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# Supercritical carbon dioxide assisted silicon based finishing of cellulosic fabric: A novel approach

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ABSTRACT

Usage of supercritical carbon dioxide as a medium for finishing cotton fabrics with modified dimethylsiloxane polymers terminated with silanol groups was investigated, different cross-linkers namely 3-isocyanatepropyltriethoxysilane (IPES) and tetraethylorthosilicate (TEOS) were used for covalently bonding between silicon and cellulose. The presence and the amount of PDMS compounds on the treated fabrics were characterized by FT-IR. Qualitative and quantitative information on the distribution of the silicon molecules across the fibre cross section was provided by SEM/EDX analysis and Confocal Raman microscopy (CRM) respectively. The results confirm that all fibres treated with PDMS and IPES have larger silicon amounts than those treated with TEOS. SC-$CO_2$ medium provides good coating of cotton surface with a 3D network of DMS compound and cross linker, and leads to forming highest DMS concentration in a layer between 1 and 2 μ under the surface of cotton fabrics.



## 1. Introduction

Supercritical fluids are well established as a processing solvent in various polymer applications such as polymer modification, formation of polymer composites, polymer blending, microcellular foaming, particle production and polymerization (Nalawade, Picchioni, & Janssen, 2006). They have special properties that could lead to substantial improvements when utilized as replacements of water in textile wet processing (Hendrix, 2001; Saus, Hoger, Knittel, & Schollmeyer, 1993; Saus, Knittel, & Schollmeyer, 1993), since considerable amounts of waste water are currently produced during the dyeing and finishing of textiles, and it is very difficult to treat the wastewater containing many additives by conventional biological process (Munshi & Bhaduri, 2009).

Carbon dioxide is the most commonly used supercritical fluid (SC-f). It is inexpensive, non-toxic, non-flammable, environmentally friendly and chemically inert under most of conditions (Hyatt, 1984). In addition, its critical point (CP) of carbon dioxide is 7.31 MPa at 31 °C and it is a suitable solvent for less polar and non-polar molecules(Gebert, Saus, Knittel, Buschmann, & Schollmeyer, 1994). Beyond its critical point, Supercritical Carbon Dioxide SC-$CO_2$ has unique properties; for example, SC-$CO_2$ exhibits density and solvating powers similar to those of liquid solvents. Due to these attributes, SC-$CO_2$ has been proposed as an environmentally friendly replacement of water and organic solvents for many industrial applications. However, only two classes of polymeric materials (amorphous fluoropolymers and silicones) have been shown to exhibit appreciable solubility in SC-$CO_2$ at readily accessible temperatures and pressures (McClain et al., 1996; Montero, Smith, Hendrix, & Butcher, 2000).

The potential of SC-$CO_2$ in textile dyeing has been investigated e.g. synthetic (Hendrix, 2001; Li-qiu, Shu-fen, Liang, Wei, & Jin-zong, 2013; Maeda, Kunitou, Hihara, & Mishima, 2004; Montero et al., 2000) and natural fibre such as cotton (Beltrame et al., 1998; Brunner, 2010; Fernandez Cid et al., 2007; Gebert et al., 1994; Maeda, Hongyou, Kunitou, & Mishima, 2002; Saus, Hoger, et al., 1993; Saus, Knittel, et al., 1993; Schmidt, Bach, & Schollmeyer, 2003a; Schmidt, Bach, & Schollmeyer, 2003b) and wool (Montero et al., 2000; Sawada, Takagi, Jun, Ueda, & Lewis, 2002). Solubility of the dye in SC-$CO_2$ is obviously a critical parameter, so that disperse dyes are generally used due to their acceptable solubility in SC-$CO_2$. However, the pressure and temperature dependence behaviour of solubility of such dyes in SC-$CO_2$ is a complex phenomenon and not fully understood. Organic solvents for dry cleaning of textiles were also replaced with SC-$CO_2$, because it has the same cleaning effect for several kind of textile (Munshi & Bhaduri, 2009; Sousa, Melo, Casimiro, & Aguiar-Ricardo, 2007). Another challenging field of application for SC-$CO_2$ in textile industry is the disinfection and sterilization of e.g. medical textiles and clothes before use (Bach,

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Schmidt, Cleve, & Schollmeyer, 2003; Schmidt, Beermann, Bach, & Schollmeyer, 2005).

Several investigators have attempted to dye cellulose fibres in SC-$CO_2$ (Maeda et al., 2004). Unfortunately, dyeing of cellulosic fibres in SC-$CO_2$ was not successful. The major limitation is the fact that SC-$CO_2$ is a hydrophobic solvent, which does not swell the polar hydrophilic cotton fibre (Saus, Hoger, Knittel, et al., 1993).

Carbon dioxide alone is unable to break hydrogen bonds between adjacent molecular chains of the fibrous cellulose material because it does not swell the fibres and the diffusion of the dye into the fibre is significantly reduced (Saus, Hoger, Knittel, et al., 1993). At the same time, SC-$CO_2$ extracts the natural moisture present in the cotton fibres. As a result, the cotton loses its flexibility, and its glass transition temperature ($T_g$) increases up to 493 °K which causes cotton damage (Beltrame et al., 1998; Fernandez Cid et al., 2007). The solubility and the rheology of silicones in SC-$CO_2$ was studied previously by many researchers (Mertsch & Wolf, 1994; Royer, DeSimone, & Khan, 1999; Wignall, 1999), and it has been established that SC-$CO_2$ reduces the viscosity of silicones at 50 °C (Gerhardt, Manke, & Gulari, 1997).

In this study, we describe a strategy for environmentally friendly finishing of cotton fabrics, with siloxanes compounds of different molecular weights dissolved in supercritical carbon dioxide instead of water. The results of the finished cotton fabric in water and in SC-$CO_2$ are compared and the effect of the medium on the deposition behaviour of silanol compound (—Si—OH compounds) on the fabric surface is studied. The effect of cross linker type on the deposition process was shown and we studied the influence of finishing agents and media on textile performances.

Conventional reactive silicones are modified dimethylsiloxane polymers with silanol groups. In the presence of water, reactive silicones form silanol groups by hydrolysis, and polymerization may take place by means of the silanol condensation process, resulting in the formation of a polymer network that entraps fibres within the matrix. This polymer network imparts an improved durability. However, there are no stable chemical bindings between the siloxane polymer and cellulose due to the small difference in electro negativities of carbon and silicon. Several approaches have been attempted to facilitate better fixation of reactive silicone polymers on the fibre surface. A special class of poly-functional silicone monomers called silane coupling agents (SCA) has been employed to improve the cross-linking of reactive silicone polymers. The silane coupling agents are used commercially in conjunction with reactive silicone softeners to provide better wrinkle recovery, durability, and other performance properties.

Organo-functional silicone softener is a poly-functional silicone monomer that can facilitate cross-linking of reactive silicone polymers as well as condensation with the substrate. Hydrolyzable groups of the silane coupling agent are believed to first hydrolyze under an acidic condition and convert to reactive silanol groups. Then, under catalysis and curing conditions, a polyfunctionalsilane coupling agent is believed to crosslink reactive silicone polymers to produce a stable polymer network over the surface of the fibre through silanol condensation. Furthermore, condensation to form cross-links with the substrate has also been reported (Arkles, 1977; Pawlenko, 1986).

As condensation proceeds, the reaction rate decreases due to increasing steric hindrance, decreasing mobility and the diminishing availability of silanol groups. Therefore, silicone softeners generally require high temperature treatment to remove moisture from the substrate and to accelerate the condensation reaction between silicone polymers (Turner, 1988). However, high temperature treatment generally has an adverse effect on the mechanical properties of the fibre. Moreover, a high temperature promotes conversion of the molecular structure of a silicone polymer from a coiled helical structure to a straightened chain (Guise & Jones, 1987).

