CELLULOSE CHEMISTRY AND TECHNOLOGY

SYNTHESIS, CHARACTERIZATION AND APPLICATION OF SILICA NANOPARTICLES ON COTTON FABRICS FOR ENHANCED FLAME RETARDANCY AND HYDROPHILICITY

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The sol-gel method was employed to synthesize silica nanoparticles on cotton fabric using two precursors: tetraethyl orthosilicate (TEOS) and sodium silicate, under acidic and basic conditions, in order to compare their effects on the fabrics' properties. This method aimed to simplify the synthesis process, thereby reducing the number of steps and associated costs. Additionally, the physical and chemical properties of the treated fabrics were studied. Various analytical techniques were used to evaluate the properties, including the water drop test, X-ray diffraction (XRD), inductively coupled plasma (ICP), and scanning electron microscopy (SEM). The flame-retardant properties were also investigated through the char yield method. Morphological analysis showed that the nanoparticles were spherical, and the acidity or alkalinity of the medium influenced particle formation. The use of acid or base as a catalyst affected nanoparticle formation. XRD patterns revealed typical broad peaks, indicating the amorphous nature of the synthesized nanoparticles. ICP analysis confirmed the stability of nanoparticles on the fabrics after washing. *In situ* synthesis of SiO_2 nanoparticles significantly enhanced the fabric's flame retardant properties, although the residual char increased. The water drop test demonstrated an improvement in the fabric's hydrophilic properties. The mechanical properties of the treated fabrics were examined and the properties were generally improved.

Keywords: SiO_2, nanoparticle, sol-gel, cotton, tetraethyl orthosilicate, sodium silicate

INTRODUCTION

Nanoscience and technology refer to the ability to control matter at the nanometer scale and exploit the properties and phenomena associated with this dimension in materials, tools, and systems. It represents a new approach in the production of products needed by humans. Nanotechnology has a significant impact on all modern products. Manufacturing is essentially about arranging atoms. The current products in the world will undergo a fundamental transformation if we can combine atoms with greater precision, flexibility, and reduced costs.

In recent years, biological methods have been used to produce metal oxides, such as titanium dioxide (TiO_2) and zinc oxide (ZnO) nanoparticles, which possess photocatalytic, antimicrobial, and other properties. Among various uses, such nanomaterials have been increasingly applied to enhance the flame resistance and mechanical performance of cotton fabrics. Studies using N-methylol dimethylphosphonopropionamide (Pyrovatex) with melamine resin, phosphoric acid, and ZnO or nano-ZnO co-catalysts have shown that co-catalysis and plasma pretreatment improve compressional recovery and tensile strength, while neutralization minimizes the adverse effects of acidic finishing. Furthermore, the incorporation of TiO_2 as a co-catalyst enhances crosslinking efficiency and flame retardancy, though higher curing temperatures may adversely affect fabric softness and handle.

Silicon is the most abundant element in the Earth's crust, followed by oxygen. In nature, silicon exists as an oxide, either in its free form or in the form of silicates. Over the past decade, due to the widespread application of silica nanoparticles, extensive research has been conducted on the production of these nanoparticles.[1-5] Silica nanoparticles have special mechanical, optical, electronic, and physicochemical applications. These particles are used as catalysts,[6-8] gas absorbers,[9] heavy metal ion absorbers,[10] mineral carriers,[11] drug carriers,[12] semiconductors,[13-14] and polymer additives, including in plastics and rubber.[15] Recently, nano-silica has been produced in the form of spherical nano-powders,[16] porous nano-powders,[1] nano-tubes,[17] and thin films,[18] depending on the specific applications.

