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A practical approach to emulsify silicone oil and attaining superhydrophobic fabrics

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Abstract

Silicone oil (polydimethylsiloxane, PDMS) was dispersed in water by virtue of stearic acid (SA)/triethanol amine (TEA) system as an emulsifier. Factors affecting emulsification of PDMS and utilization of such emulsion as a water-repellent finish for cotton/polyester fabric were investigated. The results revealed that the best formulation of such PDMS mother emulsion is PDMS (5%), TEA (2.4%), SA (4.5%), as well as equal molar ratio of $AlCl_3$ and SA. Treating cotton/polyester fabric with 40 g/L of such emulsion followed by drying at 100 ^{O}C acquired that fabric with water repellency, softness, and stiffness properties accompanied with a decreasing in air permeability and coefficient of friction of the water repellent fabric. The TEM image indicated that such emulsion particles size ranges between 6 to 10 nm. The treated fabric surface was characterized via water contact angle and SEM as well as EDX analysis.

Keywords: Silicone oil emulsion; Water repellent fabrics; Textile finishing; Stearic acid; Triethanol amine.

1. Introduction

Currently, the consumer needs for comfortable, functional, durable, high performance, and eco-friendly fabrics has attracted the interest of R&D institutions and textile industry. The R&D activities are strongly desired to innovate and evolve ingredients benign to the environment, finishing formulations, and new applications techniques to substitute the conventional ones [1-9]. Many functional properties can be imparted to cellulosic -based textiles such as antibacterial, self cleaning, anti-UV, anti radiation, softness, flame retardency, water repellency …etc [10-22].

Water repellent fabric is that resist wetting by water to a degree of rolling off the water drops over the fabric surface. Water repellency can be achieved by means of various types of chemical finishes such as paraffin wax, silicones, polyurethanes, hydrophobins, fluorochemicals, nano-particles (NPs) like SiO_2-NPs [23-31]. Repellent fabrics are used for producing raincoats, tents, medical bandages, and carpets resistant to water and oily dirt [15,18].

Silicones function as water repellents, impart their treated fabrics with high degrees of water repellence and softness, improved shape retention and sewability, resistance to heat, degradation in environment as well as improved appearance [29,32].

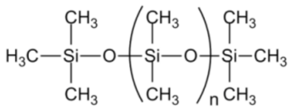

Figure 1: Chemical structure of polydimethylsiloxane.

Linear polydimethylsiloxanes molecules (Figure 1) are colourless, odourless, viscous, and water insoluble organosilicon compounds. They are used, either in their native or emulsion form, in a wide range of food, pharmacological, medical applications [33]. In the textile field, polydimethylsiloxanes form hydrogen bonds with fibres as a result of the difference between the oxygen and silicon atoms electronegativities causing the hydrophobic methyl groups to be in their orientation away from the fibres surface [23,33,34].

The present work aims at preparation of polydimethylsiloxane emulsion using stearic acid/triethanolamine emulsifying system to be used as water repellent finish for cotton/PET blended fabric.

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1. Experimental

1.1. Materials

Mill bleached cotton/polyester fabric (50/50), produced by Misr Spinning and Weaving Co., Egypt, was used. Polydimethylsiloxane (PDMS) (cas No. 63148-62-9) of density: 0.973 g/ml and viscosity: 500 mPa.s was used. Triethanolamine (TEA), Stearic acid (SA), ammonium chloride, zinc chloride, aluminium chloride, magnesium chloride, as well as zinc sulphate were laboratory grade chemicals.

1.2. Methods

1.2.1. Emulsification of PDMS

The PDMS was emulsified using stearic acid/triethanol amine (SA/TEA) system using the following method:
Certain weights of PDMS and SA were melted with each other in a 250 mL glass beaker at 70 ^{O}C in a water bath. To such melt, a certain weight of TEA solution was added and stirred using a homogenizer followed by completing the emulsion weight to 100 g with distilled water and stirring to obtain the mother emulsion [18].

