Modification of Textiles to Impart Hydrophobicity using Combination of Silica Nanoparticles & Water Repellent Agent

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Abstract

In this study the hydrophobic modification of cotton fabric was done by using combination of silica nanoparticles and water repellent agent. The silica nanoparticles were synthesized by the alkaline hydrolysis of the tetraethyl orthosilicate followed by the dehydration, condensation reaction through a typical Stober method. The characterization of silica nanoparticles on the surface of cotton fabric was done using scanning electron microscope. The properties of finished fabric such as water spray rating, hydrostatic head pressure, air permeability, tearing strength, GSM, & bending length was checked. It was found that the finished fabric shows the rating of 90 & above for all the combinations of silica nanoparticles and water repellent agent in case of spray test.

"1. Introduction"

Probably one of the first applications of the textiles was the protection of man against the weather, for example, against rain and snow. Water and soil repellency has been one of the major targets for fiber and textile scientists and manufacturers for centuries. Combinations of new materials for fiber production with a variety of surface treatments have been developed to reach the condition of limited wettability. Nevertheless, additional efforts are needed to create fiber and textile materials with ideal repelling properties. Nature has already developed an elegant approach that combines chemistry and physics to create super repellent surfaces. Lotus leaves are unusually water-repellent and keep themselves spotless, since countless miniature protrusions, coated with water-repellent hydrophobic substance, cover their surface. [1, 2]

Water repellency is the capacity of the fabric to delay the entry of water under its own pressure. Water repellent finishes achieve their properties by reducing the free energy at fiber surfaces. If the adhesive interactions between a fiber and drop of liquid placed on the fiber are greater than the internal cohesive within the liquid, the drop will spread. If the interactions between the fiber and the liquid are less than the internal cohesive interactions within the liquid, the drop will not spread. Surfaces that exhibit low interactions with liquid are referred to as low energy surfaces.[3]

Simple inorganic nanosols like silica sols are already more hydrophobic than some of the natural fiber materials such as cotton or other cellulosic materials. Increased water repellency can only be achieved if the coating surface energy is below that of the substrate. In general the simple inorganic nanosol will be not meet the demands of the textile industry for water repellent textile. By suitable modification using compounds with hydrophobic functionalities nanosols can be prepared yielding low surface energies and thus guaranteeing certain repellence. Such modifications can either be carried out by a covalent bonding between the hydrophobic components and the inorganic building blocks or by physical embedding hydrophobic substances in the network. So, in this case the nanoparticles act as a micrometer-scale hills and valleys and provide rougher surface and the hydrophobic agent act as waxy crystals. So this combination helps us to impart lotus effect on the fabric surface to get super hydrophobicity.[1]

Hydrophobic finishes lower the surface energy and can give a maximum water contact angle of roughly 120^0. To get higher contact angle and to have self-cleaning ability, super hydrophobic finish with a contact angle of above 160^0 is required. This type of finish can not be obtained only by surface coating. Super hydrophobicity increases with increase in surface roughness which provides larger geometric area. The roughened surface generally takes the form of a substrate membrane with a multiplicity of microscale to nanoscale projections or cavities. Water repellency of rough surface was due to the air enclosed between the gaps in the surface. This enlarges the air/water interface while the solid/water interface is minimized. In this situation, spreading does not occur and the water form a spherical droplet. SiO_2, Al_2O_3 nanoparticles are mainly used for super water repellent finishes.[4]

In this paper we have also tried to impart such superhydrophobicity on the cotton fabric by using silica nanoparticles.

“2. Experimental”

2.1 Materials.

2.1.1. *Fabric:* Desized, scoured bleached cotton fabric is used for study.

2.1.2. *Chemicals and Auxiliaries* Tetraethyl orthosilicate [Si $(OC_2H_5)_4$ (TEOS)], ethanol, ammonia solution were used for the synthesis of silica nanoparticles. The distilled water was used for the synthesis of silica nanoparticles. The commercially available as a water repellent agent TUBIGUARD was used.