Various researchers have employed the sol-gel method in different ways. In some cases, stabilizers such as surfactants are used in the sol-gel process. These surfactants can be either synthetic (chemical) or natural. Surfactant substances are amphiphilic molecules that, when placed at the interface between two phases with different polarities, reduce the surface and interfacial tension, leading to the formation of microemulsions due to partial dissolution of the organic phase in water, or water in the organic phase. Natural surfactants have the advantage of biodegradability, while retaining the capabilities of chemical surfactants.[19] In the sol-gel process, the primary raw materials are mixed with initiators to prepare the colloid, which contains a metal or quasi-metal surrounded by various ligands (excluding metals bound to other metal atoms).[20] Alkoxides are a group of primary raw materials widely used in sol-gel process research and are the best precursors for preparing sol-gel coatings. Metal alkoxides are organometallic compounds that have an organic ligand attached to a metal. Examples of such alkoxides include tetraethoxysilane or tetraethyl orthosilicate.[21] Chemical synthesis of the powder can enhance chemical uniformity and purity, and reduce processing temperature, as the mixing of raw materials is performed in a solution state, resulting in fine particles. Chemical methods have advantages in terms of chemical uniformity and controllability of parameters, which allow for the control of particle nucleation and growth, compared to most physical methods. Key control parameters in this method include temperature, substance concentration, additives, solvents, and pH. However, there are limitations in selecting suitable materials and the possibility of impurities in these methods. The sol-gel chemical method also utilizes the liquid phase to produce materials. Among methods that use the liquid phase to produce nanoparticles, this method is the most widely used.[22]

The sol-gel process typically involves mixing metal alkoxides with initiators to form colloidal suspensions. These alkoxides, such as tetraethyl orthosilicate (TEOS), are organometallic compounds containing organic ligands attached to a metal atom.[23] In this study, sodium silicate was also used directly in the sol-gel method, alongside these conventional precursors. The results were compared to evaluate the amount of silica nanoparticles produced from each material and to assess their effects on the properties of cotton fabric. In essence, this work extends and complements previous research. The chemical synthesis of silica nanoparticles through the sol-gel technique enables precise control over particle size and distribution, which is crucial for a wide range of applications. Parameters, such as temperature, concentration, additives, solvents and pH, play critical roles in governing particle formation.

EXPERIMENTAL

Materials

Desized, scoured, and bleached plain weave 100% cotton fabric, with 36 and 26 wefts/cm, was supplied by the Momtaz Fabrics Company (Tehran, Iran). The precursors used were tetraethyl orthosilicate [$Si(OC_2H_5)_4$ (TEOS)] and sodium silicate (Na_2SiO_3), both purchased from Merck, Germany. Ethanol (CH_3CH_2OH), ammonia (NH_3, >70%), and hydrochloric acid (HCl, 37%) were also sourced from Merck, Germany. All chemicals were used without further purification, and distilled water was employed throughout the experiment.

Sample preparation and synthesis of SiO_2 nanoparticles

Three methods were used for synthesizing SiO_2 nanoparticles. Cotton fabric samples were immersed in the prepared solutions and treated accordingly.

Solution 1: To prepare Solution 1, 31.3 mL of ethanol was mixed with 38.3 mL of distilled water for 15 minutes, stirred at high speed (pH: 6.56). Then, 30.3 mL of tetraethyl orthosilicate (TEOS) was added and stirred vigorously for one hour. Hydrochloric acid was added to adjust the pH to 2.74.

Solution 2: Solution 2 was prepared by mixing 13.3 mL of TEOS with 37.5 mL of ethanol, stirred for 15 minutes. Then, 11.8 mL of distilled water and 0.3 mL of ammonia were added to the solution, followed by stirring for another 15 minutes. The resulting solution was added to Solution 1 and stirred for 3 hours (pH: 8.20).

Solution 3: To prepare Solution 3, 15 mL of sodium silicate was mixed with 85 mL of distilled water to make a 15% solution. Then, 97 mL of distilled water was added, and 100 mL of diluted sodium silicate was mixed with 1 gram of cetyltrimethylammonium. The mixture was stirred at 55 °C (pH: 11.73). Hydrochloric acid was added gradually to reduce the pH to 3.0-3.5.

Characterization techniques

The morphology of the SiO_2 nanoparticles and treated cotton fabrics was examined using scanning electron microscopy (SEM; EM3200, KYKY, China), at an accelerating voltage of 30 kV. Samples were precoated with gold using a sputter coater. Inductively coupled plasma (ICP) spectroscopy was used to analyze the elemental composition of the samples. The ICP relies on the fact that excited electrons emit energy at the irradiated wavelength, which was done in the ICP by the hot argon plasma. The crystallinity and structural properties of the synthesized SiO_2 were characterized by X-ray diffraction (XRD) using Cu-Kα radiation at 40-60 kV and 200 mA (PANalytical X'pert pro MPD, Netherlands).