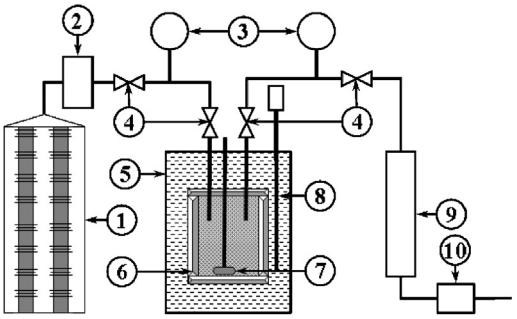


**Fig. 1.** Diagram of SC-$CO_2$ finishing technology.

The aim of this work is to estimate the possibility of finishing cotton fabric in supercritical carbon dioxide instead of water. This would help reducing the pollution associated with the usual textile wet processing.

## 2. Experimental

### 2.1. Materials

100% cotton fabric (WFK Testgewebe GmbH 10000) was provided by WFK Testgewebe GmbH (Germany); silanol terminated polydimethylsiloxanes (DMS) with different molecular weights (DMS-S12 Mwt. 0.4–0.7 KDa; DMS-S14; Mwt. 0.7–1.5 KDa and DMS-S15; Mwt. 2–3.5 KDa) were purchased from ABCR GmbH & Co. KG. 3-Isocyanatepropyltriethoxysilane (IPES, Mwt. 247.37) and tetraethylorthosilicate (TEOS,Mwt. 208.33) were provided from Sigma–Aldrich, and the WfKE colabel light Duty reference detergent (an anionic, silicate free detergent) was purchased from Ecolab GmbH.

### 2.2. Methods

#### 2.2.1. Treatment in SC-$CO_2$ medium

The static high-pressure apparatus used for the finishing experiments is shown in Fig. 1. It consists of a gas supply, diaphragm compressor, and a heatable stainless steel vessel. The finishing vessel is equipped with a perforated stainless steel beam and a stirrer. Experiments of finishing can be made with this system up to 400 bars and 50 °C.

Cotton fabrics to be treated are wrapped around the treatment beam and mounted around the stirrer. 1% (w/w) of PDMS is placed on the bottom of the treatment container before starting, and cross-linker (IPTES or TEOS) is added to the container at a weight equivalent to two -OH groups of DMS. 1.1 equivalents cross-linker (respect to each OH group) is also added. The device is sealed and heated to 50 °C as selected finishing temperature (suitable for dissolving of DMS) while SC-$CO_2$ is pumped simultaneously to the 400 bar as settled pressure. The finishing treatment is run for 120 min after which the pressure is reduced in steps while the temperature is still maintained at finishing temperature until the pressure reaches the atmospheric pressure.

#### 2.2.2. Treatment in aqueous solution

Fine, stable, mechanically prepared micro-emulsions have been made using sonificator (Bandelin electronic UW60) and magnetic stirrer for a variety of polyorganosiloxanes compounds. Cotton fibres were immersed in the previously prepared emulsions in a liquor ratio (LR) of 1:20 for 30 min. The treatment bath was of a

concentration of 0.5, 0.7 and 1% (w/w) respectively, at pH = 5.4, at room temperature.

After the finishing process in any of the treatment media, the finished samples were submitted to the thermal treatment, during which one expects to occur the condensation reaction between the PDMS/cross linker, and PDMS/cellulose respectively. The fabrics are treated in dry oven at 70 °C for 60 min. After that, the treated fabrics is rinsed in cold water then washed in aqueous solution containing 1% v/v silicate free detergent, at 50 °C for 10 min, to remove the unreacted or adhered silicon compound, which might dissolve in the washing solution (Thoss, Hesse, Höcker, Wagner, & Lange, 2003).

### 2.3. Measurements

#### 2.3.1. Fourier transform infra-red spectroscopy (FT-IR)

Attenuated Total Reflection-FT-IR using diamond cells, offers the possibility for evaluating the concentration and the presence of siloxane compound in the fabrics (both bulk and the surface of the treated fabric). It gives the overview of the silicon concentration in the fabric, being able to monitor the migration of functional groups to the polymer bulk or on the surface of the fabric (HSU, 1997; Rasmussen, Stedronsky, & Whitesides, 1977). The attenuated total reflection with diamond cells 45○, spectra resolution of 4 $cm^{-1}$, 400 scans, were used to determine the relative concentration of the silicone polymer in the untreated and treated cotton fabrics (Fourier Transform Infra-Red Spectroscopy (FT-IR) model NEXUS 470, Thermo Nicolet Co. ATR technology). The presence of silicon compounds requires the presence of the peaks at 2960–2965, 1260–1265 and 795–805 $cm^{-1}$ in the FT-IR spectrum.

#### 2.3.2. Confocal Raman microscopy (CRM)

Confocal Raman microscopy (Raman RFS 100/S from Bruker Optic Co, laser Nd:YAG 1064 nm (NIR), Laser Power 200 mW) was used to evaluate the relative proportion of the element Si distribution across a single cotton fibre because of the valence oscillation of the Si—C moiety of the Si—$CH_3$ group using a signal between 710 and 720 $cm^{-1}$ in the Raman spectrum. All Raman spectra were integrated during 20 s with a 4 $cm^{-1}$ resolution from the fibre surface to 4 μm depth below the fibre surface using 1 μm depth steps.

#### 2.3.3. Energy dispersive X-ray spectroscopy (EDX)

A combination of Energy Dispersive X-ray spectroscopy (EDX) coupled on the Scanning Electron Microscopy (SEM) was used for measuringthe silicone distribution over the fibre cross section.After carbon coating, the EDX (Energy dispersive X-ray spectroscopy) coupled to the scanning electron microscope (HITASHI S–300 microscope S, at 15–KV acceleration voltage) gave access to a qualitative mapping of the Silicon element distribution.

#### 2.3.4. Moisture sorption and desorption

Evaluation of the hydrophilicity and the ability of untreated and treated cotton fabric to absorb the moisture were investigated by using IGAsorpAnalyzer produced by HIDEN ISOCHEMA with relative humidity ranging from 0% to 95%. All the samples were tested at 25 °C.

The moisture regain defines as the ability of the fibre to recover the moisture at a given relative humidity environment. The formula for calculation is given by:

$$\text{Moisture regain } (\%) = \frac{W_t - W_o}{W_o} \times 100 \quad (1)$$

where $W_t$ and $W_o$ are the moisturized and dry weights of the film composites, respectively

We have tested the effect of finishing cotton fabric with DMS compounds on the moisture absorption. This property defines the ability of the material to absorb water and perspiration and plays an important role in feeling comfortable when wearing these materials.

The tests were run in IGASorp moisture absorbance measuring device and we measured the moisture absorption at relative humidity of 65%, and 25 °C (room temperature).

#### 2.3.5. Mechanical measurements

The Kawabata Evaluation System (KES) tensile, shear, bending, compression and surface testing instruments (Barker, Shalev, An, & Scruggs, 1992; Orzada, 2001) were used to characterize the physico-mechanical properties of the treated fabric. Several tests were performed, namely: tensile & shear, pure bending, compression and surface test. Measurements were carried at five different places on every sample in both warp and weft directions. For these experiments we used samples of 25 cm × 25 cm treated cotton fabric left 24 h at standard temperature 22 °C and 65% relative humidity.

The characteristic values (Tensile; Linearity of load-extension curve (LT), Tensile energy (WT), Tensile resilience (RT), Shearing; Shear rigidity (G), Hysteresis of shear force at 0.5° shear angle (2HG), Hysteresis of shear force at 5° shear angle (2HG5), Bending; Bending rigidity (B), Hysteresis of bending moment (2HB), Compression; Linearity of pressure-thickness curve (LC), Compressional energy (WC), Compressional resilience (RC), Surface; Coefficient of friction (MIU), Mean deviation of MIU, frictional roughness(MMD), Geometrical roughness(SMD),Weight; Weight per unit area (W) and Thickness; Thickness at 0.5 gf/$cm^2$ (T)) are calculated from the recorded curves obtained by each tester in both warp and weft direction. Tensile properties (force-strain curve) and shear properties (force-angle curve) are measured by same machine. Bending properties (torque-angle curve) are measured bending first reverse sides against each other and after that the face sides against each other. Pressure-thickness curves are obtained by compression tester. The measurements of surface friction (friction coefficient variation curve) and surface roughness (thickness variation curve) are made with the same apparatus using different detectors.

