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Synthesis and Application of New Silicone Based Water Repellents

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Abstract

Water repellent finishes are highly needed to achieve water repellent clothing, home and technical textiles. In that regard, new CPS1000/TDI and CPS5000/TDI adducts were synthesized upon reacting monocarbinol terminated polydimethylsiloxanes (CPS) having molecular weight of 1000 and 5000 Da respectively with 2,4-Toluene di-isocyanate (TDI) in a molar ratio of 2:1 respectively at 100 OC for 90 min. The chemical structure of CPS1000/TDI adduct was confirmed by the FTIR analysis. The synthesized adducts were dispersed in water using stearic acid/triethanol amine system to obtain water repellents. The TEM analysis confirmed that the particles size of such adducts emulsions is in the nano scale. Incorporation of that adducts emulsions in easy care finishing formulation of cotton/polyester (50/50) blended fabric imparts that fabric with multifunctional properties namely anti-crease, water repellency, and soft hand. The SEM images and EDX analysis of CPS1000/TDI adduct emulsion treated fabric were investigated.

Key words*:* Monocarbinol Polydimethylsiloxanes, 2,4-Toluene di-isocyanate, Water repellency, Cotton/polyester fabric, Textile finishing.

Introduction

Functional textiles have been occupied significant standing in human life as they confer man's protection and comfort. In recent years, many attempts have been carried out to develop and manufacture high added value textile products having functional properties such as anti-crease, antimicrobial, water and oil repellency, self-cleaning, and UV-blocking, taking in consideration comfort, ecological, economic and fashion demands [1-14].

A wide range of chemical finishes can be used to impart textile products with new functional properties; multi-functional products can be also achieved. The extent of improvement in the desired functional properties extremely depends on the substrate type, finishing agent chemical structure and method of application [13,15].

Water repellent textiles refer to the ability of that textiles to resist wetting with water and the water drops will run off the surface of such textiles but they will come through under sufficient pressure. They are extremely important for diverse end uses in home, clothing, and technical textiles. The key for achieving water-repellent textiles is to reduce the free surface energy of fibers to become lower than water surface tension [16-18].

The water repellency property of textiles can be obtained by using paraffin wax, silicone compounds, fluorochemicals, polyurethanes, dendrimers and hydrophobins, as well as nano-materials like SiO2 nano-particles and carbon nano-tubes [7, 16-24].

Beside the silicones function as textile water repellents, they can improve softness, tear strength, abrasion, and wrinkle resistant properties of fabrics [25]. Polydimethylsiloxanes molecules can form hydrogen bonds with fiber surface because of the difference in electronegativity between silicon and oxygen atoms, causing the hydrophobic methyl groups to orient themselves away from the fiber surface [25].

On the other hand, polyurethanes are commonly used as textile hydrophobic coatings because of their merits

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of the good adhesion to textile surface, softer handle, high flexibility, good abrasion resistance, high moisture permeability, high gloss, dry-cleanability, resistance to water and solvents, and cheapness [7,26].

The main goal of this study is to synthesis new silicone based adducts that can be emulsified using stearic acid/triethanol amine system to obtain water repellents textile finishes. Such prepared water repellents will be incorporated in easy care finishing formulations of cotton/polyester (50/50) blended fabric to impart that fabric with multifunctional properties namely anti-crease, water repellency, and soft hand.

Materials and Methods

Materials

Mill-scoured and bleached cotton/polyester (50/50) blended fabric of plain weave structure, weight of 125 g/m2 and count (Ne) of 30/1 was supplied by Misr Spinning and Weaving Co., Mehalla EL-Kobra, Egypt. Two monocarbinol terminated polydimethylsiloxanes (CPS) (Figure 1) having molecular weights of 1000 (CPS1000) and 5000 (CPS5000) Da, USA, were used. 2,4-Toluene di-isocyanate (TDI) was supplied by Sigma-Aldrich. Fixapret® ECO, low formaldehyde dimethylol dihydroxyethylene urea (DMDHEU), BASF, Germany, was used. Stearic acid (SA), triethanol amine (TEA) and ammonium chloride were all of laboratory grade chemicals.