2.2 Characterization

The surface morphology of cotton fabric treated with silica nanoparticles and combination of silica nanoparticles & water repellent agent was recorded on scanning electron microscope (SEM) (JSM-6360 JEOL/EO). The water repellency and hydrostatic head pressure properties of treated fabrics were measured according to AATCC 22, ISO 4920 & ISO 811, AATCC 127 test methods respectively. The air permeability and tearing strength properties of treated fabrics were measured according to ASTM B 737 & IS 6359:1971SP-15 respectively. The GSM and bending length were measured according to ASTM B 3776 & ASTM D 1388-96 respectively.

2.3 Synthesis of Silica Nanoparticles.

The silica nanoparticles were synthesized by the alkaline hydrolysis of the tetraethyl orthosilicate followed by the dehydration, condensation reaction through a typical Stober method. [5, 6, 7, 8]

The mixture of tetraethyl orthosilicate and ethanol was prepared, and then it was mixed with the mixture of distilled water, ethanol and ammonia solution. The synthesis was carried out for 3 hours at 30^0c.

2.4 Application of Silica Nanoparticles & the Water Repellent Agent on cotton fabric.

The previously desized, combined scoured & bleached fabric was dipped in the silica sol & then padded using two dips & two nips to achieve the wet pick up of 80 % with a pressure of 4 Kg/ Cm^2 of a padding mangle. The sample then dried at 80^0c for 3 minute & cured at 160^0c for 3 min with a laboratory stenter. Then this fabric was again treated with the water repellent agent with varying concentration of 15 - 40 gpl & dried at 80^0c & cured at 160^0c. The composition of chemicals for the synthesis of silica nanoparticles & the composition for nano water repellent finish had shown in the following tables 1 & 2 respectively.

“Table 1. Composition of Chemicals for the Synthesis of Silica Nanoparticles”

Sr No	TEOS (Mol)	Ethanol (Mol)	Water (Mol)	Ethanol (Mol)	Ammonium hydroxide (Mol)	Time (Hour)
1	0.2	2.5	2.0	2.5	0.05	3
2	0.4	3.0	2.0	2.5	0.05	3
3	0.6	3.5	2.0	2.5	0.05	3

“Table 2. Composition of water repellent agent and silica nanoparticles for water repellent finish”

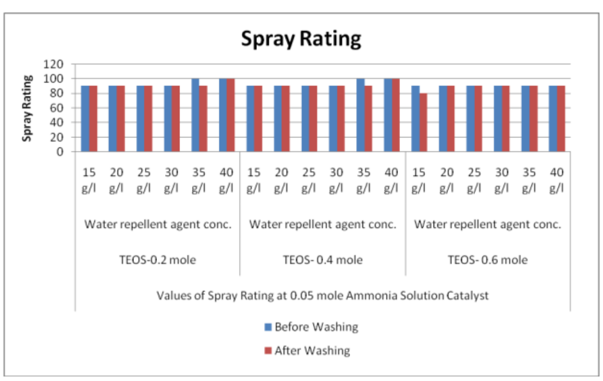
Sr. No.	TEOS (Mol)	Ethanol (Mol)	Water (Mol)	Ethanol (Mol)	Ammonium hydroxide (Mol)	Water Repellent Agent (gpl)
Recipe 1	0.2	2.5	2	2.5	0.05	15
	0.2	2.5	2	2.5	0.05	20
	0.2	2.5	2	2.5	0.05	25
	0.2	2.5	2	2.5	0.05	30
	0.2	2.5	2	2.5	0.05	35
	0.2	2.5	2	2.5	0.05	40
Recipe 2	0.4	3	2	2.5	0.05	15
	0.4	3	2	2.5	0.05	20
	0.4	3	2	2.5	0.05	25
	0.4	3	2	2.5	0.05	30
	0.4	3	2	2.5	0.05	35
	0.4	3	2	2.5	0.05	40
Recipe 3	0.6	3.5	2	2.5	0.05	15
	0.6	3.5	2	2.5	0.05	20
	0.6	3.5	2	2.5	0.05	25
	0.6	3.5	2	2.5	0.05	30
	0.6	3.5	2	2.5	0.05	35
	0.6	3.5	2	2.5	0.05	40

"3. Results and Discussion"

3.1 Effect of Concentration of TEOS, Water Repellent Agent on Spray Rating at 0.05 Mol Ammonia Solution Catalyst

"Table 3. Effect of Concentration of TEOS, Water Repellent Agent on Spray Rating at 0.05 Mol Ammonia Solution Catalyst".

