Carbohydrate Polymers 96 (2013) 305–313

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Suitability of Confocal Raman microscopy for monitoring the penetration of PDMS compounds into cotton fibres

Amina L. Mohamed[a,*], Meriem Er-Rafik[b], Martin Moller[b]

[a] Textile Research Division, National Research Centre, Dokki, Giza, Egypt
[b] DWI an der RWTH Aachen and Institute of Textile Chemistry and Macromolecular Chemistry (ITMC), Aachen University, Pauwel Straße 8, D-52056 Aachen, Germany

ARTICLE INFO

Article history:
Received 26 February 2013
Received in revised form 18 March 2013
Accepted 26 March 2013
Available online 3 April 2013

Keywords:
PDMS compounds
Confocal Raman microscopy
Scanning electron microscope
Penetration and cotton

ABSTRACT

PDMS compound was chosen as a molecule-model for investigating the diffusion of silicon products into cotton bulk. The study demonstrates the suitability of Confocal Raman microscopy (CRM) to monitor the distribution of poly(dimethylsiloxane) (PDMS) molecules into cotton fibres. Different molecular weights of PDMS compounds were used in two different solvents (water and hexane) at various temperatures (25, 50 and 60 °C). The surfaces of the fibres were studied with scanning electron microscopy and Confocal Raman microscopy was run to detect the PDMS on the surface and in the bulk of treated fabrics. We concluded that all PDMS compounds, irrespectively their molecular weights and the silicon oil infiltrate into cotton fibre. The penetration is strongly dependent on the solvent used. Water proved suitable for assisting the infiltration of low and medium molecular weight PDMS, at elevated temperatures. High molecular weight PDMS infiltrates better from hexane and at room temperature than from water.

1. Introduction

Textile finishing provides a way to impart new and diverse properties to textiles while retaining comfort and mechanical strength (Rooks, 1972). Chemical compounds containing silicon—oxygen (Si—O) bonds (such as polydimethylsiloxane; PDMS) are used in the textile industry as finishing agents: softeners, antistatic, antisoil and anticrease.

Silicones have wide applications in the textile industry from fibre, yarn and fabric production to final product finishing. Their distinctive chemistry imparts a range of characteristics, including improved softness, dimensional stability, fabric physical properties, wrinkle recovery, and stretch (Jang & Yeh, 1993). Silicones can also be used to provide hydrophilicity (Mehta, Somasundaran, Maldarelli, & Kulkarni, 2006) or hydrophobicity, static control, lubrication, antimicrobial treatments and anti-slip properties (Abidi, Hequet, & Cabrales, 2009; Gao, Zhu, Guo, & Yang, 2009; Xue, Jia, Zhang, & Ma, 2010). A variety of silicone technologies have different applications in the textile industry (Abidi et al., 2009).

The vast majority of silicon compound used in the textile sector are linear polydimethyl siloxanes (PDMS). Because of their inorganic–organic structure and the flexibility of the silicone bonds, silicones have some unique properties including low surface energy, excellent lubricity, heat stability, high compressibility, low surface tension, hydrophobicity, good electric properties, low fire hazard and limited solubility in organics coupled with water insolubility. (Abidi, Hequet, & Tarimala, 2007) At the molecular level, the fabric softening properties of siloxanes are believed to be derived from the flexibility of the siloxane backbone, that results from the freedom of rotations about the Si—O—Si linkages and the low interaction energies of the methyl groups (Owen, 1981; Skinner, Caibao, Grigoras, Halloran, & Zimmerman, 1999). Siloxane functional groups provide strong attractive interactions between the fabric softener and the cotton surface (Stark, Falender, & Wright, 1982).

Different analytical techniques were used to detect the silicon compounds on textile fabrics (Smith, 1991). The most common one is Infrared spectroscopy and, in particular, Fourier Transform Infrared spectroscopy (FT-IR), is widely available and the easiest technique for detecting the presence of silicones in textile fabric (Murthy, Leyden, & D'Alonzo, 1985) and obtaining information about their structure. Silicones have strong absorption bands in the IR spectrum range, at 1260, 1100–1000 and 770 cm^{-1}, meaning that, levels as low as 1% can be detected. X-ray photoelectron spectroscopy (XPS) and time of flight-secondary ion mass spectrometry (TOF-SIMS) are more sophisticated techniques that can also be applied to detect and characterise silicones within the 10–50 Å depth layers from the surface of materials (Brunon et al., 2011; Hoefnagels, Wu, de With, & Ming, 2007; Vilcnik et al., 2009).

Confocal Raman microscopy (CRM) is now commonly used as a complementary adjunct to other molecular spectroscopy techniques such as UV–vis, FT-IR, and NMR. It is particularly

* Corresponding author. Tel.: +20 1129769992.
E-mail addresses: alo.mohamed12@hotmail.com, alo.mohamed@yahoo.com (A.L. Mohamed).

0144-8617/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carbpol.2013.03.087

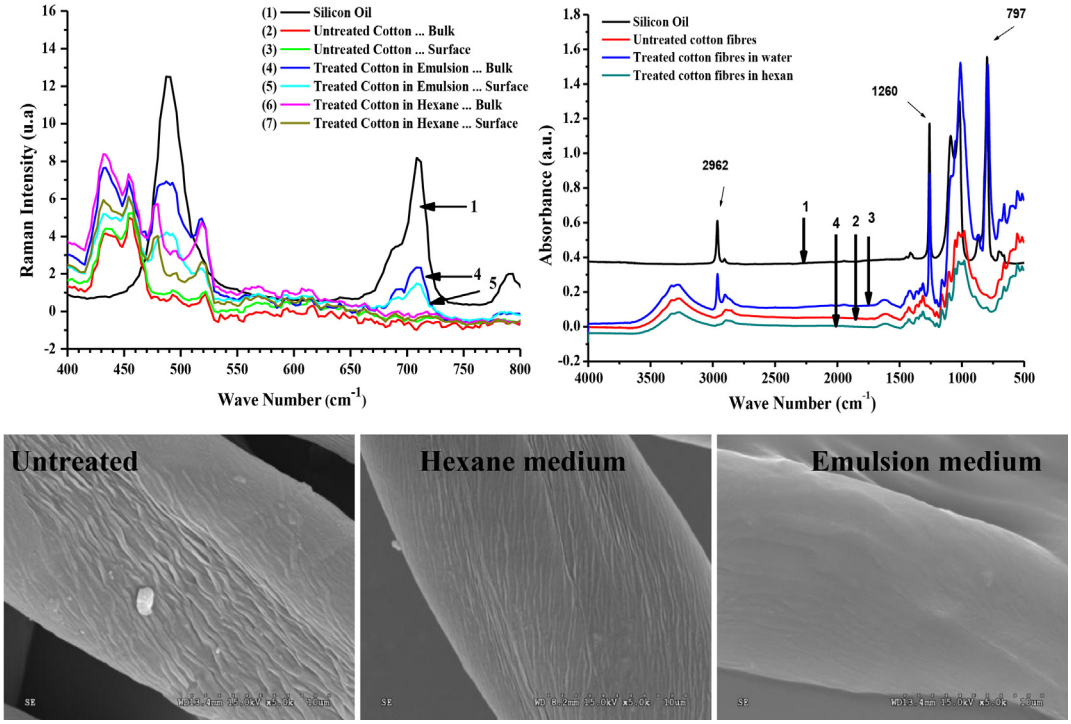

Fig. 1. Raman spectra, FT-IR spectroscopy and SEM micrographs of untreated and treated cotton fibres with silicon oil (on surface and in bulk) in water emulsion and hexane medium treatment for 30 min at 50 °C and drying at 25 °C.