1.2.2. Fabric treatment

To prepare certain concentration of the PDMS emulsion, a specific weight of the mother emulsion is weighed and diluted with water with stirring. Fabric samples are padded in baths containing 0–70 g/L of the PDMS emulsion to 100% wet pick up followed by drying at 100 - 160 ^{O}C/3 min in an oven.

1.3. Testing and analysis

- The weight of fabric (W) was assessed according to ATSM (D 3776 – 79).
- The rating of water repellency (WRR) was evaluated using the spray test according to AATCC Test Method 22-1989.
- The friction coefficient (MIU) and roughness (SR) of fabric surface were assessed using Kawabata evaluation system, Surface tester KESFB4-A, Kato Tech Co., LTD, Japan.
- Stiffness (S) was evaluated in the direction of fabric warp according to ASTM (D 1388-96) using Jika (Toyoseiki) apparatus.
- Air permeability of the fabric (AP) was assessed according to ATSM (D 737-96).
- Water contact angle of the water repellent was measured on OCA-15EC (Data physics GmbH, Germany) with software using 10 µL drops of triple distilled water.
- The particles size (TEM) and morphology (SEM) of the above mentioned hybrid emulsion was assessed using a JEOL, JEM 2100 F electron microscope at 200 kV.
- The SEM images of untreated and treated fabric samples were assessed using SEM Model Quanta 250 FEG (Field Emission Gun) linked to EDX unit (Energy Dispersive X-ray Analyses), with accelerating voltage 30 kV, magnification 14× up to 1,000,000 and resolution for Gun, FEI company, Netherlands.

2. Results and Discussion

Herein PDMS is emulsified using SA/TEA system as an emulsifier. Factors affecting emulsification of PDMS in addition to utilization of its emulsion as a water-repellent finish for cotton/polyester fabric are investigated.

2.1. Factors affecting PDMS emulsification and application as water repellent finish

2.1.1. PDMS concentration

Table 1: Effect of PDMS concentration on the treated fabric WRR. The PDMS emulsion ingredients: TEA (2.4%) and SA (4.5%). The fabric is treated with 50 g/L of mother emulsion and then dried at 100 ^{O}C/5min.

PDMS conc. (%)	WRR
5	50
7.5	50
10.0	50
12.5	50

Table 1 shows the impact of PDMS concentration in the mother emulsion on the treated fabric WRR. It is obvious that all the aforementioned PDMS concentrations bring about treated fabric samples having water repellency rating that does not exceed 50, which may be related to coating of the fabric surface with a low surface energy film composed of PDMS as well as the TEA salt of SA. The latter, i.e. TEA salt of SA, has a hydrophilic nature that impairs the hydrophobicity of the PDMS and subsequently the treated fabric [18].

2.1.2. Stearic acid concentration

Table 2: Effect of SA concentration emulsion on WRR of treated fabric. The PDMS emulsion ingredients: PDMS (5%) and triethanolamine (2.4%). The fabric is treated with 50 g/L of mother emulsion and then dried at 100 ^{O}C/5min.

SA concentration (%)	WRR
0	0
4.5	50
9	50
13.5	50

Table 2 clarifies the effect of SA concentration on treated fabric WRR. It is clear that, increasing of the SA concentration in the mother emulsion from 4.5 to 13.5% does not affect rating of the hydrophobicity of treated samples and keeps it at 50 which is the lowest repellency rating in the test scale reflecting the existence of the hydrophilic TEA salt of SA in the mother emulsion [18].

2.1.3. Degree of stearic acid neutralization

Table 3: Effect of SA neutralization degree on WRR of treated fabric. The PDMS emulsion ingredients: PDMS (5%); SA (4.5%). The fabric is treated with 50 g/L of mother emulsion and then dried at 100 OC/5min. a Oily spots are formed.