	Values of Spray Rating at 0.05 mole Ammonia Solution catalyst																	
TEOS (mole)	**0.2**						**0.4**						**0.6**					
Conc. (g/l)	15	20	25	30	35	40	15	20	25	30	35	40	15	20	25	30	35	40
Before washing	90	90	90	90	100	100	90	90	90	90	100	100	90	90	90	90	90	90
After Washing	90	90	90	90	90	100	90	90	90	90	90	100	80	90	90	90	90	90



"Figure 1. Effect of Concentration of TEOS, Water Repellent Agent on Spray Rating at 0.05 Mol Ammonia Solution Catalyst" .

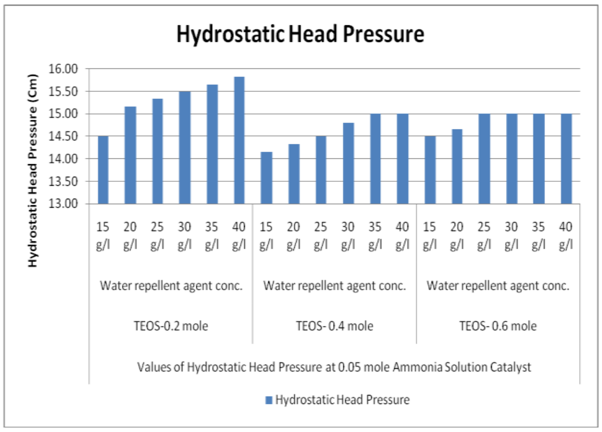
The Table 3 and Figure 1 shows that as the concentration of water repellent agent increases from 15 to 40 gpl, also the concentration of TEOS increases from 0.2 mol to 0.6 mol at fixed concentration ammonia solution of 0.05 mol. The fabric finished with 0.2 mol concentration of TEOS shows the spray rating of 90 at 15 gpl concentration and spray rating of 100 at 35 gpl concentration of water repellent agent, while the fabric finished with 0.4 mol concentration of TEOS shows the spray rating of 90 at 15 gpl concentration and spray rating of 100 at 35 gpl concentration of water repellent agent & the spray rating of 90 was observed for 15 gpl to 40 gpl water repellent agent concentration in case of 0.6 mol TEOS.

The maximum spray rating 100 was observed for 0.2 mol, 0.4 mol TEOS at 35 gpl, 40 gpl concentration of water repellent agent. This may be because of the formation of layer of silica nanoparticles on the surface of fabric which helps in formation of rough surface which helps in increase in water droplet contact angle with the surface of the fabric and with increase in the water repellent layer on the fabric surface. The washing of fabric does not affect the spray rating mostly was observed, which shows the durability of applied finish to washing.

3.2 Effect of Concentration of TEOS, Water Repellent Agent on Hydrostatic Head Pressure at 0.05 Mol Ammonia Solution Catalyst

"Table 4. - Effect of Concentration of TEOS, Water Repellent Agent on Hydrostatic Head Pressure at 0.05 Mol Ammonia Solution Catalyst".