## 3. Results and discussion

It was expected that the mixture of SC-$CO_2$/PDMS will penetrate easily inside the fibres at the end of this treatment, the pressure will reduce gradually to release the SC-$CO_2$ and keep the PDMS and the cross linker inside the fibre. During the thermal treatment, which occurred at 70 °C for one hour, condensation reaction will happened between the hydroxyl group of PDMS and isocyanatopropyl group of IPES, which has extremely high reactivity or with the ethoxy group of TEOS. The idea behind using IPTS is that, the organo functional isocyanate group can bond with the available hydroxyl groups (Lung & Matinlinna, 2010) of Silanol terminated polydimethylsiloxanes (DMS) and also the hydroxyl group of cotton fabrics). In addition, both of these cross linker can reacted with their ethoxy groups to the hydroxyl group of cotton or PDMS (Bartram & Moffat, 1996) to form 3D silane network inside the treated fabric.

### 3.1. Characterization of the treated fabrics

#### 3.1.1. Determination of the silicon concentration in the fibre by ATR-FT-IR

The ATR-FT-IR spectra (Fig. 2A) recorded for untreated and treated cotton fabrics, confirm the presence of silicon peak in all treated fabrics. The use of IPES as cross-linker provides higher silicon concentration for all type of DMS compounds. This may be

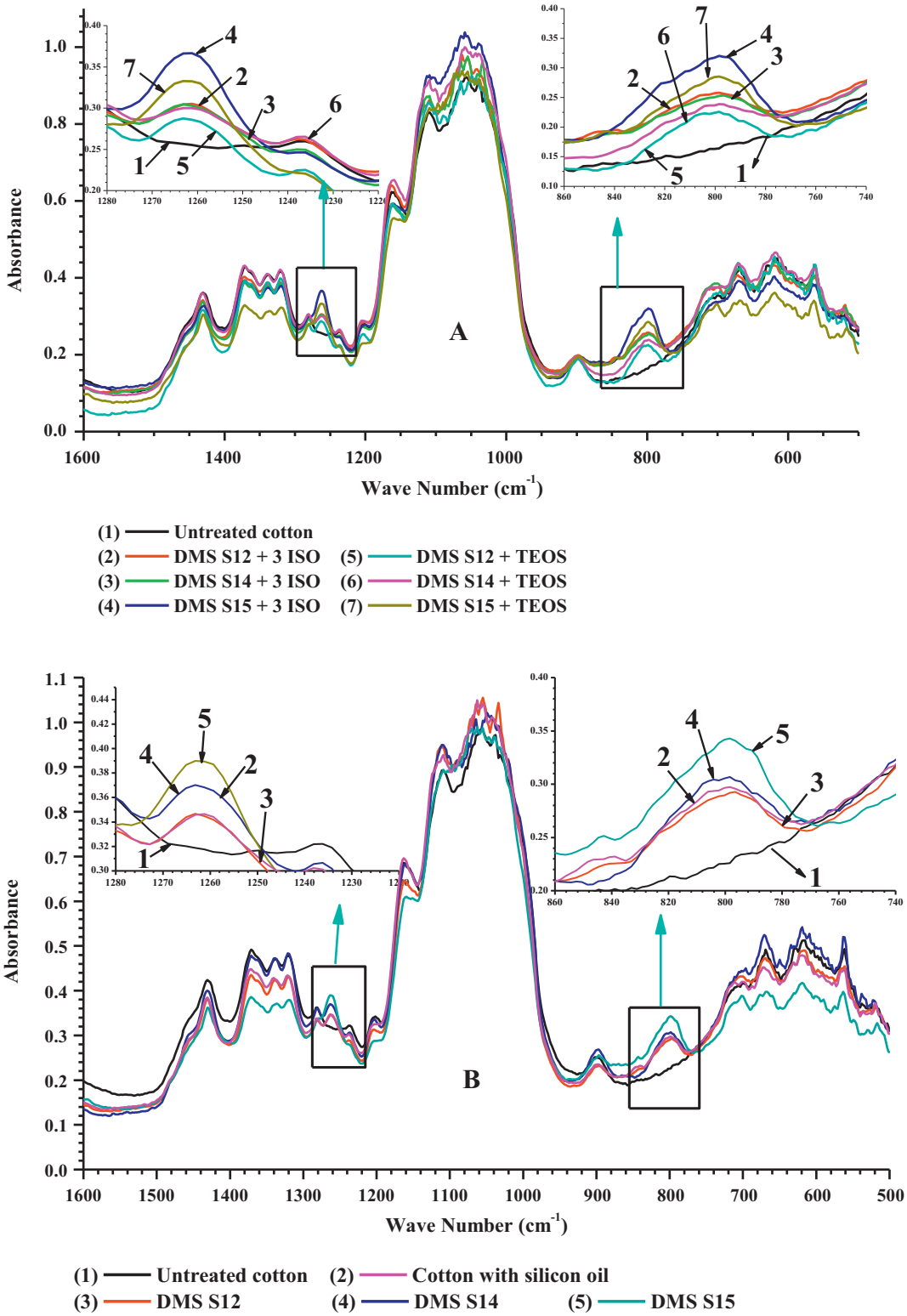


**Fig. 2.** FT-IR spectra of treated cotton fibre with 1% DMS compounds in (A) SC-$CO_2$ and (B) water media.

attributed to the highly reactive isocyanatopropyl group of IPES, which can react quickly with hydroxyl groups of both cotton and DMS compounds. On the other hand, the fabrics treated with DMS-S15 show the higher silicon concentration than the other two DMS compounds. In addition, one can say that, by increasing the molecular weight of DMS compound, the silicon concentration in the fabrics increased, in case of using the same cross-linking agent.

Cotton fabrics, which are treated with DMS compounds in water medium, were analyzed by using FT-IR. The FT-IR spectra show the presence of silicone in all treated cotton fibres (Fig. 2B). One can observe that fibre treated with DMS-S15 compound has highest