Degree neutralization (%)	Emulsion state	WRR
25	No emulsion	0
50 [a]	Poor emulsion	0
75 [a]	Unstable emulsion	0
100	stable emulsion	50

The reason behind neutralization of SA with TEA is to form the emulsifier SA/TEA for emulsification of the PDMS [18,29]. Table 3 clarifies the impact of the SA neutralization degree on state of the mother emulsion as well as the treated fabric WRR. It is clear that: (a) no emulsion was formed below a neutralization degree of 50%, (b) at neutralization degree of 50%, poor emulsion was formed and its treated fabric sample suffers from oily spots with WRR of zero, (c) at 75%, two layered unstable emulsion is formed along with treated fabric having tinny oily spots and WRR of zero, and (d) at a neutralization degree of 100%, successful emulsion is formed along with treated sample having WRR of 50.

2.1.4. Deactivation of the emulsifier SA/TEA

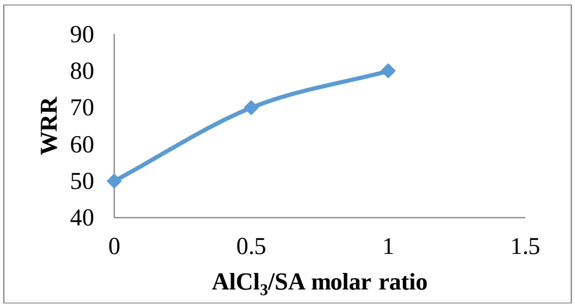


Fig. 2. Effect of $AlCl_3$/SA molar ratio on WRR of treated fabric. The PDMS emulsion ingredients: PDMS (5%); SA (4.5%) and TEA (2.4%). The fabric is treated with 50 g/L of mother emulsion and then dried at 100 ^{O}C/5min.

Despite the merit of SA/TEA system as an emulsifier, it has a drawback of being detract the PDMS hydrophobicity due to the hydrophilic nature of TEA. Deactivating of such emulsifier is necessary to enhance the WRR of treated fabric. Accordingly, four polyvalent metal salts, namely aluminium chloride, zinc chloride, zinc sulphate, and magnesium chloride were added in an equimolar ratio to SA to the PDMS mother emulsion to deactivate the emulsifier. The cations of such salts are attracted to the SA polar ends at the fabric surface that causes SA cohesion to the fabric surface during heating of that fabric [18,29,30]. Except the aluminium chloride, the other salts precipitate the emulsion ingredients immediately; the aluminium chloride forms a paste that upon dilution a stable emulsion is formed. Thus, aluminium chloride was chosen to be as a deactivating agent. Figure 2 shows the effect of $AlCl_3$/SA molar ratio on WRR of treated fabric. It is obvious that increasing of that ratio from 0 to 1 brings about a progressive enhancement in the treated fabric WRR from 50 to 80 suggesting the role of the aluminium chloride in deactivation of the emulsifier.

2.1.5. Emulsion concentration

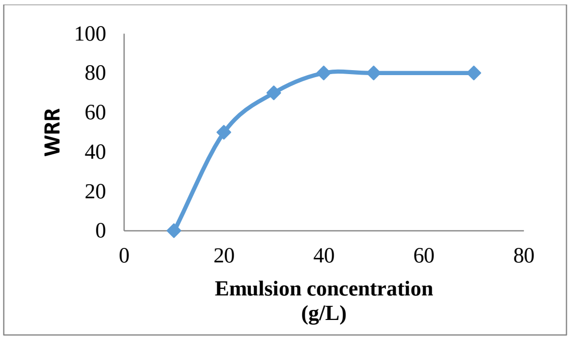


Fig. 3. Effect of emulsion concentration on WRR of treated fabric. The PDMS emulsion ingredients: PDMS (5%); TEA (2.4%); SA (4.5%); and $AlCl_3$/SA molar ratio 1. The fabric is treated with different emulsion concentrations and then dried at 100 ^{O}C/5min.