	Values of Hydrostatic Head Pressure at 0.05 mole Ammonia Solution catalyst																	
TEOS (mole)	**0.2**						**0.4**						**0.6**					
Conc. (g/l)	15	20	25	30	35	40	15	20	25	30	35	40	15	20	25	30	35	40
Hydrostatic head pressure ($Cm^3/Cm^2/Sec$)	14.50	15.16	15.33	15.50	15.66	15.83	14.16	14.33	14.50	14.80	15.00	15.00	14.50	14.66	15.00	15.00	15.00	15.66

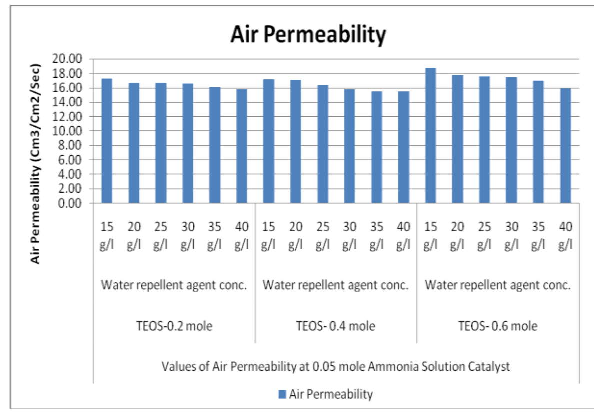


"Figure 2. - Effect of Concentration of TEOS, Water Repellent Agent on Hydrostatic Head Pressure at 0.05 Mol Ammonia Solution Catalyst".

The Table 4 and Figure 2 shows that the hydrostatic head pressure for the fabric treated with combination of silica nanoparticles and water repellent agent. As the water repellent agent concentration increases from 15 gpl to 40 gpl, also the concentration of TEOS increases from 0.2 mol to 0.6 mol at fixed concentration ammonia solution of 0.05 mol. It was observed that for 0.2 mol TEOS the hydrostatic head pressure increases from 14.50 to 14.83 for water repellent agent concentration of 15 gpl to 40 gpl respectively, while for 0.4 mol TEOS the hydrostatic head pressure increases from 14.16 to 14.50 for water repellent agent concentration of 15 gpl to 40 gpl respectively & the hydrostatic head pressure of 14.50 to 14.66 was observed for 15 gpl to 40 gpl. This is may be due to the fact that silica nanoparticles along with increase in water repellent agent concentration help to resist the drop of water penetration inside the fabric surface. As there is a continuous film formation of silica nanoparticles & water repellent agent.

3.3 Effect of Concentration of TEOS, Water Repellent Agent on Air Permeability at 0.05 Mol Ammonia Solution Catalyst.

	Values of Hydrostatic Head Pressure at 0.05 mole Ammonia Solution catalyst																	
TEOS (mole)	**0.2**						**0.4**						**0.6**					
Conc. (g/l)	15	20	25	30	35	40	15	20	25	30	35	40	15	20	25	30	35	40
Air permeability (Cm³/	17.29	16.65	16.64	16.54	16.01	15.77	17.19	17.01	16.40	15.80	15.48	15.48	18.69	17.76	17.52	17.48	16.96	15.91



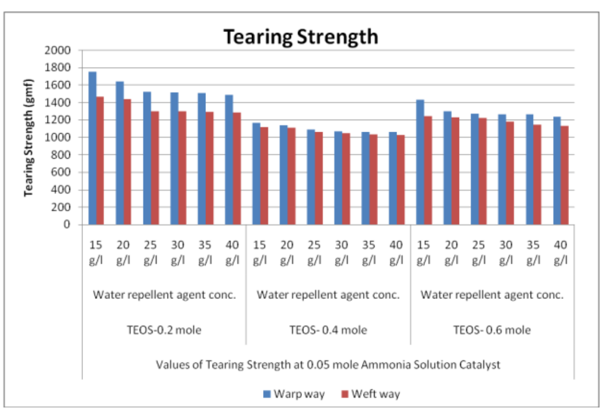
"Figure 3- Effect of Concentration of TEOS, Water Repellent Agent on Air Permeability at 0.05 Mol Ammonia Solution Catalyst".

The Table 5 and Figure 3 shows that the concentration of water repellent agent increases from 15 gpl to 40 gpl, also the concentration of TEOS increases from 0.2 mol to 0.6 mol at fixed concentration ammonia solution of 0.05 mol. It was observed that for 0.2 mol TEOS the air permeability decreases from 17.29 to 15.77 for water repellent agent concentration of 15 gpl to 40 gpl respectively, while for 0.4 mol TEOS the air permeability decreases from 17.19 to 15.48 for water repellent agent concentration of 15 gpl to 40 gpl respectively & the air permeability of 18.69 to 15.91 was observed for 15 gpl to 40 gpl in case of 0.6 mol TEOS. This is may be because as concentration of water repellent agent goes on increasing the film form goes on becoming continuous along with the silica nanoparticles due to which air transmission rate decreases, which results in superhydrophobicity.