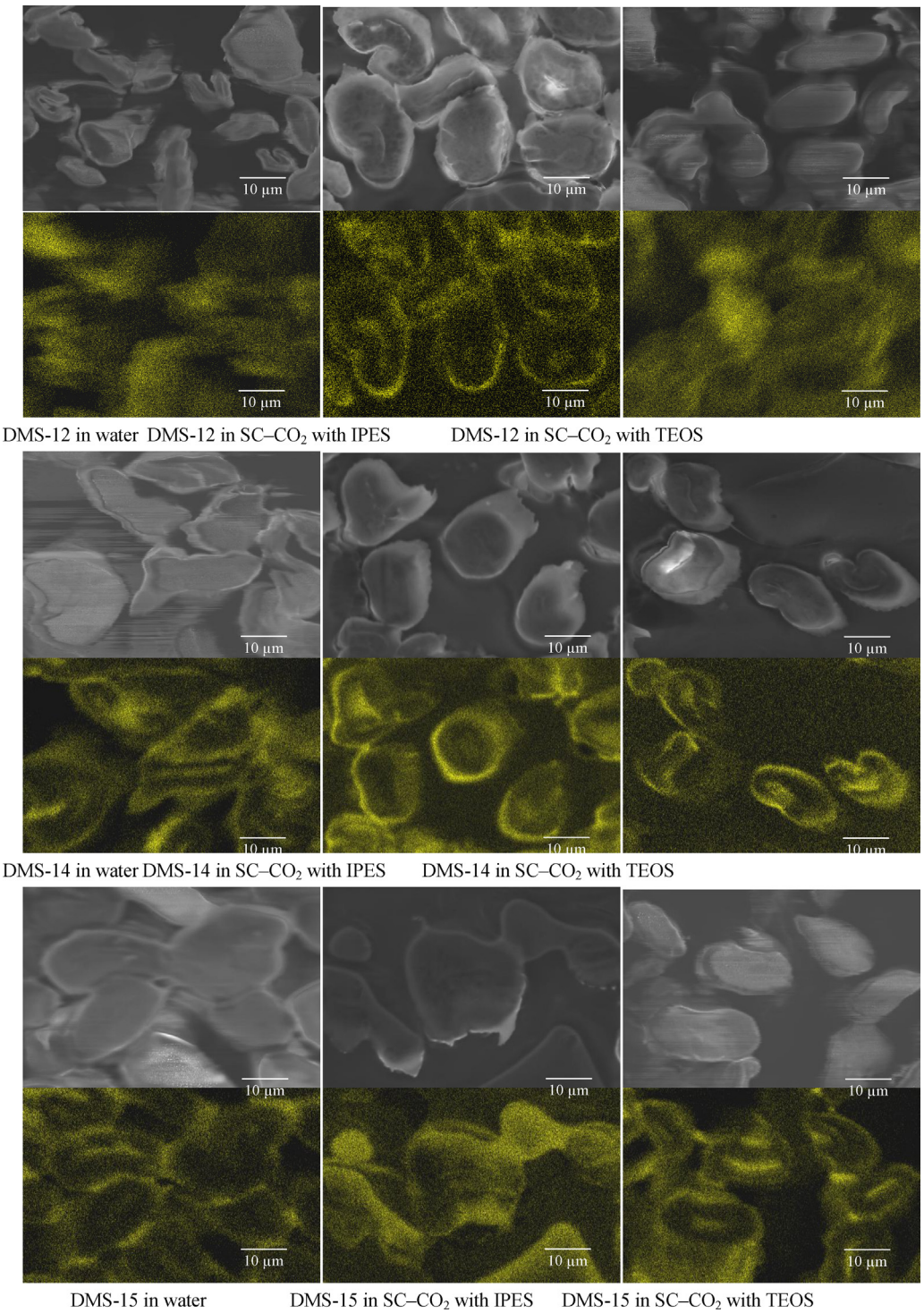


**Fig. 3.** SEM/EDX micrographs for distribution of DMS molecules over the cross-section of the finished cotton fibres.

intensity silicon peak compared to those treated with other PDMS compounds. By comparing the fibres treated with these compounds and fibres treated with the same concentration of silicone oil (i.e. 1% (w/w)) in water media, we may see that the fibre treated with any PDMS compound has higher silicon concentration than those treated with silicone oil.

One can also observed that, for the same PDMS polymer, there is no difference of the concentration of silicon deposited on cotton fabrics from any finishing media (water or SC-$CO_2$).

### *3.1.2. Distribution of the silicone through the cross-section of the fibre*

Qualitative information on the distribution of the silicon molecules across the fibre are provided by SEM/EDX analysis. Confocal Raman spectroscopy was also used as analytical tool to gather quantitative information about the silicon distribution.

By means of SEM/EDX the distribution of PDMS molecules over the cross-section of the finished cotton fibres was determined for various finishing formulas for any media of treatment. Comparing

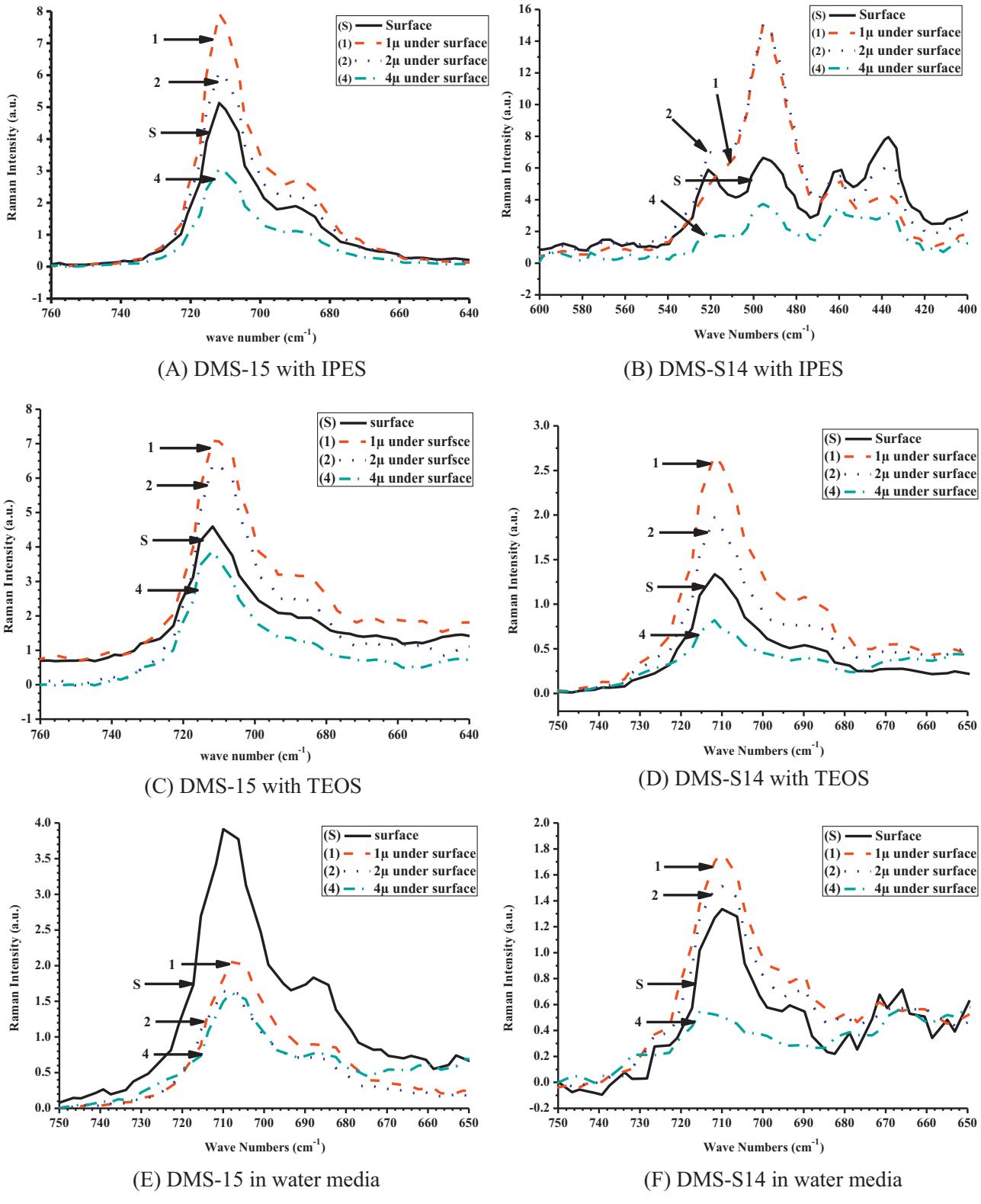


**Fig. 4.** Raman spectra of treated cotton fibres by DMS–S15 and DMS–S 14 with IPES andTEOS in SC-$CO_2$ media and in water media on the surface and in different depth from the surface.

the SEM micrographs and the silicon EDX mapping, one notices that the silicon element from PDMS is located in most cases on the surface and near to the fibre surface. The amount of PDMS on the fibre treated in SC-$CO_2$ medium is higher than the fibre treated in water medium. PDMS distributed in different ways in water medium and SC-$CO_2$ medium. It can distribute in the both fibre surface and fibre lumen in case of using SC-$CO_2$ medium while it distribute only on the fibre surface in case of using water medium. In most cases the results of SEM/EDX confirmed the results of FT-IR. The EDX micrographs (Fig. 3) of treated cotton fibres show the presence of DMS for