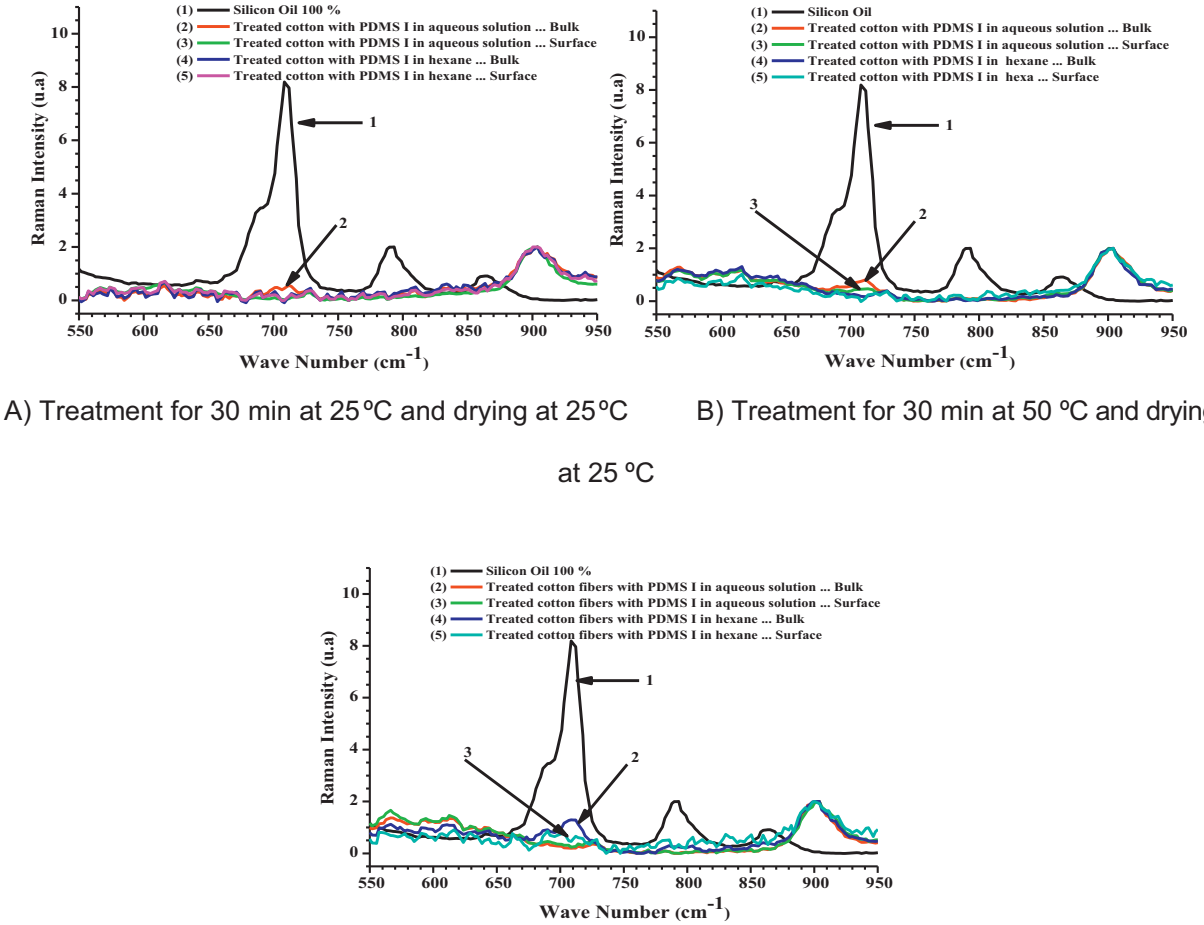

Fig. 2. Raman spectra of treated cotton fibres with PDMS I in emulsion and hexane medium in different temperature (on surface and in bulk).