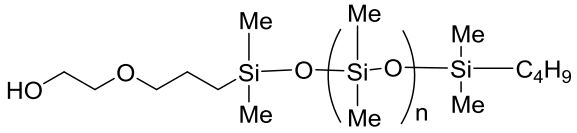


Figure 1: Chemical structure of monocarbinol terminated polydimethylsiloxanes.

METHODS

Synthesis of CPS/TDI adducts

The CPS/TDI adducts were synthesized by adding a specific weight of TDI to a thermostated CPS in 100 ml stoppered round glass bottle under dry nitrogen in an air circulated oven at a specific temperature (70 – 100 OC) for a certain time (30 – 120 min) until completion of the reaction.

Purification of the CPS1000/TDI adduct for FTIR analysis

The synthesized CPS1000/TDI adduct was purified before FTIR analysis by adding 10 g of it to 250 ml of isopropyl alcohol in 500-mL stoppered separating funnel to dissolve the unreacted TDI and CPS. The medium was then left for stirring followed by separating the undissolved adduct from the solution. This process was repeated for five times. To remove the remnant isopropyl alcohol, such adduct was left under vacuum in a rotary evaporator at 80 OC for 2 h. The product was then stored over CaCl2 in a desiccators for at least 48 h before analysis.

Emulsification of CPS/TDI adducts

The unpurified synthesized adducts were emulsified using SA/TEA system as follows: specific weights of any of the prepared adducts as well as SA were melted together at 70 OC in a 250 ml flask in a water bath. To that melt, TEA aqueous solution of a specific concentration at 70 OC was added with stirring using a strong homogenizer. After that, the emulsion weight was completed with distilled water to 100 g and stirred again for extra 3 min to obtain a homogeneous mother emulsion. At the end, the flask containing the mother emulsion is cooled to room temperature.

Fabric treatment

Fabric samples of 30 × 30 cm2 were padded twice in finishing bathes containing the prepared adducts emulsions (0–70 g/l), DMDHEU (0–80 g/l) as crosslinker, and ammonium chloride as a catalyst to a wet pick up of 100%. The padded samples were then dried at100 OC/3 min in Wenner Mathis AGCH-8155 oven and then cured at 160 OC/3 min. The finished fabrics were then washed at 50 OC for10 min, thoroughly rinsed and finally dried for testing.

Analysis and Test Methods

•Fabric weight (W) was determined according to ATSM (D 3776 – 79).
•The percent total conversion was determined according to ASTM procedure D 5155 – 01.
•Water repellency rating (WRR) was performed using the spray test as described by AATCC Test Method 22-1989.

•The wrinkle recovery angle of treated fabric samples, WRA (w+f)O, was assesed according to ASTM method D-1296-98.
•Surface roughness (SR) was measured using Kawabata evaluation system, Surface tester KES-FB4-A, Kato Tech Co., LTD, Japan.
•Stiffness (S) was determined in the warp direction according to ASTM Test Method D 1388-96 using Jika (Toyaseiki) apparatus.
•Durability to wash was assessed by subjecting the fabric to 1, 3, and 5 laundering cycles. Each laundering cycle consists of washing the fabric sample with hot water at 50 OC for 10 min using 2 g/l nonionic detergent followed by rinsing and air drying at ambient conditions [6,7,9].
•The water contact angle was measured on OCA-15EC (Data physics GmbH, Germany) with software using 10 µL drops of triple distilled water.
•Air permeability (AP) was evaluated according to ATSM (D 737-96).
•Infra Red (IR) spectroscopy was carried out using FT/IR-4700 FTIR Spectrometer from JASCO.
•The morphology and particles size of the hybrid emulsion was obtained by transmission electron microscope (TEM) using a JEOL, JEM 2100 F electron microscope at 200 kV. In that regard, two drops of the prepared emulsion were placed in a 400-mesh copper grid coated by an amorphous carbon film and then left for drying at room temperature. Phosphotungestic acid (2%) was then added as a dye to the grid followed by placing it the microscope for analysis.
•Scanning electron microscope (SEM) images of the treated and untreated fabric samples were obtained using SEM Model Quanta 250 FEG (Field Emission Gun) attached with 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.