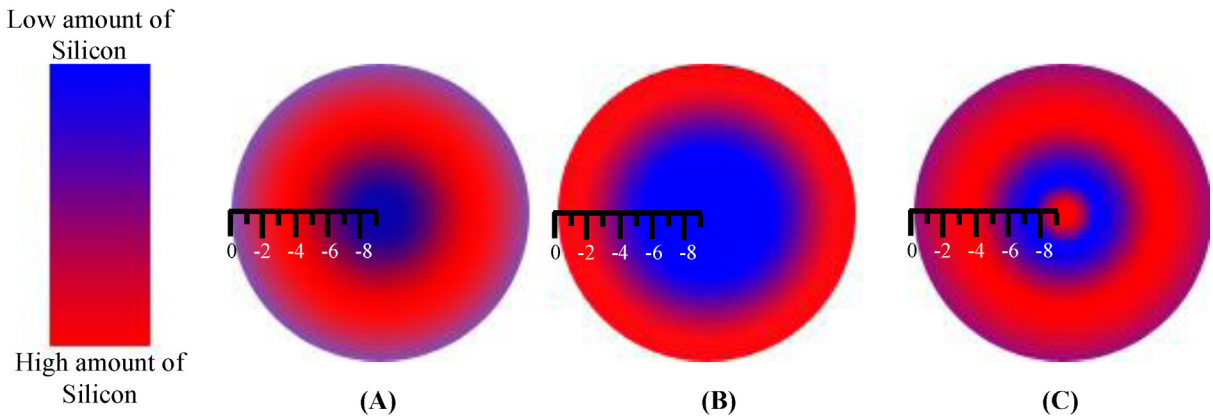


**Fig. 5.** Scheme for distribution of PDMS compounds through the single cotton fibre in aqueous solution and SC-$CO_2$ medium.

any experimental condition we used. All fibres treated with PDMS compounds and cross-linker IPES have higher silicon amounts than those treated with the same PDMS compounds using TEOS as a cross linker. PDMS distributed in the fibre lumen by using both cross linker with all PDMS compounds. Therefore we can say that SC-$CO_2$ medium provides good deposition conditions and coating of cotton surface with a 3-D network of PDMS compounds and the silicon cross linker. Treatment in aqeuoes solution provide coated surface with PDMS compounds of the treated cotton fibre without distribution into the lumen of the fibre.

Confocal Raman microscopy was run to provide quantitative estimation for the concentration of PDMS compound over the treated cotton fibres. Fibres treated with both DMS-S15 and DMS-S14 were chosen for analysis. For any experimental treatment condition, Raman spectra exhibit the presence of a silicon peak near the surface of treated fibres.

Confocal Raman spectra of finished cotton fabric with DMS-S15 in SC-$CO_2$ media indicate that the highest PDMS concentration is located in a layer between 1 μ and 2 μ depth under the surface. The concentration of PDMS on the fibre surface seems to be lower than those at 1 μ depth. The presence of PDMS is almost vanished at 4 μ depth under the surface. This result confirms the EDX mapping of silicon across the fibre cross section. (Fig. 4A–D)

The results of the treatment with DMS S15 from water media indicate also the presence of PDMS in high concentration on the surface of the treated fibres (see Fig. 4E and F). However, the treatment from aqueous solution does not show the presence of PDMS in the bulk of the treated fibres. On the other hand, the treatment with DMS-S14 and cross linker IPES from water media provides the deposition of PDMS in the fibre up to 2 μ depth.

The estimation of the quantity of PDMS deposited on the treated fibre agrees with EDX mapping. The fibres treated from SC-$CO_2$ with cross linker IPES have the highest silicon concentration compared to those treated under the same conditions with TEOS (Fig. 4C and D), or treated from water medium (Fig. 4E and F). This is shown by the high intensity of the silicon peak characterizing the product in the spectra of treated cotton fibre with DMS-S15 and IPES (Fig. 4 A and B).

Fig. 5 is a schematic presentation of the finding of the PDMS compound across the fibre cross section in both treatment media. As illustrated silicone can distributed into the lumen of the fibre and to 1–2 μm depth under the surface by using SC-$CO_2$ as treatment media, while it is deposited only on the surface by using DMS 15 and distribute in 1–2 μm depth under the surface if the treatment in aqueous solution.

### 3.2. Effect of finishing with DMS compounds on moisture absorption

Fig. 6A shows the moisture absorbance by finished cotton fabrics with 1% DMS compounds in both media. No difference was detected between the behaviour of fabrics finished from any of the medium; in both cases, the fabrics absorb well the moisture, with small enhancement compared to the untreated sample. The type of cross-linker or DMS compounds does not play an effective role in case of fabric finished from SC-$CO_2$ medium.

To investigate the effect of silicon compound on the ability of cotton fabrics to absorb moisture the fabrics were treated with different amounts of DMS compound (0.5, 0.7 and 1% (w/w)) from water environment. The results are presented in Fig 6B. This Figure illustrates that finishing cotton fabrics with any concentration of any DMS compound does not affect the moisture absorbance capacity of the finished fabric.

### 3.3. Effect of finishing with DMS compounds on the physico-mechanical properties of the finished fabrics

As stated earlier (Brooks, Das, & Smith, 1989) PDMS compound, as a softener, enhances the mechanical properties of the treated fabrics. The conventional fabric softeners have long fatty acid chains and they soften fabrics through an outstanding surface effect in which friction is reduced between the fibres in the fabric substrate. In other words, the primary effect of a fabric softener is to lubricate the surface of fibres by coating them with a thin film layer. Consequently, handle and other mechanical properties are affected by the manner in which the softener is deposited on the fibre surface. Treatment parameters such as drying and curing temperatures, as well as the type and amount of bath additives, and treatment medium are expected to influence the parameters, which determine the subjective feeling according to the Kawabata Primary Handle (stiffness, bending, tensile, shear, thickness, and weight).

#### 3.3.1. Bending stiffness properties

Bending stiffness is one of the most important properties of fabrics and it is defined as the ratio of bending moment per unit width of curvature. Not only does it affect the feel or 'handle' of a fabric but it also influences handling during assembly with the other parameters. For measuring the bending stiffness of fabrics, a "bending length" is defined by the length of a horizontally clamped fabric, when the secant from fixed to the free end makes a 41.5° angle to the horizontal. The bending stiffness affects the tailoring quality of fabrics, the design of the garment, as well as the automated handling of the fabric. Objective measurement of this