The effect of PDMS mother emulsion concentration on the treated fabric WRR is illustrated in Figure 3. It is well seen that increasing of the emulsion concentration from 10 to 40 g/L of the mother emulsion results in a promotion of the treated fabric WRR. Beyond 40, i.e. at 70 g/L, the treated fabric WRR levels off and do not exceed WRR of 80. Accordingly, it is obvious that PDMS emulsion concentration of 40 g/L is the proper concentration to achieve cotton/PET water repellent fabric.

2.1.6. Drying temperature

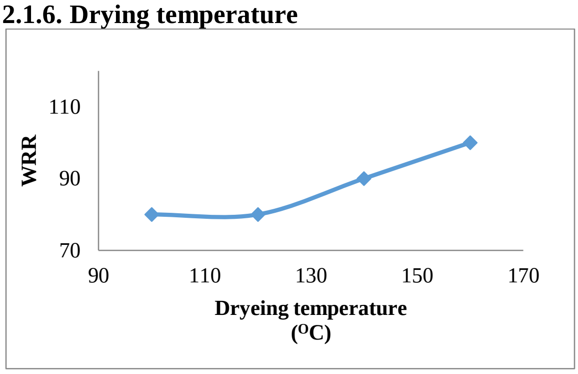


Fig. 4. Effect of drying temperature on WRR of treated fabric. The PDMS emulsion ingredients: PDMS (5%); SA (4.5%); TEA (2.4%) and $AlCl_3$/SA molar ratio (1/1). The

fabric is padded in 40 g/L of the PDMS mother emulsion to a wet pick up of 100% then dried at different temperatures.

The effect of the drying temperature of the PDMS emulsion treated fabric on WRR of that fabric is shown in Figure 4. It is clear that raising of the drying temperature from 100 to 160 ^{O}C for 5 minutes is accompanied with a gradual upgrading in WRR of treated fabric, suggesting a higher uniform distribution of the coating layer as well as a better orientation of the hydrophobic tails of the SA/TEA salt, i.e. to be in higher degree of outwarding of the fabric surface, which indeed enhances the treated fabric WRR [18,30].

2.2. Performance properties of the PDMS emulsion treated fabric

Emulsion conc. (g/L)	WRR	S (mg)	SR (µm)	MIU	AP
0	0	498	1.90	0.166	73
40	80	854	1.73	0.154	53

Table 4: Some performance properties of PDMS emulsion of treated fabric. Mother emulsion ingredients: PDMS (5%); SA (4.5%); TEA (2.4%) and $AlCl_3$/SA molar ratio 1. The fabric is treated with 40 g/L of the PDMS mother emulsion and then dried at 100 ^{O}C.

Table 4 shows some performance properties of the aforementioned prepared PDMS emulsion treated fabric expressed in water repellency rating, surface roughness, coefficient of friction, stiffness, and air permeability of treated fabric samples. It is seen that treating of fabric sample with 40 g/L of the PDMS emulsion, under the employed conditions, gives rise to an enhancement in water repellency, softness, and stiffness along with a reduction in coefficient of friction and air permeability of treated fabric, compared with an untreated sample, which can be attributed to the deposition of such emulsion ingredients onto/within the treated fabric structure [15,16,18,30].

2.3. Characterization of the prepared PDMS emulsion and its treated fabric

2.3.1. TEM image of the PDMS emulsion

Figure 5 illustrates the particles size of the above mentioned PDMS emulsion as observed by the transmission electron microscope. It is obviously seen that the particles size of such emulsion in the range of 6 to 10 nm.

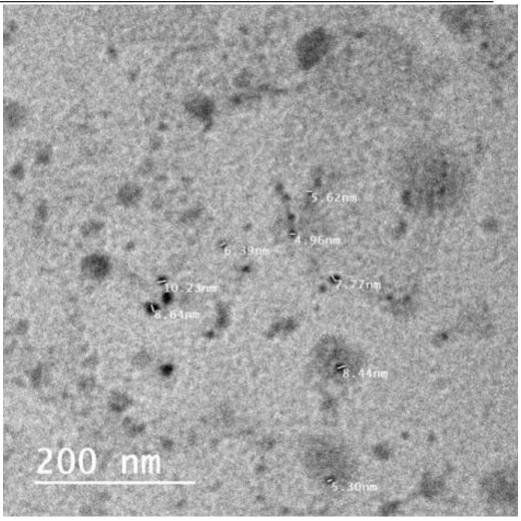


Fig. 5. TEM image of the prepared PDMS emulsion.