Results and Discussion

It was stated that the isocyanate groups of TDI can react with the primary hydroxyl groups of the aliphatic compounds, through an addition reaction, to yield urethanated compounds [6,9]. Thus, upon mixing of CPS1000 or CPS5000 with TDI, under conditions employed, the following reaction is anticipated to be occurred giving rise to a formation of CPS1000/TDI or CPS5000/TDI adduct.

2 CPS-OH + OCN-TDI-NCO ⟶ CPS-OOCNH-TDI-NHCOO-CPS …….. (1)

(CPS/TDI adduct)

Factors affecting CPS/TDI adducts formation

Reaction time and temperature

Figure 2 shows the impact of reaction time (30 - 120 min) and temperatures (70 - 120 ^{O}C) on percent total conversion of isocyanate groups of TDI to urethane groups. It is clear that either increasing of the reaction temperature at constant time or prolonging the reaction time at the same temperature, results in an enhancement the %TC which can be associated with the temperature favorable effect on providing the reactants with the required energy to reach over the process activation energy barrier [6,27]. Obviously, Figure 2 confirms that the proper conditions to achieve CPS1000/TDI adduct with high percent total conversion is raising the reaction temperature to 100 ^{O}C for 90 min.

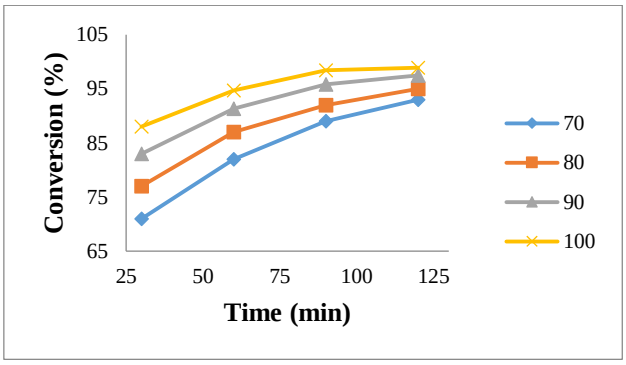


Figure 2: Effect of reaction time and temperature on percent conversion of TDI isocyanate groups.

CPS molecular weight, 1000 Da; CPS1000/TDI molar ratio, 2:1.

CPS molecular weight

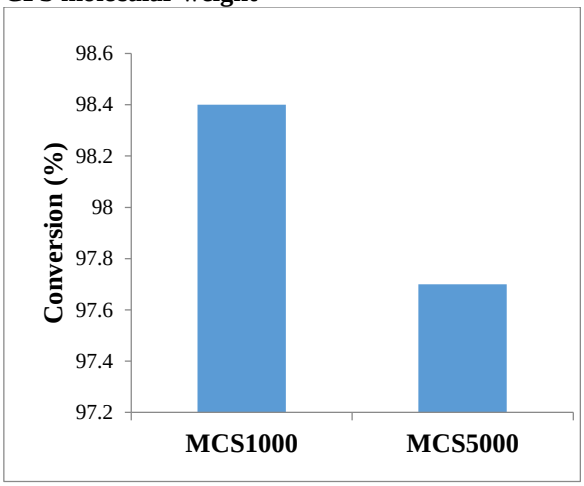


Figure 3: Effect of CPS molecular weight on percent conversion of TDI isocyanate groups.