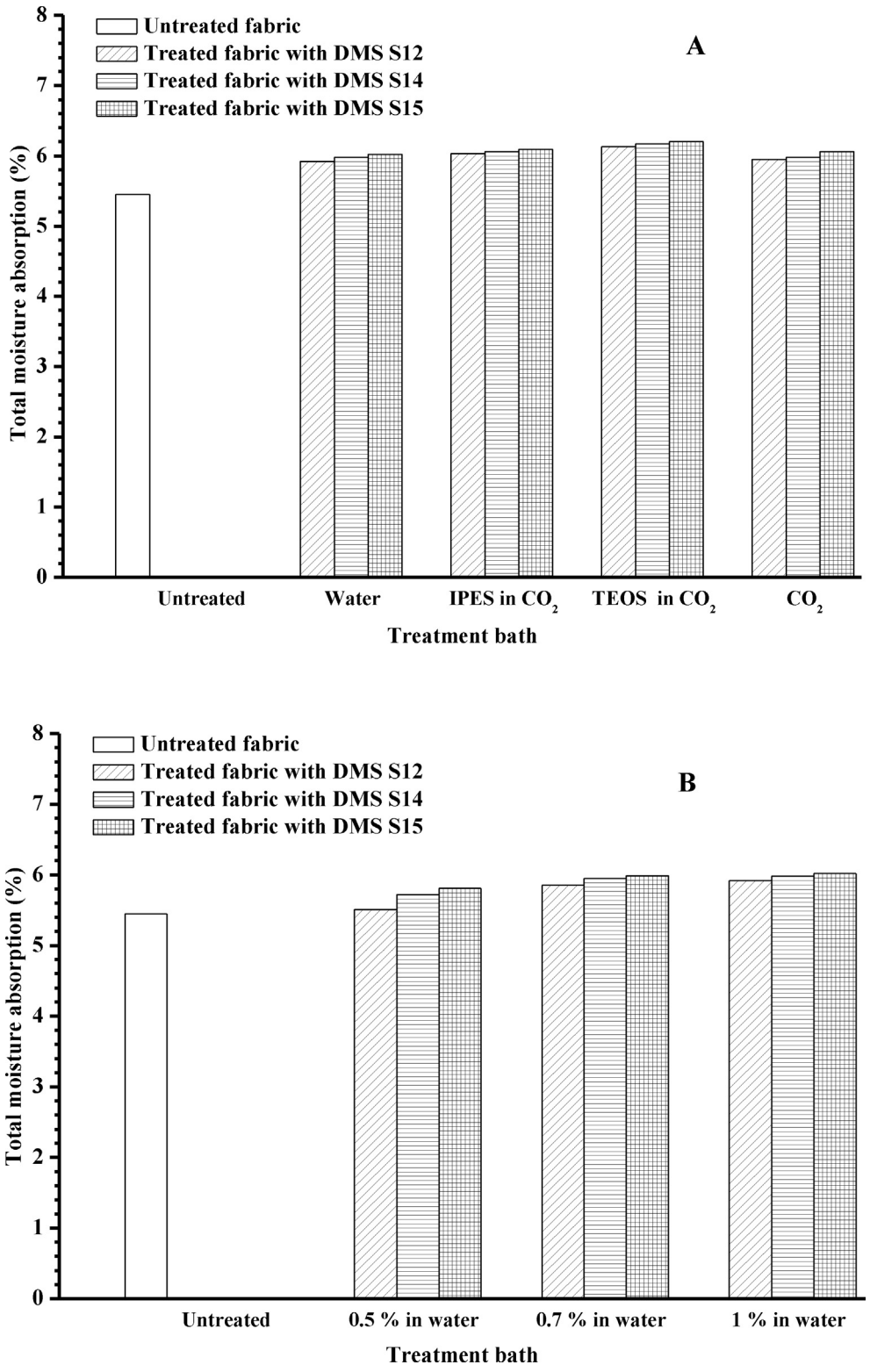


**Fig. 6.** Total moisture absorption of cotton fabric treated with DMS compounds.

characteristic leads to making rational decisions in choosing of fabrics in order to minimize the tailoring problems and improve the quality of finished garment.

Finishing cotton with DMS compound reduces bending rigidity and the hysteresis of bending amount (Fig. 7A and B), for fabrics treated from both water and SC-$CO_2$ with any finishing formula. The relative reduction in hysteresis of the finished fabrics with DMS means that the silicon compounds play an effective role as a softener of the fabrics. Hysteresis represents the energy lost during the complete deformation-recovery cycle as a direct result of the inelastic mechanical processes of inter-fibre friction and fibre viscoelasticity. DMS compound reduces the frictional resistance to inter-fibre movements at the cross-over points, thus helping the fabric to recover fully from deformation. The reduction of both

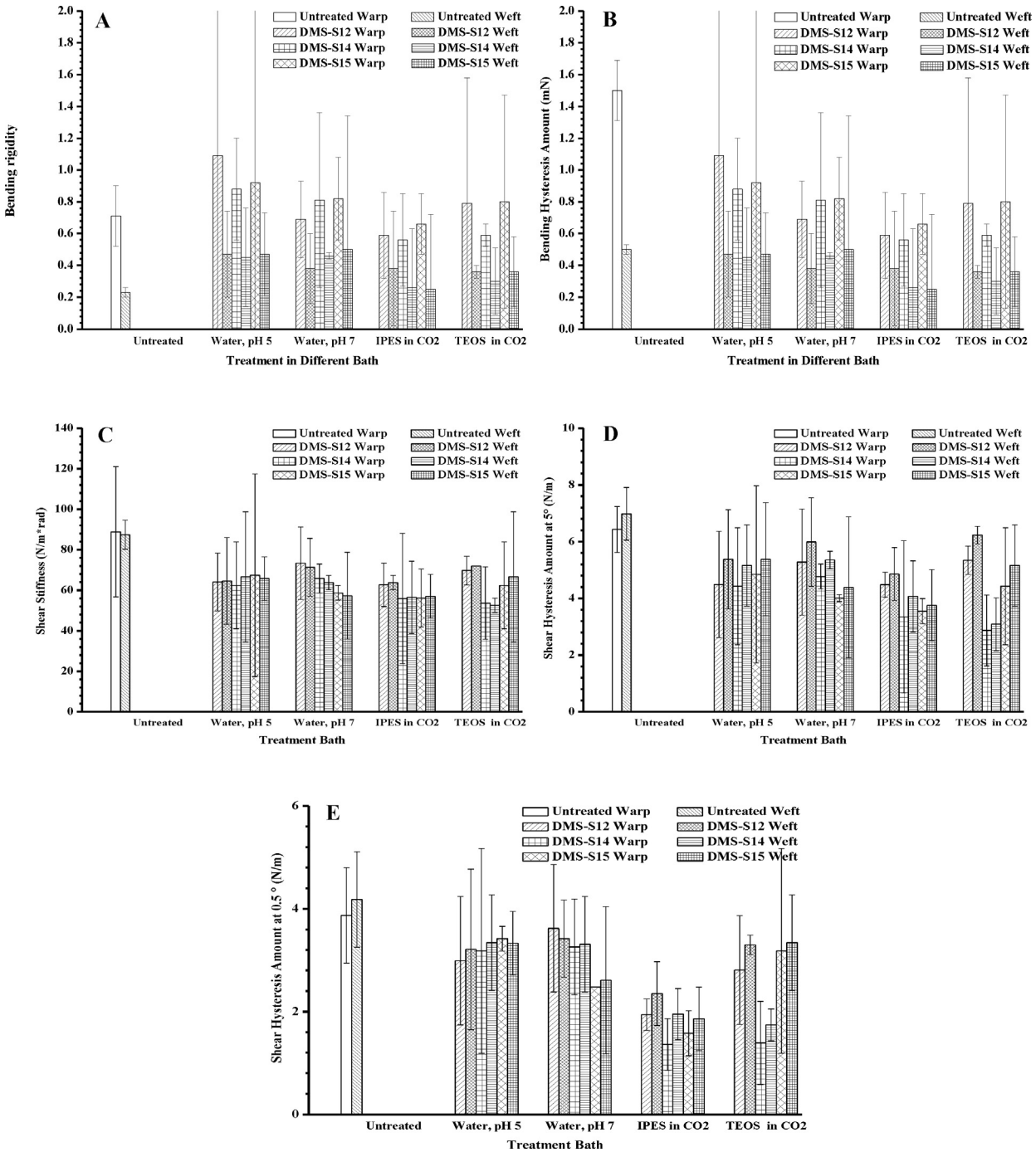


**Fig. 7.** Bending stiffness properties of treated fabrics with DMS compounds in warp and weft directions.

bending rigidity and hysteresis is enhanced in the case of fabrics treated from SC-$CO_2$ and when use IPES cross linker. This means that such treatment conditions lubricate more the fibres and reduce the friction fibre-to-fibre decreasing the stresses induced during weaving within the fabric structure.

### 3.3.2. Shearing properties

Shear rigidity ($G$) and shear hysteresis values at 0.5° (2HG) and at 5° (2HG5) were obtained from shear experiment. The reduction of shear rigidity ($G$) of the fabrics treated from SC-$CO_2$ is noticeable larger than those treated from water medium (Fig. 7C–E). The same tendency is observed in both warp and weft directions for shear rigidity (G) as well as for shear hysteresis (2HG) and (2HG5).

DMS finishes reduce shear stiffness and hysteresis (G, 2HG and 2HG5; Fig 7C–E, respectively) of the treated samples. Its application from SC-$CO_2$ is shows better results than when applied from water. Fabric shear properties are perhaps the most complex ones, because they include tensile, bending, friction, and compression at crossover points between fibres and yams in the fabric structure. All these properties, of course, depend also on fabric morphology.

### 3.3.3. Tensile properties

Linearity of tensile curve, LT, tensile energy, WT, and tensile resilience, RT and extension at 500 g load values were obtained from the tensile experiment and are presented in Fig. 8.