2.3.2. SEM and EDX analysis of treated fabric

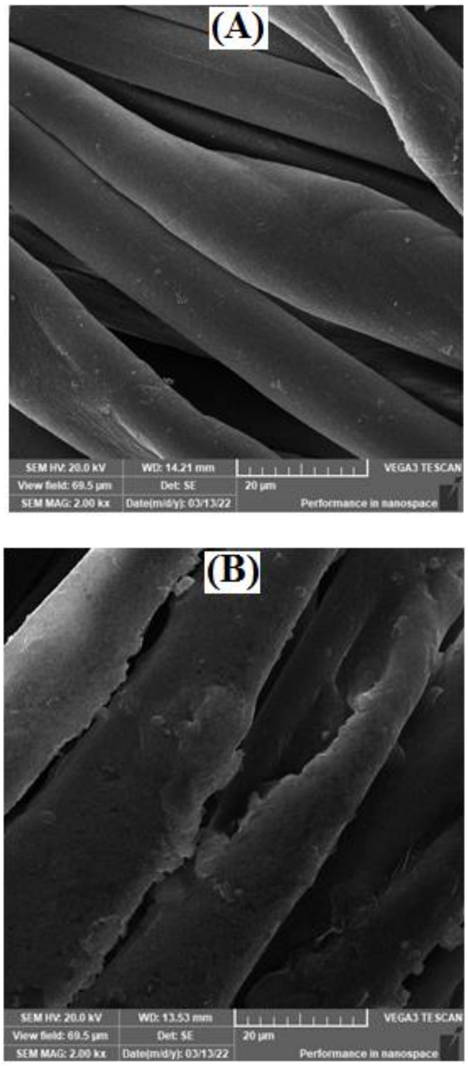


Fig. 6. SEM images of untreated fabric (A) and PDMS emulsion (40 g/L) treated fabric (B).

Figure 6 (A and B) shows SEM images of untreated as well as PDMS emulsion (40 g/L) treated fabric samples respectively. It is obvious that the treated sample surface has a soft layer of the prepared emulsion ingredients compared to the untreated sample.

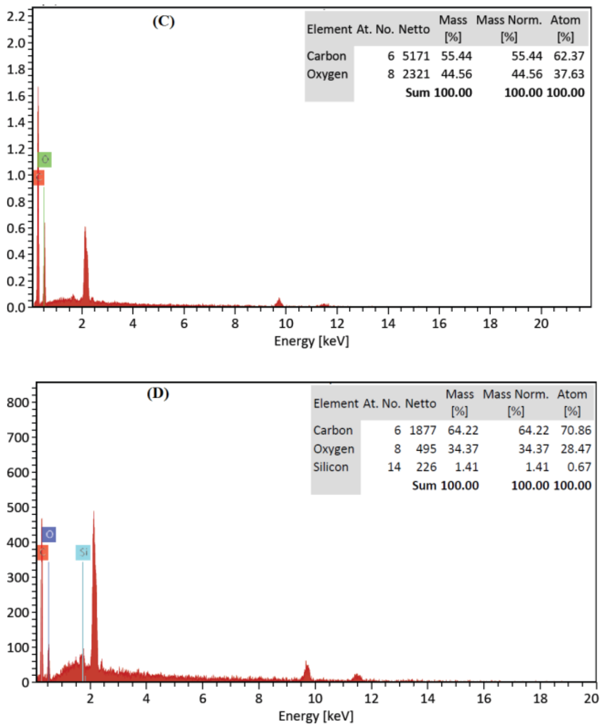
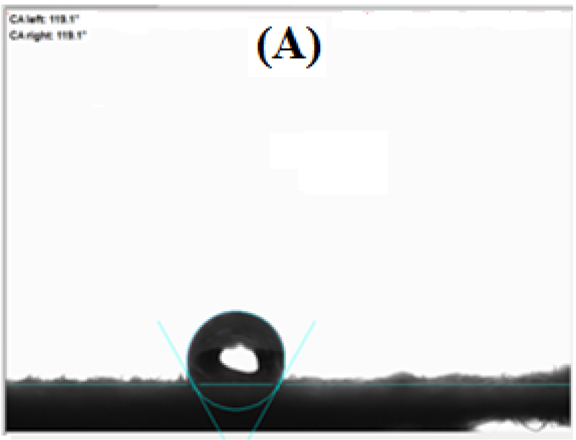