CPS/TDI molar ratio, 2:1; reaction temperature, 100 OC; reaction time, 90 min.

The effect of CPS molecular weight on percent conversion of TDI isocyanate groups is shown in Figure 3. It is clear that: i) the synthesis reaction proceeds to completion with high percent conversion, regardless of CPS molecular weight, reflecting of the TDI isocyanate groups high susceptibility to interact with CPS hydroxyl groups, and, ii) increasing of CPS molecular weight from 1000 to 5000 Da is accompanied by a reduction in percent conversion of the formed adduct, most probably due to increasing of extent of the CPS5000 chains entanglement [6].

Characterization of the CPS1000/TDI adduct

IR analysis

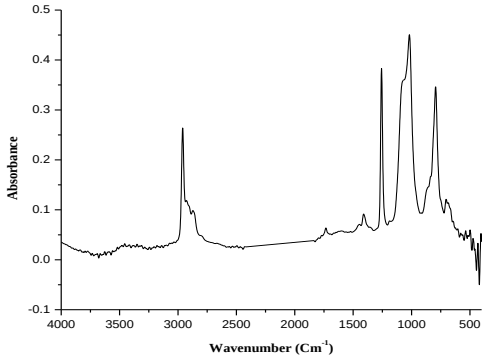


Figure 4: FTIR spectrum of CPS1000.
Characteristics of tomato fruits

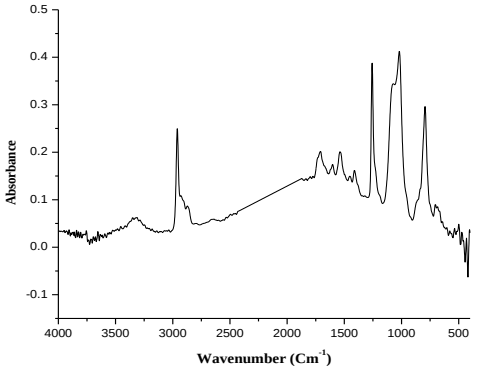


Figure 5: FTIR spectrum of the CPS1000/TDI adduct.

The FTIR spectrum of CPS1000 (Figures 4) shows strong absorption peak at 3450 cm-1 corresponding to OH stretching vibration, at 1261 cm-1 corresponding to Si-O of CPS, and at 2870-2960 cm-1 corresponding to Si-(CH3)2 stretching vibrations [28-30]. Meanwhile, the spectrum of the purified CPS1000/TDI adduct (Figure 5) shows strong absorption peak at 1261 cm-1 corresponding to Si-O of CPS, at 2870-2960 cm-1 corresponding to Si-(CH3)2 stretching vibrations [28-30], at 3317 and 1718 cm-1 corresponding to N-H and C=O stretching vibrations of the urethane group (NHCOO) as well as at 1603 cm-1 corresponding to C=C stretching of the benzene ring [6,9], which clearly confirms the formation of the synthesized adduct.

Emulsification of CPS1000/TDI adduct

Adduct concentration

Table 1: Effect of the adduct concentration on emulsion state and water repellency rating of treated fabric.

Adduct conc. in the mother emulsion (g/kg)	Emulsion state	Emulsion conc. in the padding bath (g/L)	WRR
75	Homogeneous emulsion	50	0
		60	50
		70	70
100	Homogeneous emulsion	50	50
		60	70
		70	70
125	Homogeneous thick emulsion	50	70*
		60	70*
		70	70*
150	Paste formation	-	-

[SA], 45 g/L; [TEA], 24 g/L. * Appearance of tiny oil spots on treated fabric.