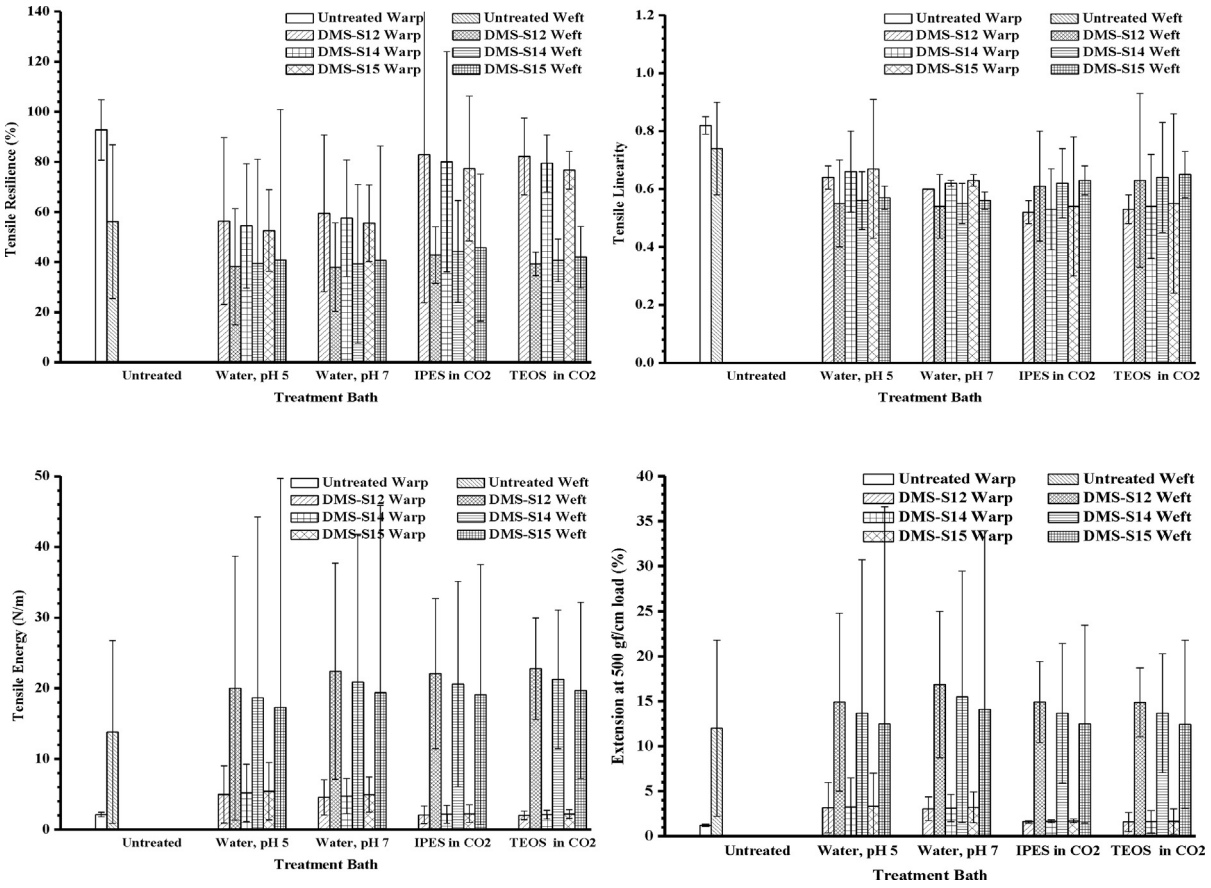


**Fig. 8.** Tensile properties of treated fabrics with DMS compounds in warp and weft directions.

In all cases, investigated fabrics treated with DMS compounds show reduced linearity of tensile curve, LT, after treatment along both warp and weft direction. This is associated with the reduction of fabric stiffness. The decrease of the tensile linearity leads to an increase of the tensile strain and tensile energy.

With the tensile test, the tensile energy (WT) of all treated samples increases significantly in warp and weft directions (Fig. 8). This means that the fabrics become more stretchable and more energy is needed to reach the same tensile load like of the untreated. The elasticity of the fabrics improves probably due to the formation of the polymer film on the surface (Jang & Yeh, 1993), which is confirmed by the results of SEM/EDX and Confocal Raman analysis. Fabric behaviour under tensile, shear, bending, and compression is very important for dimensional stability and shape deformation.

As cloth deformation is non-elastic, it exhibits a considerable amount of visco-elasticity and hysteresis. Finishing quite markedly influences resilience behaviour of fabrics. Decreasing tendency of the tensile resilience RT is observed for most of the investigated fabrics after finishing treatment. The reduction is more significant in case of treating cotton from water medium may be because the network forms preponderantly on the surface. In contrast, the cotton treated from SC-$CO_2$ appears to have the network built inside the fibre, at about 1 μ depth.

### 3.3.4. Compression properties

Compression rate (EMC), linearity of compression curve (LC), compressional energy (WC) and compressional resilience (RC) were obtained from compression experiment for untreated and finished fabrics.

Due to relaxation induced by finishing to fabrics in most cases the linearity of compression, LC, increases which means that the elasticity of the material increases by the relaxation induced by finishing with DMS compounds. LC increases for all finished samples, which means that the recovery angle slightly improves for all the samples (Fig. 9).

Compressional resilience RC increases for all treated fabrics, due to the formation of DMS on the fabric surface.

Fabric thickness changes after the treatment of cotton fabrics with DMS compounds from any of the treatment medium. There is a certain increase in the thickness of the unfinished and finished cotton fabrics. All finished samples undergo increase in thickness, which could be due to the formation of film layer on, or under the fabric surface. The thickness of fabrics treated from water is higher than those of fabrics treated from SC-$CO_2$, which may be attributed to the formation of layer of DMS on the surface, in the first case, and under surface in the second.

The compression energy increases also due to the increasing of the thickness, the increase in LC and WC of the finished fabrics. The changes in surface characteristics, thickness, and compression of the material are directly related to the subjective perception of fullness and softness of handle.

### 3.3.5. Surface properties

Coefficient of friction MIU, mean deviation MMD and surface roughness SMD before and after finishing were obtained in surface investigation experiment Fig. 10. It is observed that SMD values in warp and weft directions are close to each other. This indicates an evenness of the treatment, with no preference of the silicon compound for any of the directions.

Referring to Fig. 10, the results of the surface test exhibit a lower frictional coefficient for all treated samples compared to untreated,