3.4. Effect of Concentration of TEOS, Water Repellent Agent on Tearing Strength at 0.05 Mol Ammonia Solution Catalyst.

"Table 6. Effect of Concentration of TEOS, Water Repellent Agent on Tearing Strength at 0.05 Mol Ammonia Solution Catalyst".

	Values of Tearing Strength (gmf) at 0.05 mole Ammonia Solution catalyst																	
TEOS (mole)	**0.2**						**0.4**						**0.6**					
Conc. (g/l)	15	20	25	30	35	40	15	20	25	30	35	40	15	20	25	30	35	40
Warp way	1753.60	1644.80	1523.20	1516.80	1510.40	1491.20	1171.20	1139.20	1088.00	1068.80	1064.40	1062.40	1433.80	1299.20	1273.60	1267.20	1267.20	1235.20
Weft way	1472.00	1440.00	1299.20	1299.20	1292.80	1286.40	1120.00	1113.60	1062.40	1049.60	1036.80	1030.40	1241.60	1228.80	1222.40	1184.00	1145.60	1132.80



"Figure 4. Effect of Concentration of TEOS, Water Repellent Agent on Tearing Strength at 0.05 Mol Ammonia Solution Catalyst".

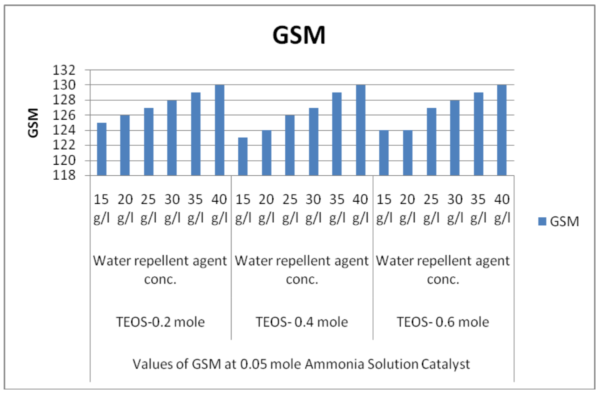
The Table 6 and Figure 4 shows that the tearing strength in both warp way and weft way for the fabric treated with combination of silica nanoparticles and water repellent agent. The concentration of water repellent agent increases from 15 gpl to 40 gpl, also the concentration of TEOS increases from 0.2 mol to 0.6 mol at fixed concentration ammonia solution of 0.05 mol. The fabric shows decrease in tearing strength in warp direction for 0.2 mol TEOS from 1753.60 to 1491.20 for water repellent agent concentration of 15 gpl to 40 gpl respectively, while the fabric shows decrease in tearing strength in warp direction for 0.4 mol TEOS from 1171.20 to 1062.40 for water repellent agent concentration of 15 gpl to 40 gpl respectively & the decrease in tearing strength in warp direction for 0.6 mol TEOS from 1433.80 to 1235.20 for water repellent agent concentration of 15 gpl to 40 gpl respectively was observed. The fabric shows decrease in tearing strength in weft direction for 0.2 mol TEOS from 1472.00 to 1286.40 for water repellent agent concentration of 15 gpl to 40 gpl respectively, while the fabric shows decrease in tearing strength in weft direction for 0.4 mol TEOS from 1120.00 to 1030.40 for water repellent agent concentration of 15 gpl to 40 gpl respectively & the decrease in tearing strength in weft direction for 0.6 mol TEOS from 1241.60 to 1132.80 for water repellent agent concentration of 15 gpl to 40 gpl respectively was observed.

This is may be due to increase in concentration of water repellent agent along with silica nanoparticles causes increase in the resistance for the slippage of yarns in both warp and weft direction. So the load applied on the fabric is beared by only the affected yarns, results in decrease in tear strength.

