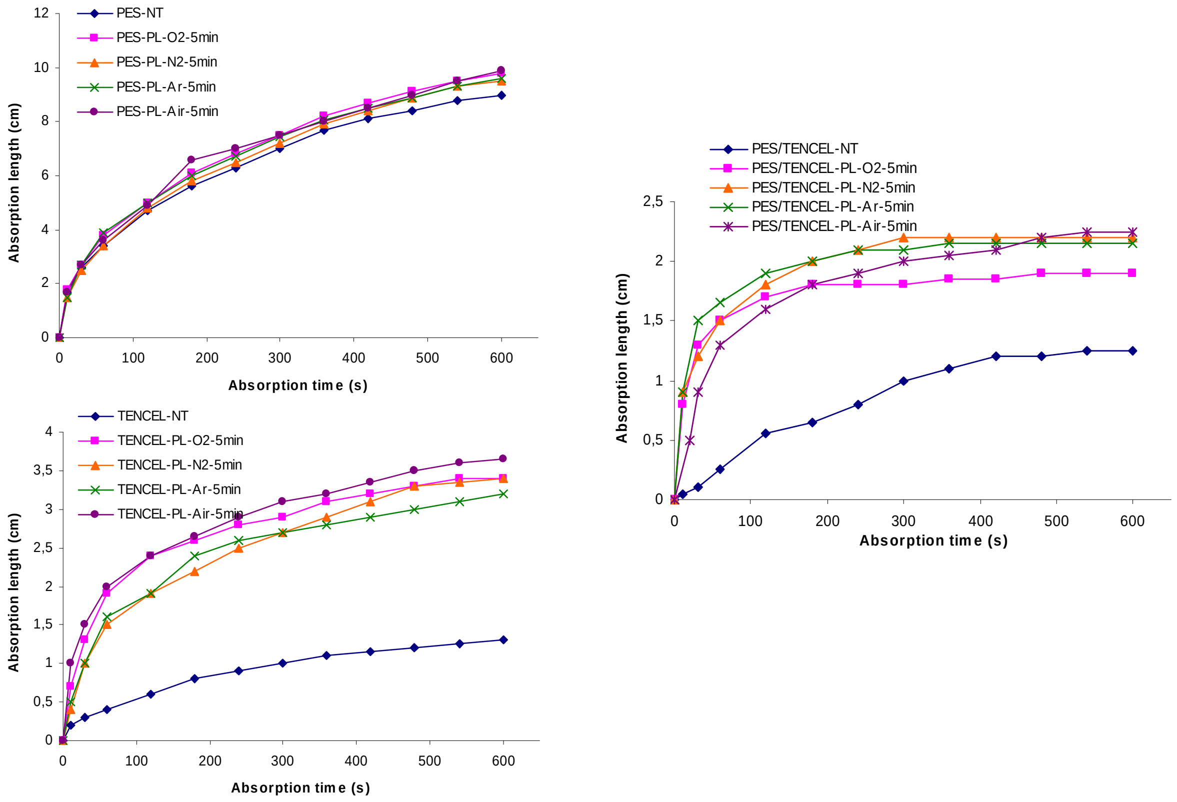

Fig. 2.- Wicking properties of non-treated (NT) and plasma-treated (PL) textiles using different gases

As a result, a five minutes activation stage using plasma of air has been selected for all PECVD treatments.

3.2. Influence of the time of treatment

Figure 3 shows that only 10 minutes of PECVD using 100% HMDSO are necessary to achieve a good hydrophobicity and the lower yellowing index on Tencel and PES/Tencel fabrics. It was not possible to obtain water repellency on polyester fabrics using the experimental conditions used in our PECVD processes. Similar results are obtained in PECVD using 100% MDMOS or 50/50 HMDSO/MDMOS.