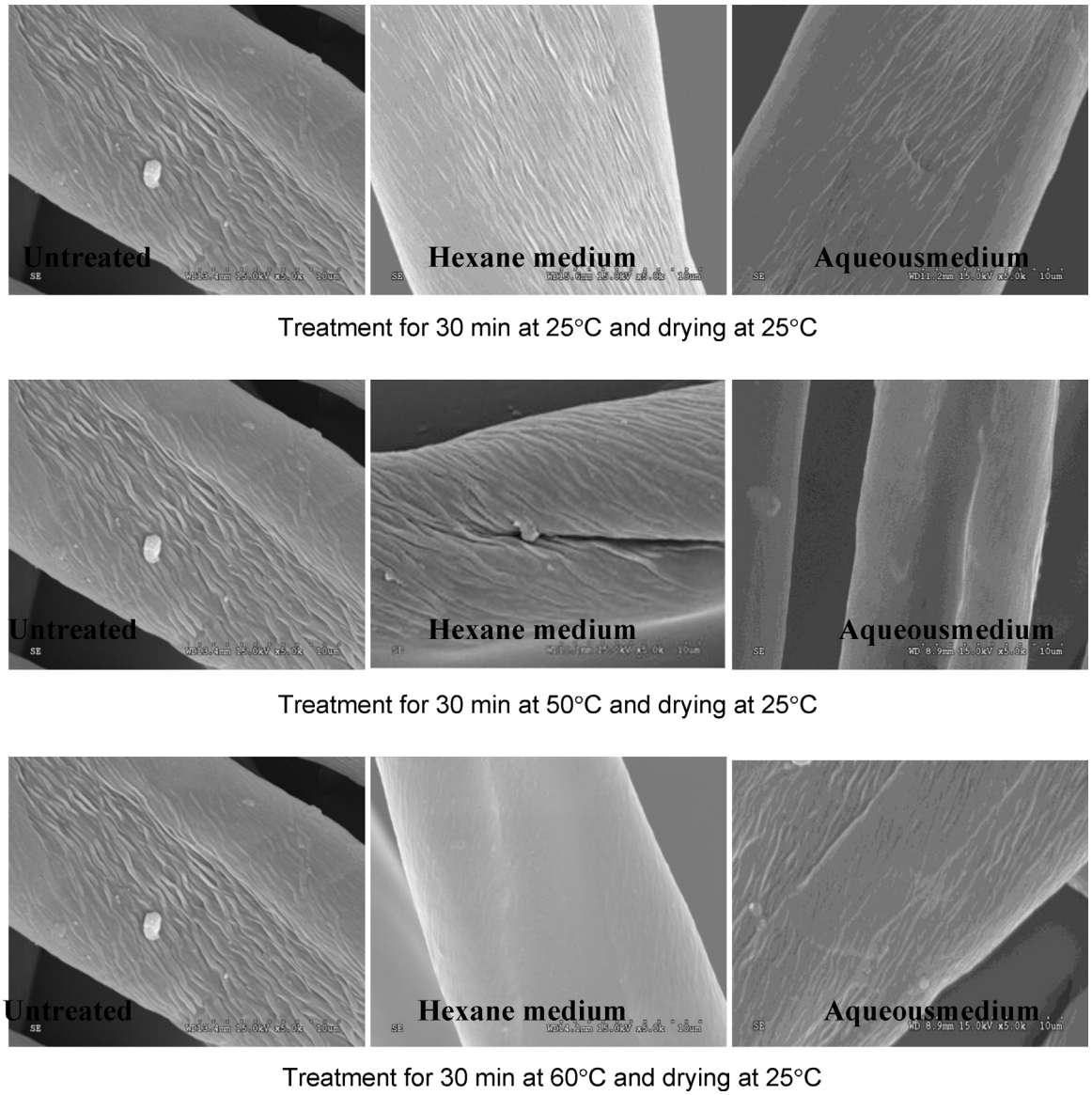

Fig. 3. SEM micrographs of treated fibre with PDMS I in emulsion and hexane medium in different temperature.

suited to investigating such distributions within polymers, as spectral information is recorded as a function of depth within the sample (Fleming, Stepanek, & Kazarian, 2005). It permits analysis of very small fragments and particles. For this reason, it is becoming an increasingly important analytical tool in the area of polymer science. However, interpretation of the Raman depth profile data is complicated by refraction effects occurring at the air/sample interface (Baldwin & Batchelder, 2001; Reinecke, Spells, Sacristán, Yarwood, & Mijangos, 2001; Vyörykkä et al., 2002). A Confocal Raman Microscopy spectrum provides information on the vibrational modes characteristic of chemical groups within a sample. Raman spectroscopy is particularly valuable for identifying natural textile fibres such as wool (Jurdana, Ghiggino, Nugent, & Leaver, 1995), cotton and synthetic fibres such as polyester and nylon (Hsu, Moore, & Krimm, 1976; Kelemen, Moss, & Glitsch, 1984; Kulshreshtha & Dweltz, 1981; Lang, Katon, O'Keefe, & Schiering, 1986). Also it has been used to study the distribution of the dye molecules inside the fibres (Fleming, Kazarian, Bach, & Schollmeyer, 2005; Kelemen et al., 1984). The CRM technique has been successfully used to determine the configuration of polypeptide' chains of constituent proteins in feather keratin (Hsu et al., 1976; Kelemen et al., 1984) and to investigate structural changes in wool fibres due to annealing (Shishoo & Lundell, 1976). CRM has also been applied (in situ) to study diffusion of penetrate species through a membrane (Schmitt et al., 2003) and the diffusion in multi-component liquid systems (Bardow, Marquardt, Göke, Koss, & Lucas, 2003).

This work is aimed to study the suitability of CRM for detecting and monitoring molecules interpenetrating cotton fibres. Liner PDMS with different molecular weight was chosen to act as a model of penetrating molecules into cotton fibres. CRM has been applied to treated cotton fibres with liner PDMS with different molecular weight and in different treatment media (aqueous and hexane) to study the distribution of PDMS into the cotton cellulose.

2. Experimental

2.1. Materials

Cotton fibres were provided from WFK Testgewebe GmbH (Germany), (hydrocarbon-based and silicone-based impurities were removed by extraction: 75 g of fabric were extracted with 1000 ml hexane in a Soxhlet during 24 h) Poly(dimethyl siloxane)