The influence of nanosilica particles on the flame-retardant, hydrophilicity and mechanical properties of the fabric was investigated using standardized testing methods. Flame-retardant properties were evaluated by measuring the char yield of the samples, which was calculated using Equation 1:

$$\text{Char yield} = \frac{W2}{W1} \times 100 \qquad (1)$$

where w_1 is the initial weight of the fabric, and w_2 is the weight after complete burning.

The wettability of the fabric was assessed by measuring the absorption time for four drops of distilled water.

Prior to mechanical testing, the samples were dried and conditioned at 65 ± 2% relative humidity and 27 ± 2 °C. For the tensile strength test, fabric samples measuring 2 cm × 8 cm were tested at a traversing speed of 100 mm/min to determine the breaking load, breaking elongation, stress, and strain. The test was conducted in accordance with British Standard B.S. 2576:1959.

The tearing strength of treated and untreated cotton fabric samples was determined using a pendulum-type (Elmendorf) tearing strength tester. Testing was performed under standard atmospheric conditions (65 ± 2% relative humidity and 27 ± 2 °C), in accordance with ASTM D1424–1996.

The crease recovery angle was measured according to AATCC Test Method 66–2003. Test specimens were folded and compressed under controlled conditions with a specified force to produce a defined crease. Each specimen was then suspended in the recovery tester to allow controlled recovery, and the recovery angle was measured after the specified time interval.

RESULTS AND DISCUSSION

The methods used in this research to characterize the samples and analyze their properties in terms of performance included scanning electron microscopy (SEM), X-ray diffraction (XRD), inductively coupled plasma (ICP), char content analysis of fabrics, the water drop test and mechanical testing.

Scanning electron microscopy (SEM)

SEM analysis was conducted to observe the morphology of the sample and determine the size of the nanoparticles. A comparison of the SEM images of SiO_2 nanoparticles' surfaces, synthesized with different concentrations of the tetraethyl orthosilicate precursor, along with acidic and basic agents in the reaction process, is presented. Additionally, a precursor substance, liquid sodium silicate, was used. SEM images of Samples 1 to 3 are presented in Figures 1-3, respectively. As mentioned earlier, in the case of Sample 1, the acidic agent used in the reaction consisted of 30.30 mL of tetraethyl orthosilicate precursor and one drop of hydrochloric acid. For Sample 2, the basic agents in the reaction consisted of 13.30 mL of tetraethyl orthosilicate precursor and 0.3 mL of liquid ammonia. For Sample 3, 15 mL of liquid sodium silicate was used as precursor, as previously described. The formation of nanoparticles was influenced by the use of the acid or base as a catalyst in the reaction, as demonstrated by comparing Figure 1 to Figure 2. Due to the repulsive forces, the particles are separated in the presence of the base catalyst, while in the acid catalyst, the particles tend to form larger aggregates by sticking together. The spherical and uniform characteristics of the silica nanoparticles formed with tetraethyl orthosilicate precursors and liquid sodium silicate, can be observed in Figures 1 to 3.

X-ray diffraction

The structural analysis of the synthesized nanoparticles was conducted using XRD, in the 2θ range from 10° to 80° (step size of 0.20°). The diffraction patterns are shown in Figures 4-6. At 2θ = 22°, a typical broad peak is observed, indicating the amorphous nature of the synthesized nanoparticles. This is due to an incomplete internal structure or smaller particle size, in contrast to spherical nanoparticles. The diffraction patterns analyzed using X'pert software provided the following information:

Sample 1: nanoparticles exhibited an amorphous form, with a peak at 2θ = 21.71°;

Sample 2: nanoparticles were also found to be amorphous, with a peak at 2θ = 22.17°;

Sample 3: a sharp peak was observed at 2θ = 31.74°, indicating crystallinity.