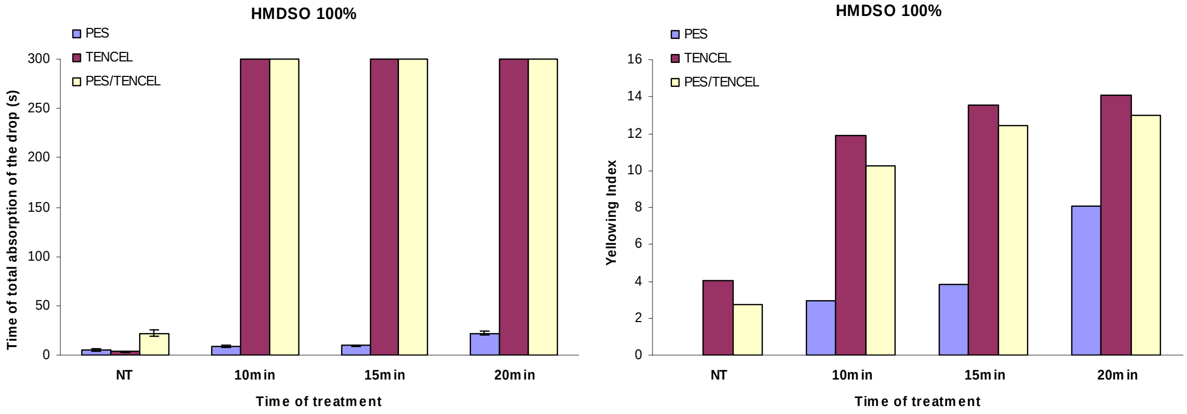

Fig. 3.- Drop test and yellowing index results of non-treated (NT) and plasma-treated textiles using different times of treatment in the plasma polymerization stage

The drop test is not able to differentiate between the hydrophobicity achieved in PECVD processes using different times of treatment (Fig. 3). However, contact angle measurements can easily quantify these differences of wettability (Fig. 4). The optimum time of treatment for 100% Tencel fabrics is 10 minutes (Fig. 4). For more than 10 minutes, the hydrophobic coating formed on the surface of the textile fibres could be partially removed due to some processes associated to plasma treatments, like sputtering and etching.

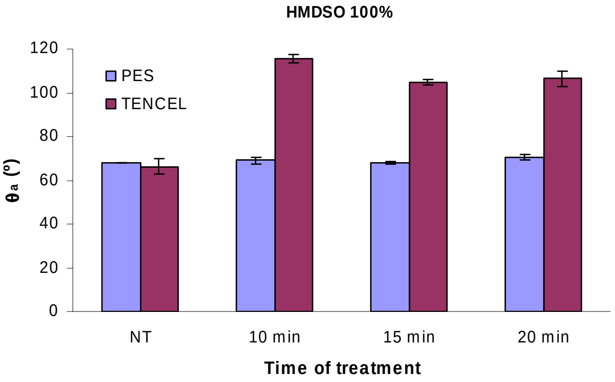

Fig. 4.- Advancing contact angle of non-treated (NT) and plasma-treated textiles using different times of treatment in the plasma polymerization stage

3.3. Influence of the type of monomer

The higher hydrophobic character for 100% Tencel or 50/50 PES/Tencel fabrics for the lower yellowing index is achieved using the combination of monomers (i.e. 50/50 HMDSO/MDMOS). The use of 100 % MDMOS do not involve hydrophobicity for any sample.

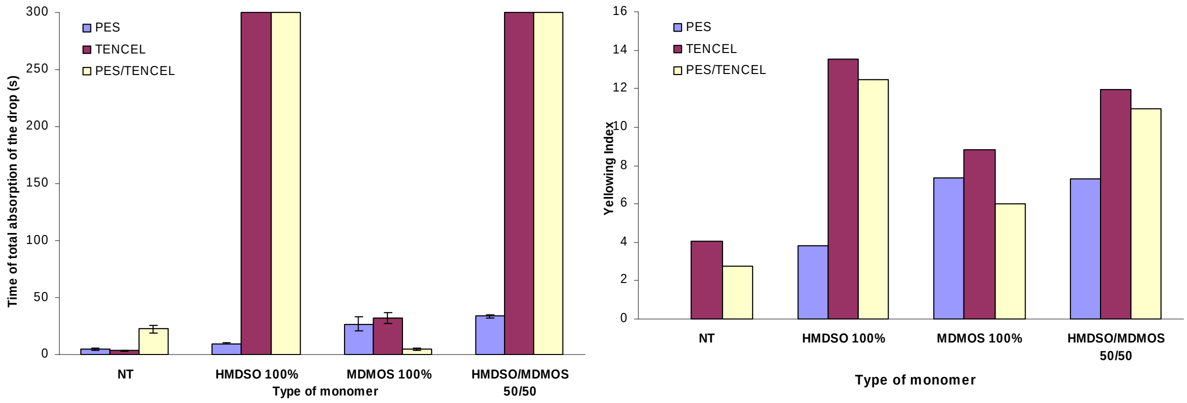

Fig. 5.- Drop test and yellowing index results of non-treated (NT) and plasma-treated textiles using different combinations of monomers in the plasma polymerization stage (time of treatment = 15 min)