3.5 Effect of Concentration of TEOS, Water Repellent Agent on GSM at 0.05 Mol Ammonia Solution Catalyst.

"Table 7- Effect of Concentration of TEOS, Water Repellent Agent on GSM at 0.05 Mol Ammonia Solution Catalyst"

	Values of GSM at 0.05 mole Ammonia Solution catalyst																	
TEOS (mole)	**0.2**						**0.4**						**0.6**					
Conc. (g/l)	15	20	25	30	35	40	15	20	25	30	35	40	15	20	25	30	35	40
GSM	123	125	127	128	129	130	123	124	126	127	129	130	124	125	127	128	129	130



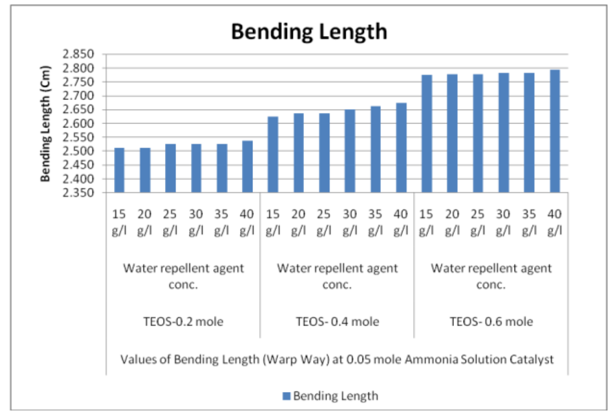
"Figure 5- Effect of Concentration of TEOS, Water Repellent Agent on GSM at 0.05 Mol Ammonia Solution Catalyst".

The Table 7 and Figure 5 shows that the concentration of water repellent agent increases from 15 gpl to 40 gpl, also the concentration of TEOS increases from 0.2 mol to 0.6 mol at fixed concentration ammonia solution of 0.05 mol. It was observed that for 0.2 mol TEOS the GSM increases from 123 to 130 for water repellent agent concentration of 15 gpl to 40 gpl respectively, while for 0.4 mol TEOS the GSM increases from 123 to 130 for water repellent agent concentration of 15 gpl to 40 gpl respectively & the increase in GSM of 124 to 130 was observed for 15 gpl to 40 gpl in case of 0.6 mol TEOS. This increase in GSM may be because of increase in mass per unit area with increase in concentration of water repellent agent along with silica nanoparticles.

3.6 Effect of Concentration of TEOS, Water Repellent Agent on Bending Length at 0.05 Mol Ammonia Solution Catalyst

"Table 8. Effect of Concentration of TEOS, Water Repellent Agent on Bending Length at 0.05 Mol Ammonia Solution Catalyst" .

	Values of Bending Length at 0.05 mole Ammonia Solution catalyst																	
TEOS (mole)	**0.2**						**0.4**						**0.6**					
Conc. (g/l)	15	20	25	30	35	40	15	20	25	30	35	40	15	20	25	30	35	40
Bending Length (Cm)	2.513	2.513	2.525	2.525	2.525	2.538	2.625	2.637	2.637	2.650	2.662	2.675	2.775	2.778	2.778	2.781	2.781	2.793



"Figure 6. Effect of Concentration of TEOS, Water Repellent Agent on Bending Length at 0.05 Mol Ammonia Solution catalyst" .

The Table 8 and Figure 6 shows that the concentration of water repellent agent increases from 15 gpl to 40 gpl, also the concentration of TEOS increases from 0.2 mol to 0.6 mol at fixed concentration ammonia solution of 0.05 mol. It was observed that for 0.2 mol TEOS the bending length increases from 2.513 to 2.538 for water repellent agent concentration of 15 gpl to 40 gpl respectively, while for 0.4 mol TEOS the bending length increases from 2.625 to 2.675 for water repellent agent concentration of 15 gpl to 40 gpl respectively & the increase in bending length of 2.775 to 2.793 was observed for 15 gpl to 40 gpl in case of 0.6 mol TEOS. This is may be because of increase in mass per unit area with increase in concentration of water repellent agent & due to the lower flexibility of the inorganic silica nanoparticles. As the concentration increases' binding of fibers & yarns goes on increasing results in increase in stiffness of fabric so bending length. The increase in bending length from 0.2 mol TEOS to 0.6 mol TEOS may be due to the silica nanoparticles with higher concentration.