Fig. 7. SEM images of untreated fabric (C) and PDMS emulsion (40 g/L) treated fabric (D).

Figures 7 (C and D) shows EDX images of untreated and PDMS emulsion (40 g/L) treated fabric samples. It is clear that both the fabric samples contain the elements of carbon and oxygen whereas the silicone element is existed only onto the treated sample structure.

2.3.3. Water contact angle of treated fabric



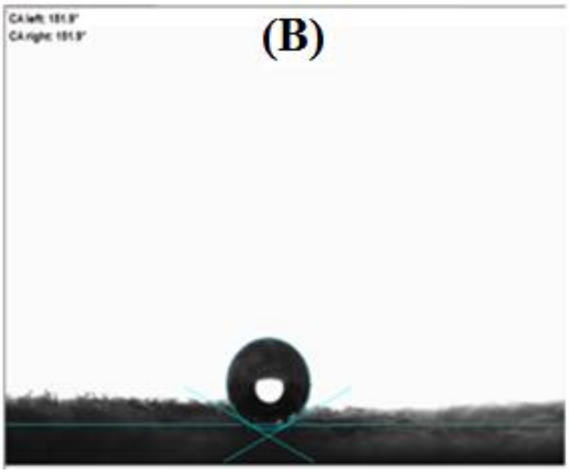


Fig. 8. Images of water droplets on surface of the water repellent fabric samples treated with the PDMS emulsion (40 g/L) and then dried at 100 ^{O}C (A) or 160 ^{O}C (B).

Figure 8 shows water contact angle of a fabric sample treated with the aforementioned PDMS emulsion (40 g/L) then dried at 100 ^{O}C (fabric A) and another fabric sample treated with the same emulsion concentration but dried at 160 ^{O}C (fabric B). It is obvious that fabric (A) has a contact angle of 119.1whereas fabric (B) has a contact angle of 151.9^{o} reflecting the role of the drying temperature in enhancement of WRR of treated fabric surface as discussed before.

Conclusions

- The PDMS mother emulsion is PDMS (5%), TEA (2.4%), SA (4.5%), and $AlCl_3$/SA molar ratio 1.
- Treating cotton/polyester fabric with 40 g/L of the PDMS emulsion followed by drying at 100 ^{O}C acquired that fabric with water repellency, softness, and stiffness accompanied with a decreasing in coefficient of friction as well as air permeability of treated fabric.
- Raising the drying temperature of treated fabric enhances its water repellency.
- The TEM image indicated that emulsion particles size ranges between 6 to 10 nm.
- The treated fabric surface was characterized via water contact angle and SEM as well as EDX analysis.

Conflicts of interest: "There are no conflicts to declare".

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References

1. A. Hebeish, H. M. Fahmy, M. H. Abo-Shosha and N.A. Ibrahim, Preparation of New Chemical Polyblend Sizing Agent via Polymerization of Acrylic Acid with Polyvinyl Alcohol, Polym. Plastic Technol. Eng., 45, 309(2006).