Contact angle measurements have been carried out again to differentiate between the hydrophobicity of 100% HMDSO-treated and 50/50 HMDSO/MDMOS-treated fabrics (Fig. 6). The contact angle of non-treated 100% Tencel fabrics is 66.2 ± 3.4º. When 100% HMDSO monomer is used, the contact angle is significantly increased until 104.7º ± 1.0º. However, if the combinations of monomers is used, the increase of contact angle is lower, 99.1 ± 2.0º (Fig. 6). Therefore, the most suitable monomer to achieve hydrophobic character in Tencel fabrics is HMDSO.

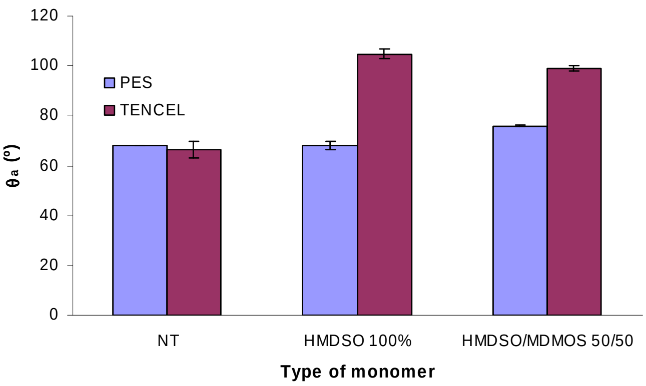

Fig. 6.- Advancing contact angle of non-treated (NT) and plasma-treated textiles using different combinations of monomers in the plasma polymerization stage (time of treatment = 15 min)

3.4. Surface and chemical analysis

It has not been possible to observe significant differences in DSC measurements of non-treated and plasma treated polyester fabrics.

The chemical structure of the deposited film when using HMDSO as a monomer in PECVD processes has been qualitatively identified. It consist of a Si:Ox:Cy:Hz compound (Fig. 7).