Table 1 shows the effect of CPS1000/TDI adduct concentration on emulsion state as well as water repellency rating of treated fabric. It obvious that: i) increasing of the adduct concentration from 75 to 125 g/kg in the mother emulsion is accompanied with a formation of homogeneous emulsions that thickens progressively, ii) the water repellency rating of treated fabric increases gradually with increasing of the padding bath concentration and does not exceed the value of 70, regardless of the adduct concentration, iii) at adduct concentration of 125 g/kg, the treated fabric samples suffer from tiny oil spots, and iv) the adduct concentration of 150 g/kg produces a pasty mother emulsion that cannot form good emulsions upon dilution. However, it seems that the adduct

concentration of 100 g/kg is a convenient choice [9,31].

Stearic acid concentration

The effect of SA concentration on CPS1000/TDI adduct emulsion state as well as water repellency rating of treated fabric is shown in Table 2. It is clear that: i) at SA concentration of 45 g/L, the produced mother emulsion is homogenous and the water repellency rating of treated fabric increases with increasing of the padding bath concentration, ii) increasing of SA concentration from 60 to 75 g/L results in a progressive increasing in viscosity of the mother emulsion as well as treated fabric having tiny oil spots, and iii) at SA concentration of 90 g/L, the mother emulsion becomes a past and cannot be diluted into successful emulsions. However, the water repellency rating of the treated fabric does not exceed the value of 70 at any of SA concentrations which can be ascribed to the constancy of the urethane adduct concentration in such emulsions [9,31].

Table 2: Effect of stearic acid concentration on emulsion state and water repellency rating of treated fabric.

SA conc. in the mother emulsion (g/L)	Emulsion state	Emulsion conc. in the padding bath (g/L)	WRR
45	Homogeneous emulsion	50	50
		60	70
		70	70
60	Homogeneous emulsion	50	50*
		60	70*
		70	70*
75	Homogeneous very viscous emulsion	50	70*
		60	70*
		70	70*
90	Paste formation	-	-

[Urethane adduct], 100 g/kg; [TEA], 24 g/L. * Appearance of tiny oil spots on the fabric.

Degree of stearic acid neutralization

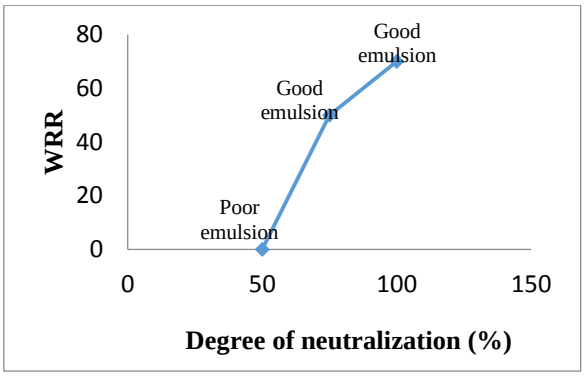
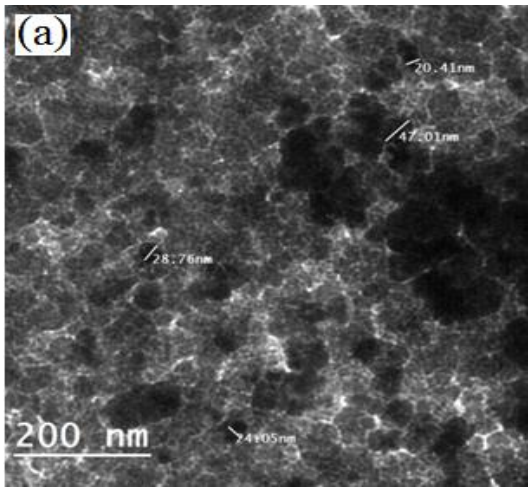


Figure 6: Effect of the degree of SA neutralization with TEA on emulsion state and water repellency rating of treated fabric.

[Urethane adduct], 100 g/kg; [SA], 45 g/L.