2. N.A. Ibrahim, M.H. Abo-Shosha, M.H. Fahmy and A. Hebeish, Effect of Size Formulation on Sizeability and Desizeability of some Soluble Sizes, Polym. Plast. Techonl. Eng., 36(1), 105(1997).
3. N.A. Ibrahim**,** A. Hebeish, H. M. Fahmy and M. H. Abo-Shosha, Synthesis Characterization and Application of Poly (Acrylamide) / Poly(Vinyl Alcohol) Polyblends, Polym. Plastic Technol. Eng., 45, 341(2006).
4. N.A. Ibrahim, M.H. Abo-Shosha , H.M. Fahmy , Z.M. El-sayed and A.A. Hebeish, Hybrids for finishing cotton fabric with durable handle performance, J. Materials Processing Technology, 200, 385 (2008).
5. H.M. Fahmy, Utilization of Poly (N-vinyl-2-pyrrolidone) in easy care finishing of cotton fabrics to improve their performance properties and antibacterial activities, Journal of Industrial Textiles, 39(2), 109 (2009).
6. H.M. Fahmy, A.A. Aly, A. Amr, Sh.M. Sayed and A.M. Rabie, An innovative SA/PVP hybrid for attaining water repellent cotton/polyester blended fabric, International Journal of ChemTech Research, 9(3), (2016) 215-227.
7. H.M. Fahmy, A.A. Aly, A. Amr, Sh.M. Sayed and A.M. Rabie, Effect of phenolic compounds and water repellents combination on performance properties of cotton/polyester blended fabric, Egyptian Journal of Chemistry, 60(1), (2017) 69 - 84.
8. N.A. Ibrahim, H.M. Fahmy, M. Abdel Rehim, S.S. Sharaf and M.H. Abo-Shosha, Finishing of Cotton Fabrics with Hyperbranched poly (ester-amine) to enhance their antibacterial properties and UV protection, Polymer-Plastics Technology and Engineering, 49, (2010) 1297–1304.
9. R.A.A. Eid, T.M. Hassan, H.M. Fahmy, A. Amr and D.E. Nada, Utilization of Triclosan to Enhance the Antibacterial Activities of Linen, Egyptian Journal of Chemistry, 58(2), (2015) 203-216.
10. N.A. Ibrahim, B.M. Eid, N.A. Abd El-Ghany, and E.M. Mabrouk, Polyfunctional cotton cellulose fabric using proper biopolymers and active ingredients, Journal of the Textile Institute, 111, (2020) 381-393.
11. N.A. Ibrahim, A. Amr A, and B.M. Eid, Multipurpose Treatment of Cellulose-Containing Fabrics to Impart Durable Antibacterial and Repellent Properties, Fibers and Polymers, 21,(2020) 513-521.
12. N.A. Ibrahim, B.M. Eid, E.M. El-Zairy, E. Emam, and S. Barakat, Environmentally sound approach for imparting antibacterial and UV-protection functionalities to linen cellulose using ascorbic acid, International Journal of Biological Macromolecules, 135, (2019) 88-96.
13. N.A. Ibrahim, E.M. Emam, B.M. Eid, and T.M. Tawfik, An Eco-Friendly Multifunctional Nano-Finishing of Cellulose/Wool Blends, Fibers and Polymers, 19, (2018) 797-804.
14. H.M. Fahmy, R.A.A. Eid, S.S. Hashem, and A. Amr, Enhancing some functional properties of viscose fabric, Carbohydrate Polym, 92, (2013) 1539–1545.
15. H.M. Fahmy, A.A. Aly, A. Amr, Sh.M. Sayed, and A.M. Rabie, SA/TDI/PEG adducts as water repellent finishes for cotton/polyester blended fabric. Prog Org Coat 99: (2016) 166–172.
16. H.M. Fahmy, A.A. Aly, and Sh.M. Sayed, Graft copolymerization of N-vinylpyrrolidone onto stearyl alcohol to impart water repellency and antibacterial properties for cotton/polyester fabric, Prog. Org. Coat., 105, (2017) 176–182.
17. N.A. Nabil, A.A. Ibrahim, B.M. Aly, B.M. Eid, and H.M. Fahmy, Green approach for multifunctionalization of cellulose-containing fabrics, Fiber and Polymers, 19, (2018) 2298-2306.
18. H.M. Fahmy, A. Amr, A.A. Aly, and S.M. Sayed, Synthesis of castor oil/2,4-toluene diisocyanate adduct to impart water repellency and antibacterial properties for cotton/polyester fabric. J Coat Technol Res 16, (2019) 31–39.
19. H.M. Fahmy, Enhancing some performance properties of ester crosslinked cotton fabric by pre-quaternization, Egypt Journal of Chemistry, 47, (2004) 627–639.
20. B.F. Abdel-Wahab, H.E. Gaffer, M.M.G. Fouda, E.M. Osman, and H.M. Fahmy, Synthesis of some new 2-(2,3-dihydroinden-1-ylidene) hydrazinyl)-4-methylthiazole derivatives for simultaneous dyeing and finishing for UV protective cotton fabrics, Journal of Applied Polymer Science, 112, (2009) 2221-2228.
21. M.H. Abo-Shosha, Z. El-Sayed, H.M. Fahmy, and N.A. Ibrahim, Synthesis of PEG/TDI/F6 Adducts and Utilization as Water/Oil Repellents and Oily Stain Release Finishes for Cotton Fabric, Polym. Plastic Technol. Eng., 44, (2005) 1189-1201.
22. M.H. Abo-Shosha, N.A. Ibrahim, H.M. Fahmy, and A. Hebeish, Utilizing Water Soluble Size Additives in Easy Care Finishing, American Dyestuffnnual Reporter, 84, (1995) 44-46.
23. A.K.R. Choudhury, Principles of Textile Finishing, The Textile Institute Book Series, Woodhead Publishing, (2017).
24. P.J. Rivero, A. Urrutia, J. Goicoechea, and F.J. Arregui, Nanomaterials for Functional Textiles and Fibers, Nanoscale Research Letters, 10, (2015) 11-22.
25. J. Vasiljevic, B. Tomsic, I. Jerman, and B. Simoncic, Organofunctional trialkoxysilane sol-