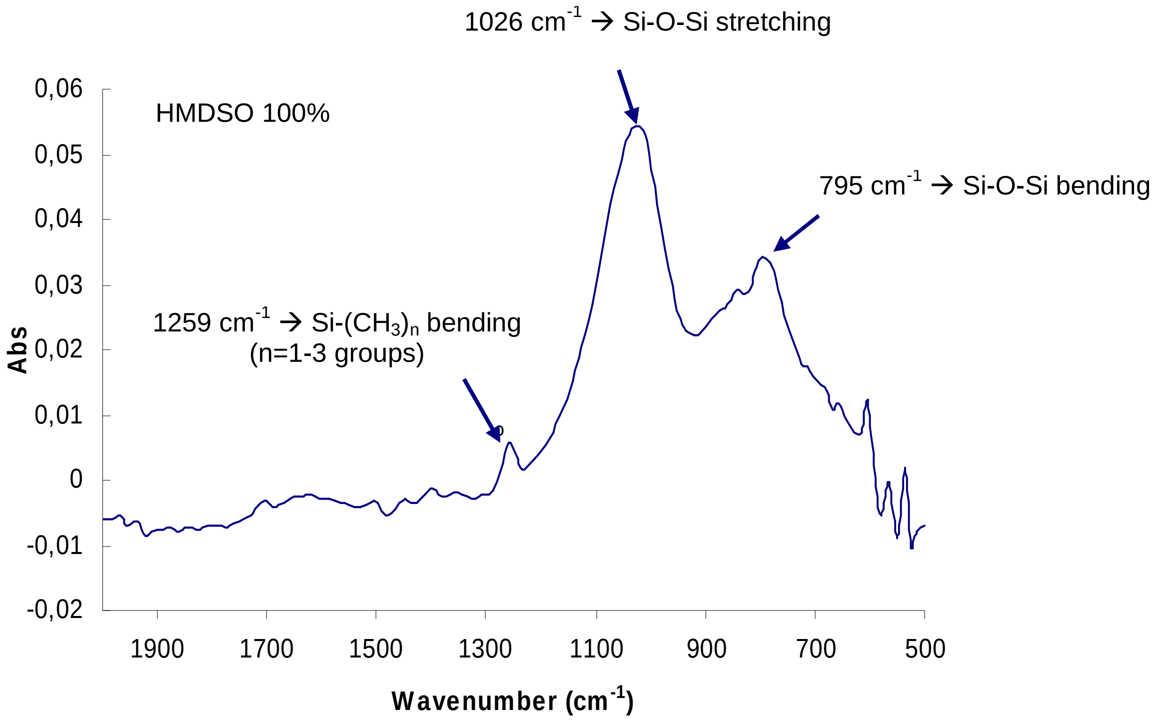

Fig. 7.- FTIR-ATR spectrum of the silicon-based coating deposited onto aluminium substrates during PECVD processes using 100% HMDSO as a monomer (time of treatment = 15 min)

It has not been possible to observe significant differences in FTIR-ATR spectra of any coated fabric. This suggests that the kind of coatings deposited onto the surface of textile fibres could by nanometric.

The topography of non-treated and plasma-treated PES and Tencel fibers has been analyzed using SEM images (Fig. 8).

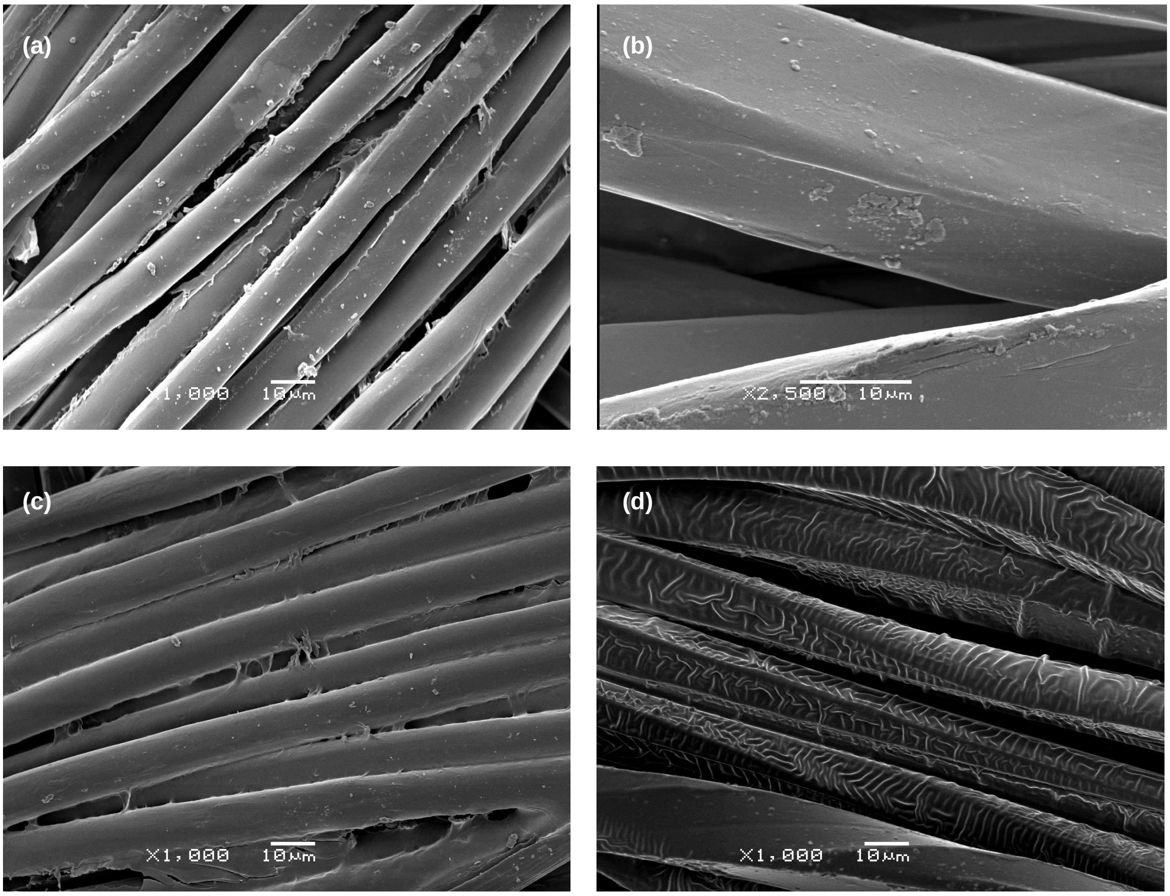

Fig. 8.- SEM images of non-treated Tencel (a), non-treated PES (b), plasma-treated Tencel (c) and plasma-treated PES (using 100% HMDSO as a monomer for 15 min)

It is observed a thin and smooth film onto plasma-treated textile fibres. However, the film deposited onto Tencel covers the fibre concentrically, while the one deposited onto polyester present a very interesting wave-like structure (Fig. 8).