In this study, SA/TEA system was used to emulsify CPS1000/TDI adduct. Since TEA has hydrophilic characters, thus, it should be added in an appropriate concentration to neutralize SA without impairing the emulsion hydrophobicity [9,31]. Figure 6 indicates the impact of the neutralization degree of SA on CPS1000/TDI adduct emulsion state as well as water repellency rating of treated fabric. It is clear that increasing of the neutralization degree from 50 to 100% is accompanied with a gradual improvement in state of the formed emulsions as well as water repellency rating of treated fabric samples; needless to say that no emulsion was formed below the neutralization degree of 50%. On the other hand, oily spots were observed onto fabric samples treated with emulsions containing SA neutralized with a degree less than 100%. This clearly suggests that the proper emulsion composition is a urethane adduct of 100 g/kg, SA of 45 g/kg, and TEA of 24 g/kg.

TEM analysis of CPS/TDI adducts emulsions



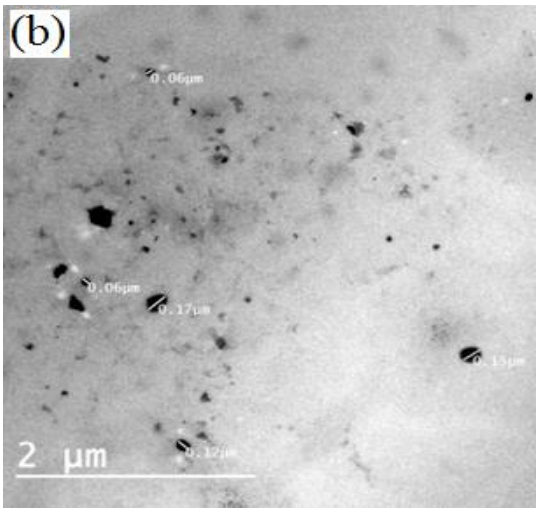


Figure 7: TEM of (a) CPS1000/TDI and (b) CPS5000/TDI adducts emulsions.

The particles size of CPS1000/TDI and (b) CPS5000/TDI adducts emulsions was evaluated by TEM analysis as shown in Figure 7 (a) and (b) respectively. It is clearly seen that such emulsions particles size is in the nano-scale but the CPS5000/TDI adduct emulsion particles are larger than that of CPS1000/TDI adduct reflecting the higher molecular weight of CPS5000.

Performance of CPS/TDI adducts emulsions as water repellents

DMDHEU concentration

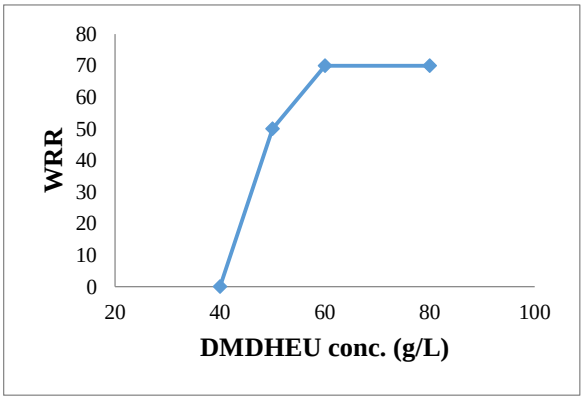
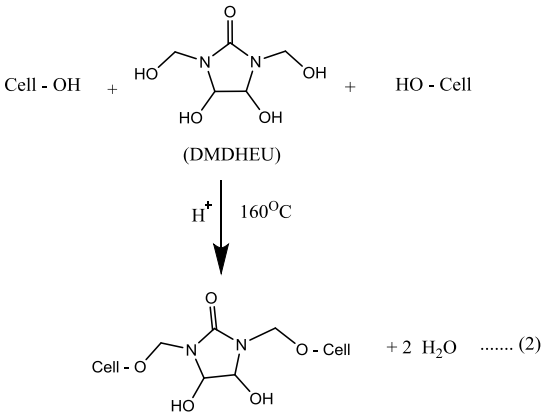


Figure 8: Effect of DMDHEU concentration on water repellency rating of treated fabric.