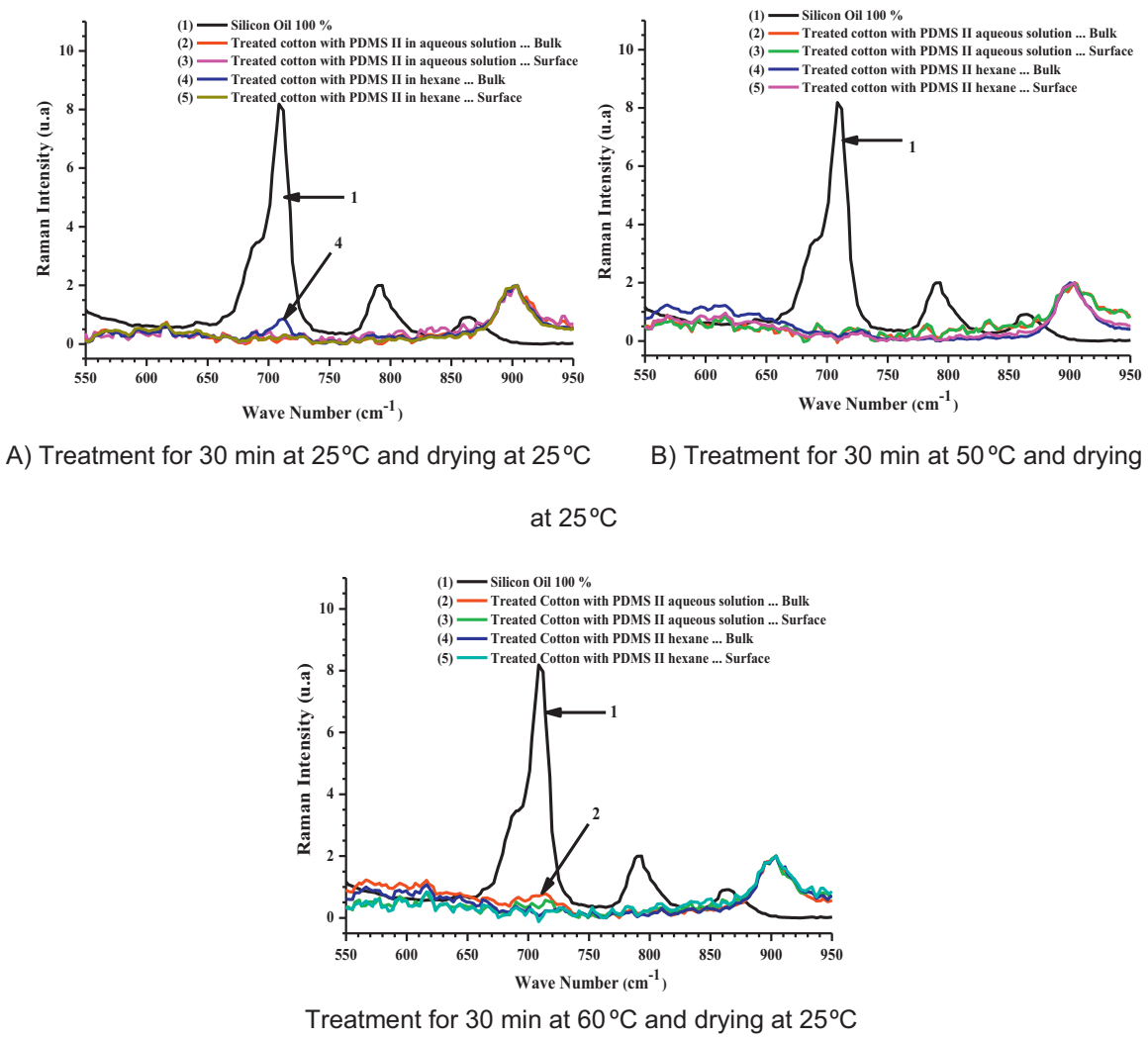

Fig. 4. Raman spectra of treated cotton fibres with PDMS II in emulsion and hexane medium at different temperature (on surface and in bulk).

(DMS alpha;- sec. Butyl omega;- trimethyl siloxy terminated) with different molecular weight (PDMS I; Mw = 1500 g/mol, PDMS II; Mw = 9600 g/mol, PDMS III; Mw = 69,000 g/mol) was produced by Polymer Source company, Silicon oil (Mw = 6000 g/mol) and hexane were purchased form Sigma–Aldrich.

2.2. Methods

2.2.1. 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 and silicon oil. Cotton fibres were immersed in the previously made emulsions with 1:20 LR and the concentration of the treatment bath was 0.5% (w/w) (PDMS/Fabric) at pH = 5.4 for 30 min at different reaction temperatures (25, 50 and 60 °C, respectively). After the treatments, all samples were washed in aqueous solution, containing 1% (v/v) silicate free detergent at 50 °C for 10 min to remove the unreacted silicon compounds and then dried at room temperature.

2.2.2. Treatment in hexane media

Because of the solubility of polydimethyl siloxane (PDMS) in hexane, it was used as a treatment media for cotton, where, it expected to provide good infiltration to PDMS compounds and silicon oil into cotton fibres. Cotton fibres were treated with mixture of PDMS or silicon oil in hexane medium. The concentration of PDMS in the treatment bath was 0.5% (w/w) (PDMS/Fabric) and the LR was 1:20. The fibres were treated for 30 min at different reaction temperatures (25, 50 and 60 °C, respectively). After the treatments, all samples were washed in aqueous solution, containing 1% (v/v) silicate free detergent at 50 °C for 10 min to remove the unreacted silicon compounds and then dried at room temperature.

2.3. Measurements

2.3.1. 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) permits to evaluate the distribution of siloxane compounds across a single cotton fibre on the surface and in the bulk (4 μm depth under on the surface). The presence of siloxane compound was providing by the presence of the peak between 710 and 720 cm^{-1} in Raman spectrum, which related to the valence oscillation of Si—C of $Si—CH_3$ group. All Raman spectrums were integrated during 20 s with 4 cm^{-1} of resolution on the surface and 4 μm depth under on the surface.

2.3.2. Scanning electron microscopy (SEM)

Scanning Electron Microscopy HITASHI S-3000 microscope S, at 15 kV acceleration voltage, after gold coating, was used to visualise