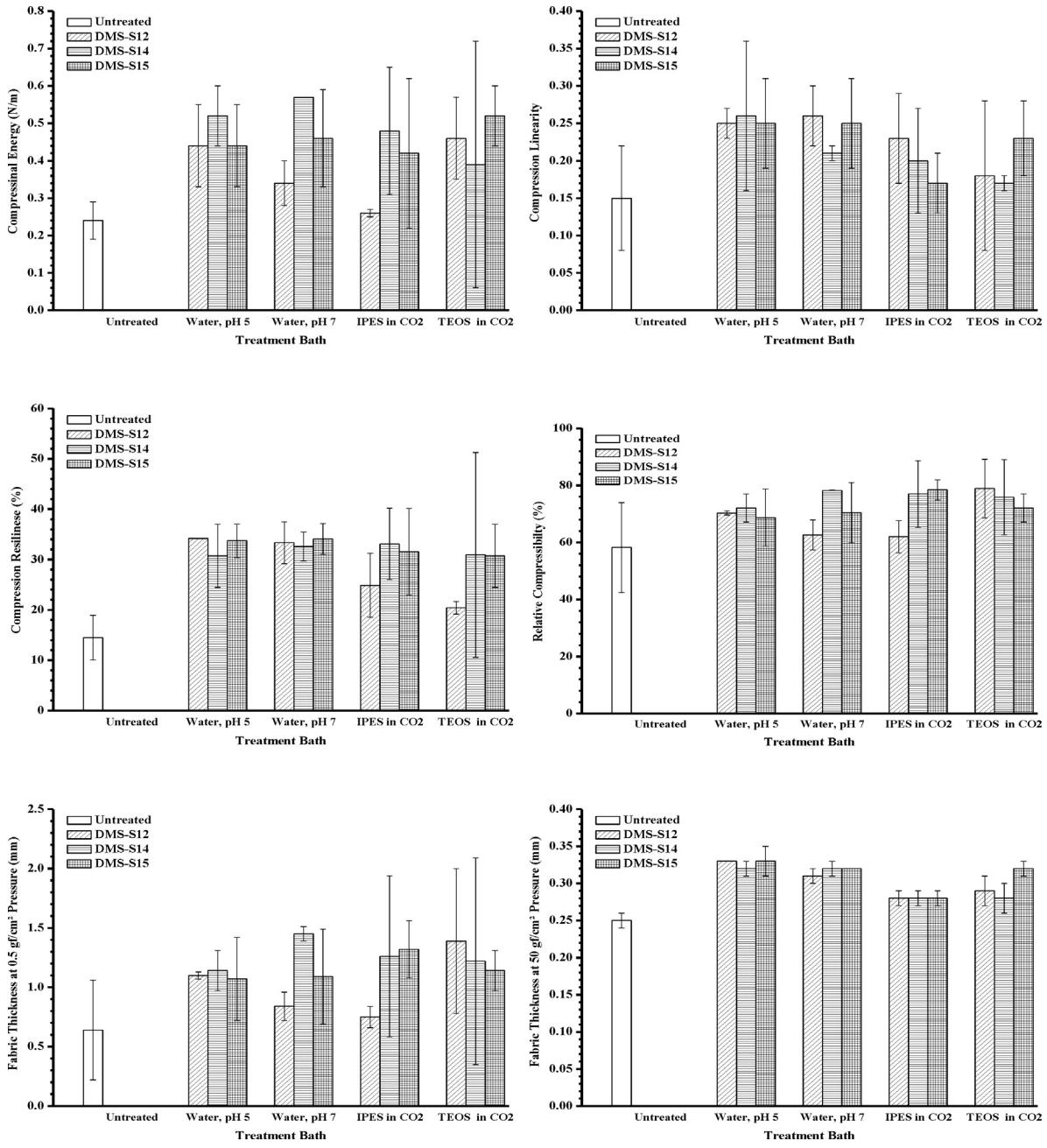


**Fig. 9.** Compression properties of treated fabrics with DMS compounds.

disregarding the finishing medium or pH. Preliminary observations of DMS compounds treated samples in aqueous solution and SC-$CO_2$ by SEM/EDX and Confocal Raman microscopy reveal the deposition of DMS on or near fibre surface and formation of a polymer film on the fabric surface, which is quite uniform and markedly pronounced in both treatment medium for all treatment formula. From the previous information, we can assume that the polymer film is the main cause for changes of the surface and mechanical properties of the DMS-treated fabrics in this study. The formation of the polymer film increases the uniformity of the surface (MMD decreases, see Fig. 10) and decreases the roughness, which is expressed in a better cohesion between the sensor of the instrument and the sample and from this, a lowering of the friction coefficient. Friction is not only determined by the contact surface, but also by deformation at the contact point (Tzanov, Betcheva, Hardalov, & Hes, 1998). This behaviour was observed for all fabrics finished from both water and SC-$CO_2$ with similar amount of DMS. It confirms that there is no difference between treating from water or from SC-$CO_2$ medium in terms of the achieved surface properties of the finished fabric.

In the context of producing soft, smooth, extensible, and flexible fabrics, according to Postle (Postle & Dhingra, 1989), the 2HG5, B, MIU, and SMD should decrease and RC, should increase. We confirmed these by the results of our study. MIU depends also on the uniformity of the silicone polymer film. Mahar et al. (Mahar, Dhingra, & Postle, 1987) noted that LT, RT, MIU, LC, and RC were not quite sensitive to changes in fibre characteristics, fibre construction, finishing, and other processing parameters, so they were not appropriate for quality control. Our experiments found the same results.

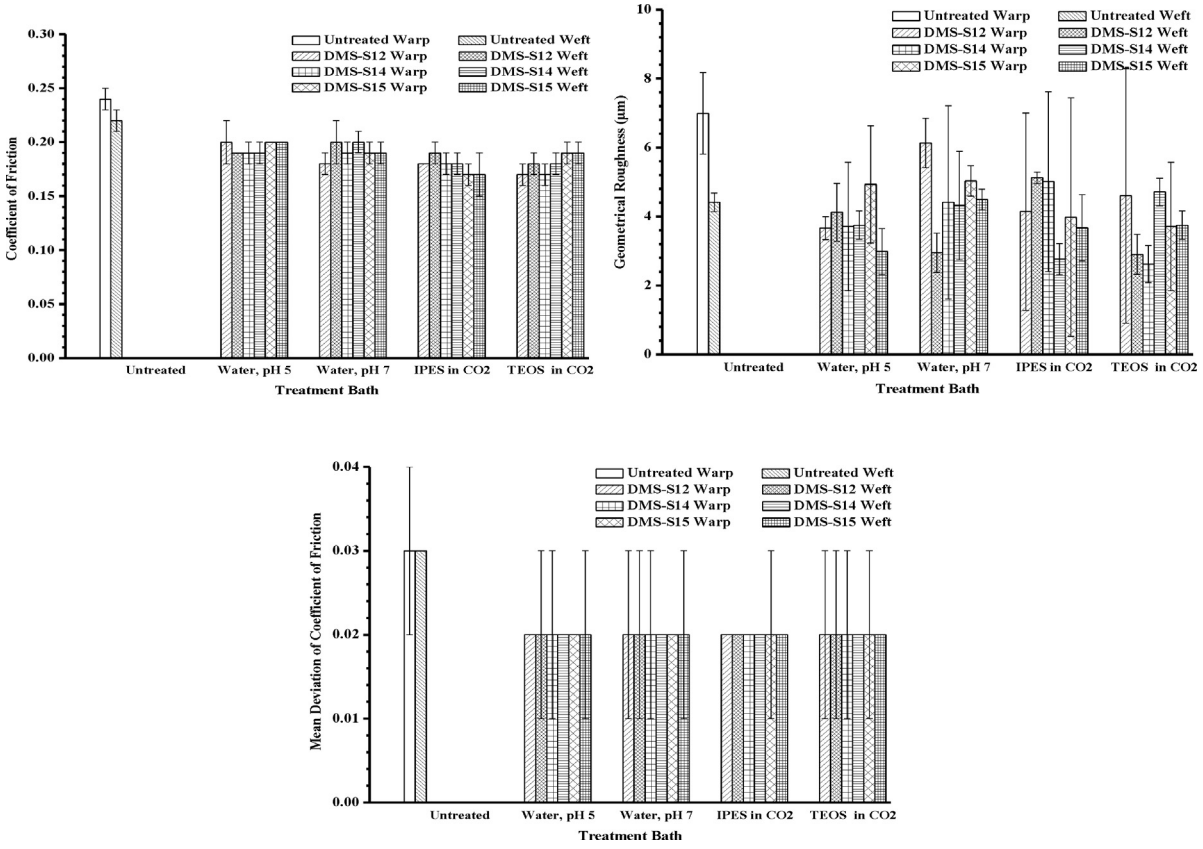


**Fig. 10.** Surface properties of treated fabrics with DMS compounds in warp and weft directions.

## 4. Conclusions

Supercritical carbon dioxide is a suitable medium for finishing cotton fabrics with PDMS-silanol compounds. The EDX and confocal Raman microscopy results of the finished fabrics are close for samples treated from water and from SC-$CO_2$, whilst the physico-mechanical properties of treated fabrics from SC-$CO_2$ show improvement compared to the fabrics treated from water media.

Aqueous medium helps the deposition of silanol compound on the surface of the fabrics, while SC-$CO_2$ supports the deposition at 1 μ under the surface. These results were confirmed by SEM/EDX in agreement with Confocal Raman analysis.

DMS-S15 shows best results of deposition on cotton surface, ATR-FT-IR and Confocal Raman analysis detecting the highest concentration of silicon for this case. Isocyanatepropyltriethoxysilane (IPTS) proved to be a better cross-linking agent than TEOS, and combining IPTS with DMS compound yields most silicon deposition on the surface of the fabrics.

Treating cotton fabric with DMS compounds from water or from SC-$CO_2$ does not affect the moisture regain of treated fabrics. Physico-mechanical properties of treated fabrics from any of the two media improve significantly with achieving good handle and soft performance.

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