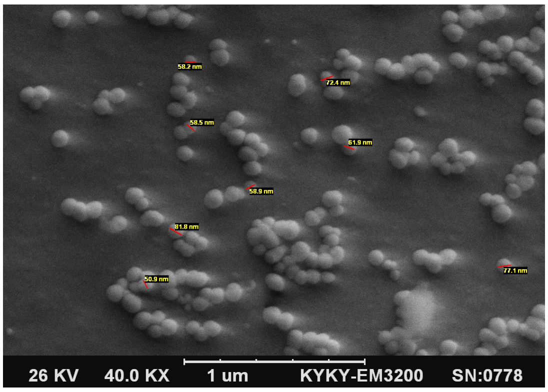

Figure 1: SEM image of silica nanoparticles formed with TEOS precursor and acid catalyst, average size of nanoparticles = 64 nm (Sample 1)

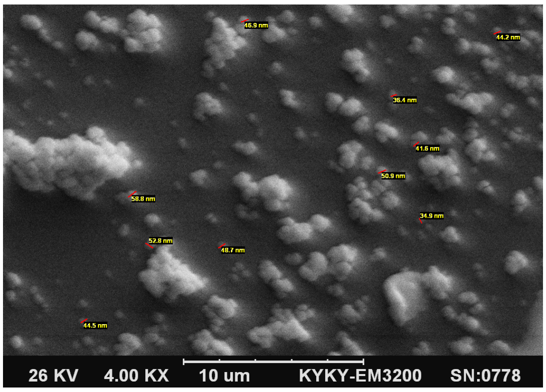

Figure 2: SEM image of silica nanoparticles formed with TEOS precursor and basic catalyst, average size of nanoparticles = 46 nm (Sample 2)

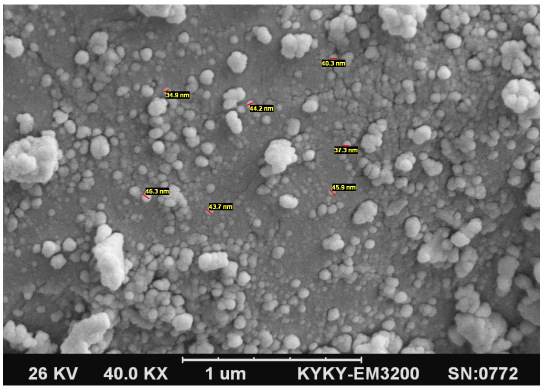

Figure 3: SEM image of silica nanoparticles formed with sodium silicate liquid precursor and acid catalyst, average size of nanoparticles = 42 nm (Sample 3)