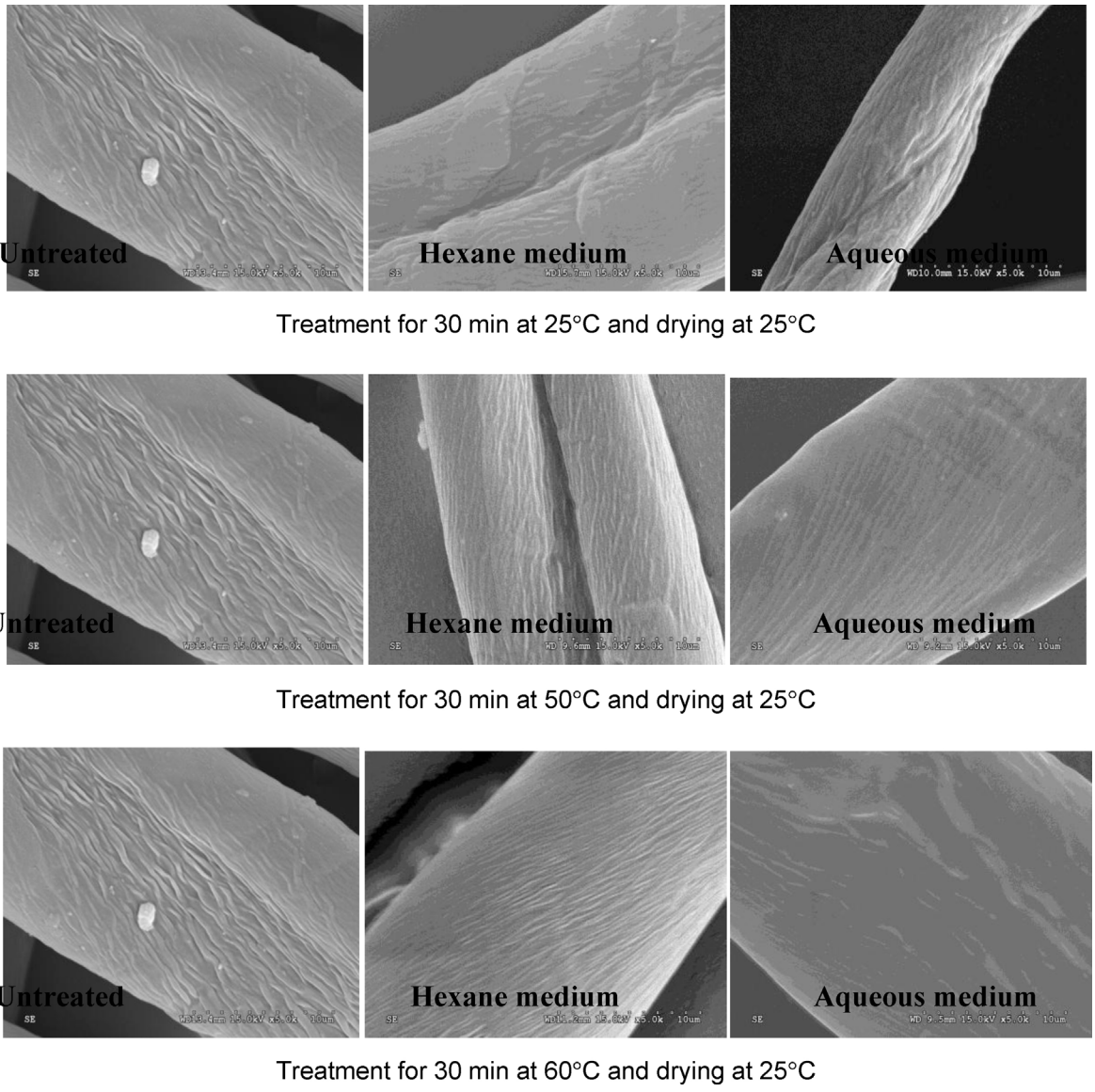

Fig. 5. SEM micrographs for treated cotton fibre with PDMS II in aqueous and hexane media at different temperature.

the distribution of the polymers (droplet or film) coated the fibre surface.

2.3.3. Fourier transform infra-red spectroscopy (FT-IR)

The FT-IR tester of Nicolet Magna-IR 560 spectrometer was used to analyse the spectrum of the treated and the untreated samples. Resolution for the infrared spectra was 4 cm^{-1} and there were 32 scans for each spectrum. KBr was used to prepare the thin film together with the samples. The tester collected transmittance of the infrared in the film between 400 and 4000 cm^{-1}.

3. Results and discussions

The interesting goal of this study is to investigate the suitability of Confocal Raman microscopy to monitoring the interpenetrated molecules into cotton fibres. PDMS compounds were used as a model for interpenetrated molecules. In this context, the infiltration of different molecular weight PDMS compounds into cotton fibre in two different media was investigated.

The study was started using silicon oil, which is the earliest silicon product used in textile sector, then, studied the infiltration of different molecular weight of the liner PDMS in aqueous solution (as a classical finishing medium) and hexane medium into cotton fibres.

CRM was used as new technical analytical tool to detect the presence of liner PDMS which deposited onto the surface or infiltrated in the bulk (4 μm depth under the surface) of the treated fibres.

3.1. Treatment with silicon oil

Cotton fibres were treated with silicon oil in two different media (aqueous solution as (oil/water emulsion) and hexane), and then the treated fibres was undergoing to CRM analysis. To establish the suitability of CRM to detect the silicon products, the CRM result were compared with the FT-IR result for the same treated fibres to see if they are agree with each other or not. SEM was used to visualise the distribution of the silicon oil (droplet or film) coated the fibres surface.

The cotton fibres were treated with silicon oil (6 kDa) in aqueous media as (oil/water emulsion) and hexane medium during 30 min at 50 °C and drying at 25 °C. The Raman spectra show the presence of characteristic peak of silicone (about 710–720 cm^{-1}) on the

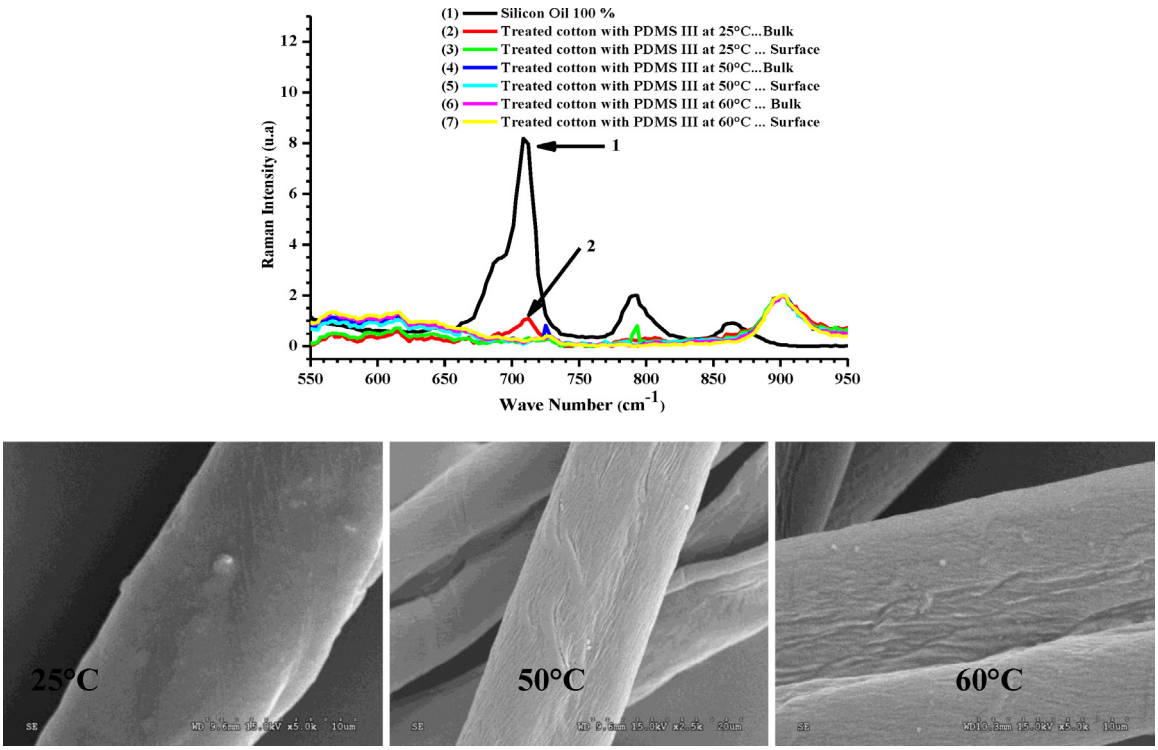

Fig. 6. Raman spectra and SEM micrographs of treated cotton fibres with PDMS III in hexane medium at different temperature.

surface and in the bulk (4 μm depth under the surface) of treated fibres in case of using aqueous medium while this peak is absent in the spectra of fibre treated in hexane medium (see Fig. 1). This means that, the treatment in aqueous medium at 50 °C provides a deposition and infiltration of silicon oil on the surface and into the bulk of treated cotton fibres.