3.7 Characterization.

The surface morphology was characterized by scanning electron microscope (SEM). It was observed that the cotton fabric treated with silica nanoparticles showed the scaly appearance on the surface, which made the surface rougher & enhance the water repellency. Also the scanning electron micrographs showed the change of the surface geometry of the cotton fabric. The figure 7 shows the SEM images of cotton fabric treated with silica nanoparticles & figure 8 shows the SEM images of cotton fabric treated with both silica nanoparticles and water repellent agent (40 gpl) using recipe 1. The figure 8 shows SEM images that the water repellent agent forms a waxy layer on the silica nanoparticles as like lotus leaves. Here silica nanoparticles act as an epidermal cells and forms rougher surface which is the necessity of the super water repellent finishes.

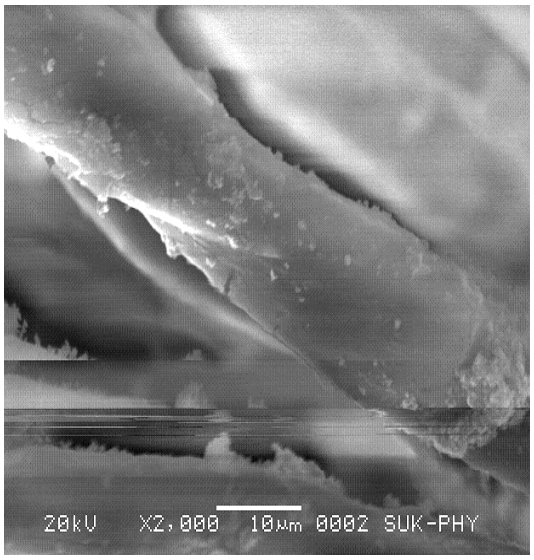


Figure 7. SEM Image of Cotton Fabric Treated with Silica Nanoparticles.

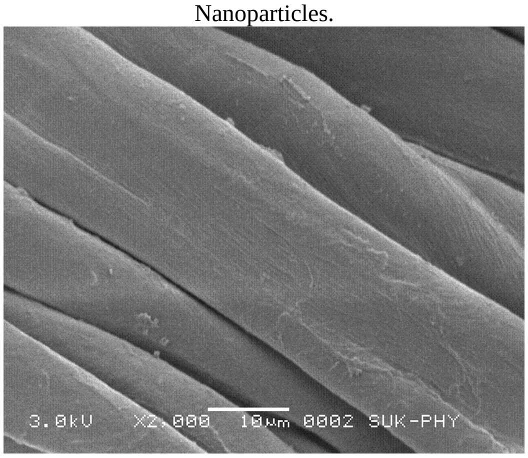


Figure 8. SEM Image of Cotton Fabric Treated with Both Silica Nanoparticles and Water Repellent Agent.

"4. Conclusion"

From this we can conclude that, silica nanoparticles synthesized by using the alkaline hydrolysis of the tetraethyl orthosilicate followed by the dehydration, condensation reaction through a typical Stober method. It is one of the excellent methods to impart superhydrophobicity. The hydrophobic modification of the cotton fabric was done by the combination of silica nanoparticles and water repellent agent finish. It was observed that the spray rating of 90 was shown by all the fabrics treated with the combination of silica nanoparticles at the concentration of water repellent agent 15 gpl. The fabric finished using first recipe shows the spray rating of 100 for 35 gpl & 40 gpl concentration of water repellent agent. This indicates that the silica nanoparticles help in imparting rougher surface on the cotton fabric. Also there was decrease in air permeability and increase in hydrostatic head pressure and decrease in tearing strength, increase in GSM & bending length was observed as the concentration of water repellent agent increased.

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