3.5. Physical and durability properties

Abrasion behaviour is significantly improved probably due to the inorganic nature of silicon-based coatings deposited onto Tencel and polyester textile surfaces (Table 1). It is interesting to observe that the use of MDMOS, alone or in combination with HMDSO, increases considerably the abrasion resistance of the textiles (Table 1).

Table 1.- Abrasion resistance of non-treated (NT) and plasma-treated textile samples (time of treatment = 15 min)

Fabric	Treatment	Abrasion cycles until the break of one yarn (cycles)
Tencel	NT	14.000
	100% HMDSO	14.000
	50/50 HMDSO/MDMOS	22.000
	100% MDMOS	16.000
PES	NT	30.000
	100% HMDSO	35.000
	50/50 HMDSO/MDMOS	45.000
	100% MDMOS	> 50.000

The durability of the coating to 5 domestic washing cycles at 40ºC for Tencel fabrics is not good (Fig. 9). More research is needed to achieve permanent properties in this case. However, an unexpected phenomenon for polyester fabrics has been observed. Washed polyester fabrics present significant hydrophobic properties than not-washed ones (Fig. 9). A better adhesion of the silicon-based coating for polyester than for Tencel is suggested. It is also possible that some component of the coating could interact with washing agents in such a way that the hydrophobicity could increase.

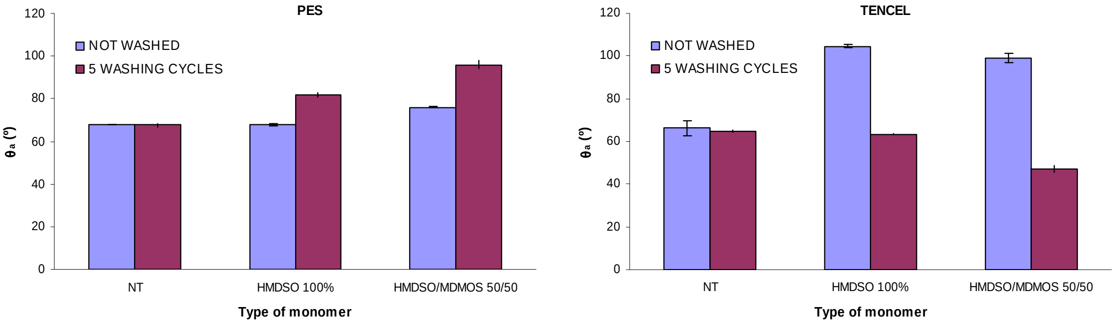

Fig. 9.- Contact angle measurements of non-treated (NT) and plasma-treated textiles using different combinations of monomers in the plasma polymerization stage (time of treatment = 15 min)

4. Conclusions

Multifunctional and environmentally friendly textiles have been developed in this study using silicon-based monomers applied by means of PECVD processes.

Low-pressure plasma treatments of PES, Tencel and PES/ Tencel fabrics with several gases (i.e. oxygen, nitrogen, air and argon) improve significantly their wettability, being air the most suitable to be used in the activation stage of plasma polymerization processes.

FTIR-ATR spectra of plasma-treated and non-treated fabrics indicate that physicochemical modifications introduced by plasma treatments are superficial.

High hydrophobic and high abrasion resistance Tencel and PES/ Tencel fabrics have been developed by PECVD using HMDSO or HMDSO/MDMOS only during 10 minutes. It has been not possible to confer hydrophobic properties to the PES 100% fabrics used.

Yellowing index increases considerably when time of treatment also increases.

The chemical structures of the films deposited onto PES, Tencel and PES/Tencel fabrics using HMDSO are based on Si:Ox:Cy:Hz.

A thin film onto plasma-treated textile fibres has been observed. The film deposited onto polyester fibres present an interesting wave-like structure.

The use of MDMOS in PECVD processes is very useful to increases the abrasion resistance of the textiles.

The durability of the hydrophobic coating deposited onto Tencel fabrics is not good. However, the hydrophobicity of washed polyester fabrics is surprisingly higher than the obtained for not washed ones.

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