FT-IR analysis was run to permit the presence of silicon oil on the surface of cotton fibres (see Fig. 1), the results of FT-IR agree with the CRM results. The FT-IR spectra of treated fibres show the presence of three characteristic peaks of silicone compound at 2962, 1260 and 797 cm^{-1} for fibre treated in aqueous medium, while these peaks are not exist in case of treated fibre in hexane medium. The scanning electron micrographs of untreated and treated cotton fibres which illustrated in Fig. 1 confirm the results of both CRM and FT-IR. The deposition of silicone is very clear as a film on the treated fibre surface in case of treatment in aqueous medium, so, the surface of treated fibre appears smoother than the untreated one. The characteristic texture of the virgin (uncoated) cotton fibres still appears in case of cotton treated in hexane medium, which confirms that, treatment in hexane did not support the deposition of silicone on the fibre surface. This is may be attributed to, deposition of the silicon oil on cotton surface in the hydrocarbon solvent is slower than in aqueous medium (Conner, Mazzeno, & Reeves, 1962).

3.1.1. Treatment with PDMS compounds according to molecular weight

The cotton fibres were treated with linear PDMS compound (0.5%, w/w) with various molecular weights (1.5, 9.6 and 69 kDa) in aqueous medium as (oil/water emulsion) and in hexane medium with LR 1:20 during 30 min at different temperatures (25, 50 and 60 °C) and drying at 25 °C.

3.1.1.1. Treatment with PDMS I (Mwt. = 1500 g/mol). Linear PDMS I compound (Mwt. 1500 g/mol) was applied to cotton fibres in two treatment media at different reaction temperatures. CRM analysis proved the deposition and the infiltration of PDMS I compound on the surface and in the bulk of cotton fibres in aqueous solution at 50 °C, while hexane media support the infiltration only at 60 °C. That is may be because this temperature (60 °C) is close to the boiling point of hexane (67 °C), when the mobility of the hexane molecules is very high, which provide more penetration into the fibres bulk carrying the PDMS I molecules. Treatment at room temperature did not have any effect in either infiltration or deposition of PDMS molecules in both treatment media.

Fig. 2A shows the Confocal Raman spectra of treated cotton fibres with PDMS I in both aqueous and hexane media, at 25 °C for 30 min and dried at 25 °C. In different experimental conditions, Confocal Raman spectra proved the presence of weak peak in the bulk of the treated fibre. Treatment in aqueous medium provides a peak in the bulk (4 μm depth under the surface) of the treated fibres, but the intensity of this peak is weak and not relevant to distinguish from the other peaks.

The treatment at 50 °C during 30 min in aqueous medium shows better infiltration and fixation of PDMS I in the bulk and on the surface of cotton fibres. Elsewhere, same treatment condition in hexane medium did not show any improvement in either infiltration or deposition of PDMS I. Fig. 2B shows the Raman spectra of treated cotton fibre in aqueous and hexane media. It is very clear that, the presence of the characteristic peak of silicone compound at 710–720 cm^{-1} on the surface and in the bulk (4 μm depth under the surface) of treated fibres in aqueous medium, while the intensity of the peaks is very low in case of using hexane as treatment medium.

By increasing the treatment temperature until 60 °C in the same treatment duration, the infiltration process takes place in hexane medium, where the Confocal Raman spectrum of the bulk of treated cotton fibre shows the presence of the characteristic silicone peak with high intensity comparing by the PDMS I (Fig. 2C). The treatment in aqueous medium did not provide the presence of PDMS in the bulk or on the surface of the treated cotton fibres.

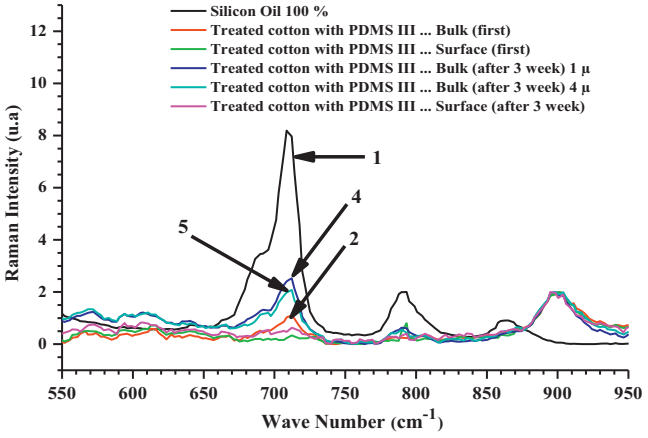

Fig. 7. Raman spectroscopy for the treated cotton fibres with polymer III in hexane medium before and after storage (on the bulk and surface) treatment for 30 min at 25 °C and drying at 25 °C.

Summing up, the PDMS I has the ability to deposit onto the surface and infiltrate in the bulk of treated fibres at 60 °C in hexane medium, while using the aqueous solution as a treatment medium at 50 °C is the best condition for infiltration of PDMS into the bulk of cotton fibre.

Concerning the surface, SEM analysis was run to detect the deposition of silicon on the surface of treated fibres, also to prove the result of CRM. The SEM micrographs have confirm the results of CRM, where it show that, the surface of the treated cotton fibres have the same equivalent texture like the surface of untreated cotton fibres (Fig. 3A) when the fibres was treated at 25 °C in both treatment media, also there is no deposition of silicon on the surface of treated fibre.

When the fibres were treated at 50 °C, the SEM micrographs confirmed that treatment of fibres in aqueous solution provide coated fibre surface with polymer layer, which proved as smooth surface, the SEM micrographs of treated fibre in hexane medium proved uncoated surface of the treated fibres (Fig. 3B).

On contrast, the SEM micrographs of the treated fibre with PDMS I at 60 °C show a smooth coated surface in hexane medium (Fig. 3C).

3.1.1.2. Treatment with PDMS II (Mwt. = 9600). Linear PDMS II compound (Mwt. 9600 g/mol) was applied to cotton fibres in two treatment media at different reaction temperatures. CRM analysis proved that, this type of PDMS can infiltrated into cotton fibres at 25 °C in case of using hexane as treatment medium, also, a weak infiltration was observed by treatment in aqueous medium at 60 °C.

CRM spectrum proved the infiltration of PDMS II, the treatment of cotton fibre with PDMS II at 25 °C during 30 min in hexane medium gives a good infiltration in the bulk (4 μm depth under the surface), while the intensity of the peak is very low on the fibre surface (Fig. 4A). On contrast, the spectra of treated cotton fibres in aqueous medium did not show any characteristic peaks of the PDMS either in the bulk or on the surface, which mean that, there is no infiltration or deposition of this PDMS compound in aqueous medium at 25 °C, or the amount of PDMS II is not enough to detect by CRM. That may be attributed to, at this temperature the fibres did not swell enough in aqueous medium to allow this big PDMS molecules (Mwt. 9600 g/mol) to penetrate inside the fibres bulk.