gel precursors for chemical modification of textile fibers, Tekstilec, 60, (2017) 198-213.
26. R. Atav and B. Bariş, Dendrimer technology for water and oil repellent cotton textiles, AATCC J. Res., 3, (2016) 16-24.
27. K. Opwis and J.S. Gutmann, Surface modification of textile materials with hydrophobins, Text. Res. J., 81, (2011) 1594-1602.
28. M. Montazer and T. Hafiri, Nanofinishing of textile materials, Woodhead Publishing, Sawston, 2018.
29. W.D. Schindler and P.J. Hauser, Chemical finishing of textiles, Woodhead Publishing Ltd and CRC Press LLC, Cambridge, England, 2004.
30. M.H. Abo-Shosha, Z.H. El-Hilw, A.A. Aly, A. Amr, and A.S.I. El-Nagdy, Paraffin Wax Emulsion as Water Repellent for Cotton/Polyester Blended Fabric, . J. Ind. Text., 37, (2008) 315–325.
31. M.H. Abo-Shosha, A.M. Rabie, Z.H. El-Hilw, A. Amr, Stearyl Alcohol/2,4-Toluene Diisocyanate /Perfluorinated Alcohols Adduct as a New Textile Water/Oil Repellent, J. Industrial Textiles, 39(2), (2009)149-161.
32. H.Z. Özek, Silicone-based water repellents, In: Waterproof and water repellent textiles and clothing, J. Williams (ed), Woodhead Publishing, Elsevier Ltd, Sawston, 2017.
33. ECETOC, 2011. Linear Polydimethylsiloxanes Cas no. 63148-62-9. Second Edition. JACC No: 55, Brussels, Available from: http://www.ecetoc.org/wp-content/uploads/2014/08/JACC-055-Linear-Polydimethylsiloxanes-CAS-No.-63148-62-9-Second-Edition
34. C. Tomasino, Chemistry & Technology of Fabric Preparation & Finishing, College of Textiles, NCSU, USA, 1992.