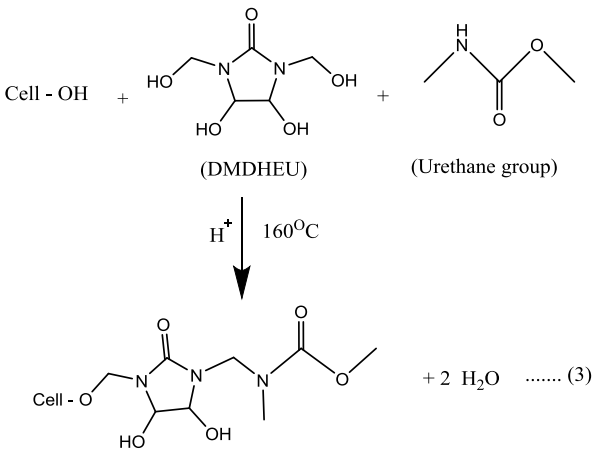
[CPS1000/TDI adduct emulsion], 60 g/L; [NH4Cl], 10% based on DMDHEU concentration; wet pick up, 100%; drying, 100 OC/3 min; curing, 160 OC/3 min.

The impact of DMDHEU concentration, 0 - 80 g/L, on WRR of treated fabric is shown in Figure 8. It is clear that increasing of the DMDHEU concentration form 0 to 60 g/L in the finishing bath results in a maximum water repellency rating value of 70. This is due unequivocally to the role of DMDHEU in fixation and deposition of a soft hydrophobic film of the CPS1000/TDI adduct ingredients onto/within the finished fabric structure via DMDHEU as a crosslinker [9,12,32-36]. The higher concentrations of DMDHEU in the finishing bath, i.e. 60 – 80 g/L, practically have no effect on the water repellency of treated fabric. Scheme 1 may illustrate the induced interactions among cotton cellulose (Cell-OH), DMDHEU and the urethane groups of the prepared adduct under the conditions employed:

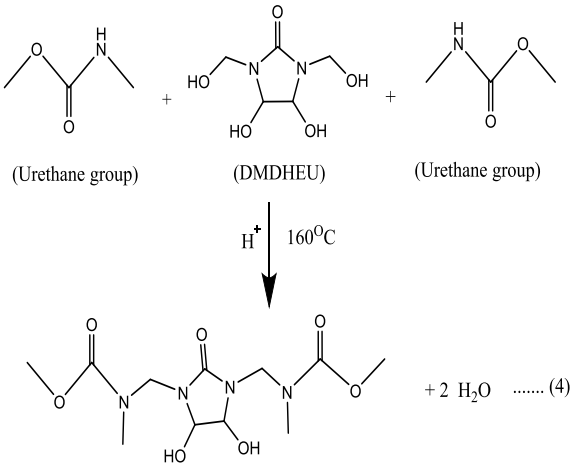
i) Crosslinking of cotton cellulose



ii) Fixation of the adduct ingredients onto/within cotton cellulose



iii) Deposition of unbound by-product layer onto/within fabric structure



Scheme 1: The induced interactions among cotton cellulose, the crosslinker and the urethane groups of the prepared adduct.

Adduct type

Table 3: Effect of adduct type on performance properties of treated fabric.

Adduct type	WRA (w+f)^{O}	SR (µm)	S (mg)	AP ($cm^3/cm^2.s$)	WRR	WCA (^{O})
Untreated	184	0.004	498	76	0	0
CPS1000/TDI adduct	292	0.003	712	62	70(50)(0)(0)	118.0
CPS5000/TDI adduct	280	0.003	819	54	80(70)(50)(0)	127.6

[Adduct emulsion], 60 g/L; [DMDHEU], 60 g/L; [NH4Cl], 6 g/L; wet pick up, 100%; drying, 100 OC/3 min; curing, 160 OC/3 min. WRA: wrinkle recovery angle; S: stiffness; SR: surface roughness; AP: air permeability; WCA: water contact angle; WRR: water repellency rating. Values in parentheses indicate the retained WRR after 1, 3, and 5laundering cycles.