The CRM spectra of treated cotton fibres in both media at 50 °C were shown in Fig. 4B. One can observed that there is no infiltration or deposition of PDMS II in both treatment media on the surface or in the bulk respectively. In the same line comes the result of treatment cotton fibre in hexane media at 60 °C, there is no significant presence of PDMS on the surface or in the bulk of treatment fibre (Fig. 4C). Moreover, treatment in aqueous medium provides weak peak in the bulk, but the intensity of the peak is not enough to distinguish from the other peaks. Therefore, the treatment at 60 °C

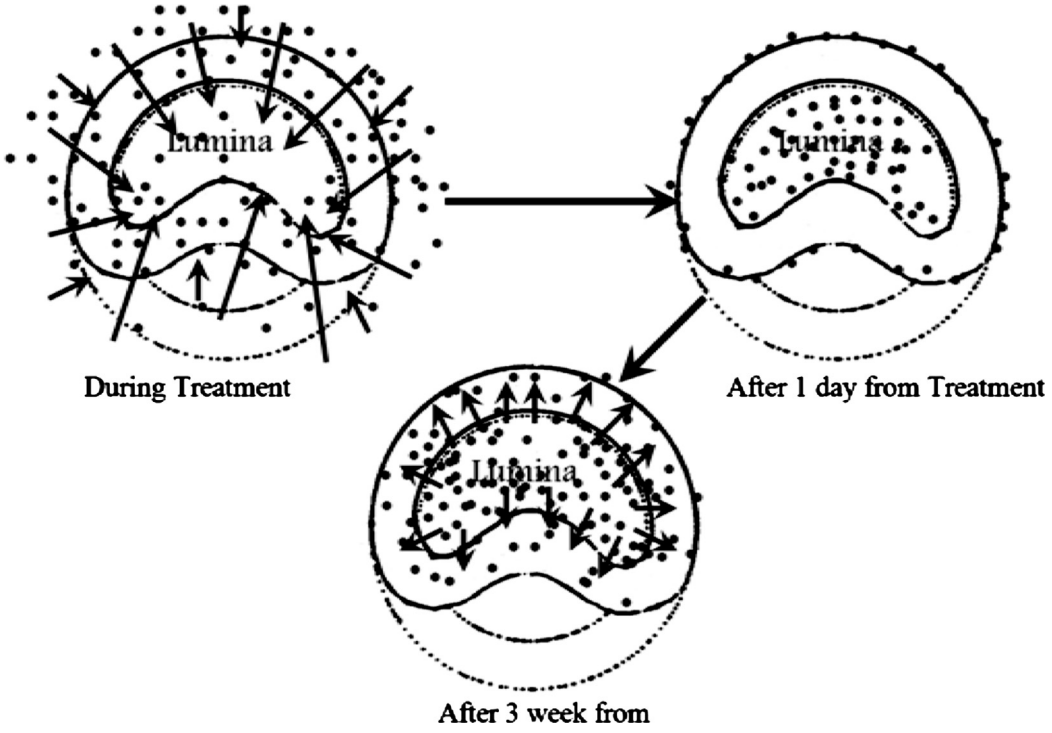

Fig. 8. The suggested mechanism for distribution of PDMS compounds across the fibre cross-section.

during 30 min in hexane and in aqueous medium did not shows good infiltration and fixation on the surface.

SEM analysis was run to confirm the CRM result and visualise the presence of the polymer on the fibre surface. SEM micrographs show that in case of treated cotton fibres at 25 °C in both aqueous or hexane media, no deposition of PDMS compound on the surface of treated fibre (Fig. 5). SEM micrographs shows the same results by treated cotton in both aqueous or hexane media at 50 or 60 °C, so, PDMS II did not deposited onto the fibre surface

3.1.1.3. Treatment with PDMS III (Mwt. = 69,000 g/mol). Due to the very high molecular weight and viscosity of PDMS III (Mwt. 69,000 g/mol), it was no possibility to have a micro-emulsion from this type of PDMS mechanically, because it cannot dispersed good to have stable micro-emulsion. Therefore, this linear PDMS were applied to cotton fibres only in hexane medium.

CRM spectra were presented in (Fig. 6), and illustrated the spectra of the surface and of the bulk of treated cotton fibres in hexane medium. Treatment in hexane medium for 30 min at 25 °C provides a strong peak in the bulk of the treated fibre (4 μm depth under the surface). For the other treatments at 50 and 60 °C, CRM show that, the peak intensity of PDMS III is very weak in the fibres bulk or on the surface. So, the treatment of cotton fibres with PDMS III in hexane medium at 25 °C has the best fixation and infiltration of this polymer in the bulk.

The SEM micrographs show that the fibres treated in hexane medium for 30 min at 25 °C have a coated polymer layer on the surface and the surface is smoother than the other treated fibres in different reaction temperature (Fig. 6).

3.1.2. Studying the effect of storing time on the PDMS compounds

CRM analyses were used to determine defiantly the position of PDMS on the fibre surface and in the bulk after storing. Therefore, the treated fibre was examined firstly after one day from the treatment and the examination were repeated after three weeks from the treatment for the bulk and the surface of the fibre. The analysis confirmed that after 3 weeks the concentration of PDMS in the bulk of treated fibre is increased by storage even under 1 μ and 4 μ depth from the fibre surface. Fig. 7 illustrates that, the peaks of the stored fibre bulk after 3 weeks of the treatment has higher intensity than stored fibre bulk after one day. Therefore, we can say that when cotton fibres treated with the PDMS compounds most of the molecules adsorbed from the treatment medium to the fibres surface and penetrated to the fibre lumen, so, the lumen has the higher concentration of the PDMS molecules. By time this molecules migrated from the lumen to the fibre bulk again. That may be explaining why the higher concentration of the PDMS is presence in 1 μ depth under the fibre surface (see Fig. 8).

4. Conclusions

Confocal Raman microscopy (CRM) has been successfully used to monitoring the distribution of different molecular weights of liner PDMS as a model of molecules interpenetrate into cotton fibres, as a function of depth in fibres treated in aqueous or hexane medium. PDMS compound with three different molecular weights can infiltrate into cotton fibres by chosen the suitable treatment medium. Hexane can used as treatment medium to applying any molecular weight of the PDMS, but aqueous medium is not suitable to use in case of high molecular weight PDMS, because PDMS cannot form a stable micro-emulsion via mechanical way. Using aqueous medium, provide a good infiltration of low and medium molecular weight PDMS into cotton fibres at 50 and 60 °C reaction temperature. Elsewhere, hexane medium is suitable to infiltrate PDMS into cotton fibre at any temperatures (below its boiling temperature) according to the molecular weight of PDMS. Information regarding to the distribution of the PDMS makes the use of CRM a powerful technique for distributive material characterisation into the treated fibres.

References

Abidi, N., Hequet, E., & Cabrales, L. (2009). Imparting multi-functional properties to cotton fabric by means of sol gel process. In *Beltwide cotton conferences* (pp. 1402–1406). San Antonio, Texas: Fiber and Biopolymer Research Institute, Department of Plant and Soil Science, Texas Tech University.

Abidi, N., Hequet, E., & Tarimala, S. (2007). Functionalization of cotton fabric with vinyltrimethoxysilane. *Textile Research Journal*, *77*(9), 668–674.

Baldwin, K. J., & Batchelder, D. N. (2001). Confocal Raman microspectroscopy through a planar interface. *Applied Spectroscopy*, *55*(12), 517–524.

Bardow, A., Marquardt, W., Göke, V., Koss, H.-J., & Lucas, K. (2003). Model-based measurement of diffusion using Raman spectroscopy. *AIChE Journal*, *49*(2), 323–334.

Brunon, C., Bessueille, F., Grossiord, C., Chadeau, E., Oulahal, N., Darroux, C., et al. (2011). ToF-SIMS and XPS characterization of antimicrobial textiles for the food processing industry. *Surface and Interface Analysis*, *43*(1–2), 604–608.

Conner, C. J., Mazzeno, L. W., & Reeves, W. A. (1962). Influence of solvent media upon polymerization of a silicone alloy water repellent. *Textile Research Journal*, *32*(7), 598–600.

Fleming, O. S., Kazarian, S. G., Bach, E., & Schollmeyer, E. (2005). Confocal Raman study of poly(ethylene terephthalate) fibres dyed in supercritical carbon dioxide: Dye diffusion and polymer morphology. *Polymer*, *46*(9), 2943–2949.

Fleming, O. S., Stepanek, F., & Kazarian, S. G. (2005). Dye diffusion in polymer films subjected to supercritical CO_2: Confocal Raman microscopy and modelling. *Macromolecular Chemistry and Physics*, *206*(11), 1077–1083.

Gao, Q., Zhu, Q., Guo, Y., & Yang, C. Q. (2009). Formation of highly hydrophobic surfaces on cotton and polyester fabrics using silica sol nanoparticles and nonfluorinated alkylsilane. *Industrial & Engineering Chemistry Research*, *48*(22), 9797–9803.

Hoefnagels, H. F., Wu, D., de With, G., & Ming, W. (2007). Biomimetic superhydrophobic and highly oleophobic cotton textiles. *Langmuir*, *23*(26), 13158–13163.

Hsu, S. L., Moore, W. H., & Krimm, S. (1976). Vibrational spectrum of the unordered polypeptide chain: A Raman study of feather keratin. *Biopolymers*, *15*(8), 1528.

Jang, K. O., & Yeh, K. (1993). Effects of silicone softeners and silane coupling agents on the performance properties of cotton fabrics. *Textile Research Journal*, *63*(10), 557–565.

Jurdana, L. E., Ghiggino, K. P., Nugent, K. W., & Leaver, I. H. (1995). Confocal laser Raman microprobe studies of keratin fibers. *Textile Research Journal*, *65*(10), 593–600.

Kelemen, J., Moss, S., & Glitsch, S. (1984). Azo-hydrazone tautomerism in azo dyes, IV. Colour and tautomeric structure of adsorbed 1-phenylazo-2-naphthylamine and 1-phenylazo-2-naphthol dyes. *Dyes and Pigments*, *5*(2), 83–108.

Kulshreshtha, A. K., & Dweltz, N. E. (1981). Analysis of flame-retardant finishes on textiles using laser-Raman spectroscopy. *Indian Journal of Fibre & Textile Research*, *6*, 135–138.

Lang, P. L., Katon, J. E., O'Keefe, J. F., & Schiering, D. W. (1986). The identification of fibers by infrared and Raman microspectroscopy. *Microchemical Journal*, *34*(3), 319–331.

Mehta, S. C., Somasundaran, P., Maldarelli, C., & Kulkarni, R. (2006). Effects of functional groups on surface pressure—Area isotherms of hydrophilic silicone polymers. *Langmuir*, *22*(23), 9566–9571.

Murthy, R. S. S., Leyden, D. E., & D'Alonzo, R. P. (1985). Determination of polydimethylsiloxane on cotton fabrics using fourier transform attenuated total reflection infrared spectroscopy. *Applied Spectroscopy*, *39*(5), 856–860.

Owen, M. J. (1981). Why silicones behave funny. *ChemTech*, *11*, 288.

Reinecke, H., Spells, S. J., Sacristán, J., Yarwood, J., & Mijangos, C. (2001). Confocal Raman depth profiling of surface-modified polymer films: Effects of sample refractive index. *Applied Spectroscopy*, *55*(12), 1660–1664.

Rooks, R. J. (1972). New development in silicone emulsion polymers as textile finishes. *American Association of Textile Chemists and Colorists*, *4*(1), 47.

Schmitt, M., Leimeister, B., Baia, L., Weh, B., Zimmermann, I., Kiefer, W., et al. (2003). Characterization of diffusion processes of pharmacologically relevant molecules through polydimethylsiloxane membranes by confocal micro-resonance raman spectroscopy. *Chemphyschem*, *4*(3), 296–299.

Shishoo, R., & Lundell, M. (1976). Investigation of structural changes in wool fibers due to annealing. *Journal of Polymer Science: Polymer Chemistry Edition*, *14*(10), 2535–2544.

Skinner, M. W., Caibao, Q., Grigoras, S., Halloran, D. J., & Zimmerman, B. L. (1999). Fundamental aspects of aminoalkyl siloxane softeners by molecular modeling and experimental methods. *Textile Research Journal*, *69*(12), 935–943.

Smith, A. L. (1991). *The analytical chemistry of silicones*. New York: John Wiley & Sons, Inc.

Stark, F. O., Falender, J. R., & Wright, A. P. (1982). In G. Wilkinson, F. G. A. Stone, & E. W. Abel (Eds.), *Comprehensive organometallic chemistry*. Oxford: Pergamon Press.

Vilcnik, A., Jerman, I., Surca Vuk, A., Kozelj, M., Orel, B., Simoncic, B., et al. (2009). Structural properties and antibacterial effects of hydrophobic and oleophobic sol–gel coatings for cotton fabrics. *Langmuir*, *25*(10), 5869–5880.

Vyörykkä, J., Halttunen, M., Iitti, H., Tenhunen, J., Vuorinen, T., & Stenius, P. (2002). Characteristics of immersion sampling technique in Confocal Raman depth profiling. *Applied Spectroscopy*, *56*(6), 776–782.

Xue, C.-H., Jia, S.-T., Zhang, J., & Ma, J.-Z. (2010). Large-area fabrication of superhydrophobic surfaces for practical applications: An overview. *Science and Technology of Advanced Materials*, *11*(3), 033002.