The performance properties of cotton/polyester fabric samples treated with easy care finishing formulations containing either CPS1000/TDI or CPS5000/TDI adduct emulsion are monitored in Table 3. It is clear that treating of fabric samples with the aforementioned finishing formulations brings about an enhancement in resiliency, smoothness, stiffness, water repellency and water contact angle (Figure 9 (a) and (b)) accompanied with a reduction in air permeability of treated fabric which can be associated with a fixation and deposition of such adducts ingredients onto/within the fabric structure as illustrated before by equations 3 and 4. Moreover, CPS5000/TDI adduct emulsion, compared to CPS1000/TDI adduct, imparts the treated fabric with higher stiffness, durable water repellency, and water contact angle along with lower resiliency and air permeability magnitudes, the matter which can be attributed to the CPS5000 higher molecular weight that renders the adduct ingredients to coat treated fabric fibres with higher extent than to penetrate that fibres. However, fabric softness is unchanged suggesting the high lubricating effect of that silicone based adducts whatever the CPS molecular weight used [17,37].

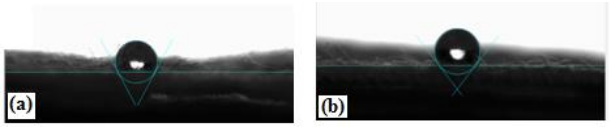


Figure 9: Photograph of water droplets on water repellent fabric surfaces treated with (a) CPS1000/TDI and (b) CPS5000/TDI adducts.

SEM and EDX analysis

Figures 10 (a,b) and **11** (c,d) represent SEM and EDX analysis of an untreated and CPS1000/TDI adduct emulsion treated fabric samples respectively. It is clearly seen that the treated fabric is coated with a soft hydrophobic layer of the adduct emulsion, compared to the untreated sample. Meanwhile, the EDX elemental analysis confirms the presence of carbon and oxygen elements onto both fabric samples but the silicone element is present only onto the treated sample

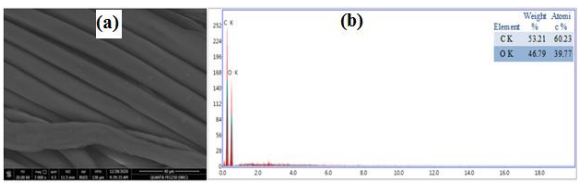


Figure 10: (a) SEM image and (b) EDX spectrum of untreated fabric.

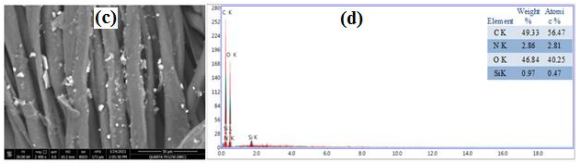


Figure 11: (c) SEM image and (d) EDX spectrum of CPS1000/TDI adduct emulsion treated fabric.

Conclusions

- New CPS1000/TDI and CPS5000/TDI adducts were synthesized upon reacting of CPS1000 and CPS5000 with TDI at a molar ratio of 2:1 respectively at optimum reaction conditions of 100 OC for 90 min.
- Dispersing the aforementioned adducts in water using SA/TEA system results in good emulsions.
- Incorporation of such adducts emulsions in easy care finishing formulation of cotton/polyester (50/50) blended fabric imparts that fabric with anti-crease, water repellency, and soft hand properties.
- The chemical structure of the CPS1000/TDI adduct was confirmed using FTIR analysis.
- The SEM images and EDX analysis confirmed a deposition of a soft hydrophobic layer of the CPS1000/TDI adduct ingredients onto treated fabric.
- The TEM images confirmed that the particles size of either CPS1000/TDI or CPS5000/TDI adduct emulsion is in the nano scale.

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