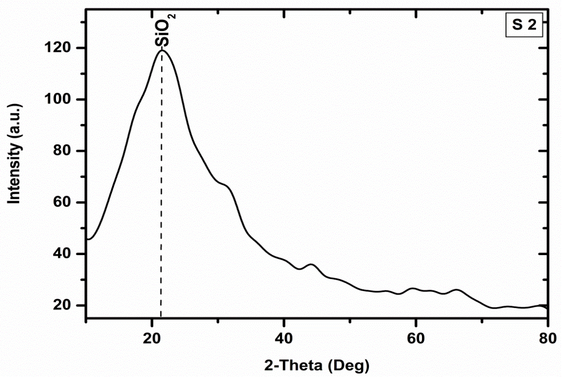

Figure 4: XRD pattern of Sample 1

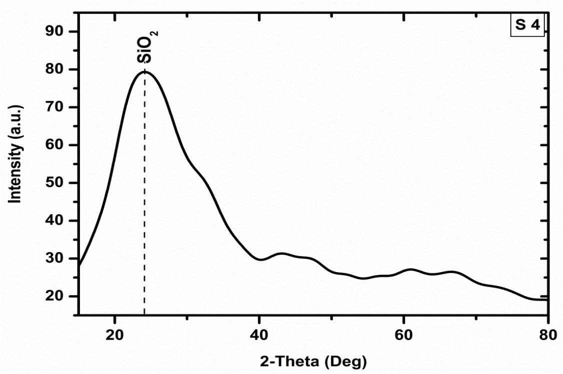

Figure 5: XRD pattern of Sample 2

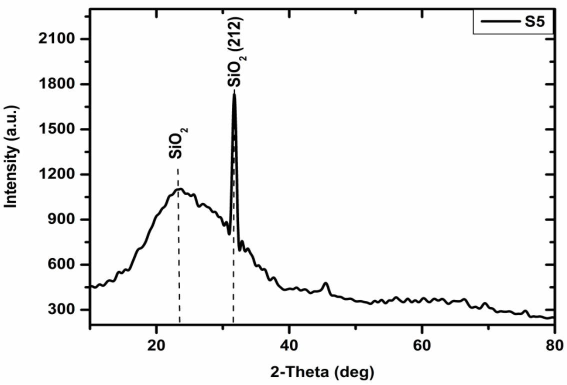

Figure 6: XRD pattern of Sample 3

Table 1
Analysis of X-ray diffraction patterns for Samples 1-3

Sample	2θ (deg.)	β	D (nm)	Number card	Oxide	Hkl	I (%)	Structure crystal
S_1	21.71			00-076-0931	SiO_2	__	100	Cubic
S_2	22.17			00-081-0066	SiO_2	011	100	Hexagonal
S_3	23.91			00-047-0715	SiO_2	---	31.68	Amorphous
S_3	31.74	0.28	30	00-047-1300	SiO_2	212	100	Tetragonal

The Debye-Scherrer equation was used to calculate the nanoparticle size as follows:

$$D = K\lambda/\beta \cos\theta \quad (2)$$

where D is nanoparticle crystallite size in nanometers, λ is the wavelength of the X-ray radiation (0.154 nm), β is the full width at half maximum (FWHM) of the peak, which should be entered in radians, K is a constant that depends on the shape of the particles, θ is the Bragg angle, which is half of the value measured on the diffraction pattern's horizontal axis.

The Debye-Scherrer equation suggests that the nanoparticle size is 30 nm, and the particles exhibit a tetragonal structure.

The data resulting from diffraction pattern analysis for all three samples are tabulated in Table 1.

It is important to note that the XRD method provides the grain size, not the particle size. Therefore, SEM results are generally more accurate than XRD results. The two methods will yield the same results only when the particle consists of a single grain. Also, the patterns reveal a clear difference in the peaks of Sample 3.

Inductively coupled plasma optical emission spectrometry

ICP-OES is one of the most important instrumental methods for elemental analysis. This method allows the measurement of approximately 70 elements from the periodic table, with detection limits in the ppb range, in various samples, such as soil, water, metals, ceramics, and organic materials. The technique is based on the excitation of electrons from different elements in a plasma environment, and high-accuracy results are obtained through the emission of light after the electrons return to their ground state, owing to its adaptability and reproducibility.

After 20 wash cycles of the cotton fabrics at 300 °C for 4 minutes, ICP analysis was employed to measure the amount of remaining SiO_2 nanoparticles on the samples. The results were presented in Table 2. Upon comparison, it was observed that Sample 1 had the highest content of SiO_2, followed by Sample 3, and then Sample 2. These results indicate that the stability of the particles to washing is highest in Sample 2. Additionally, this arrangement demonstrates that the amount of precursor is directly related to the stability of nanoparticles on fabrics after washing. As observed in Samples 1 and 2, it can be concluded that a higher amount of precursor leads to increased nanoparticle stability on the fabrics during washing.

Water drop test

The water drop test was used to assess the hydrophilicity of the samples. In this process, drops of a controlled size were placed at a constant rate onto the fabric surface, and the time required for the water to penetrate the fabrics was measured.

The absorption times for the samples were recorded and are presented in Table 3.

By comparing the time it takes for water drops to penetrate the raw fabric and Samples 1 to 3, it was found that the absorption time for the raw fabric is much longer than for the fabrics of Samples 1 to 3. This indicates that fabrics impregnated with SiO_2 nanoparticles develop a highly hydrophilic surface. The results suggest that changes in the type and concentration of the precursor do not significantly affect this outcome. Overall, it can be concluded that the use of SiO_2 nanoparticles improves the water hydrophilicity and durability of fabrics against washing.

Table 2
Inductively coupled plasma (ICP) analysis results

Sample	El	Wavelength	Calc. conc.	Unit
1	Si	251.611	94546	ppm
2	Si	251.611	15094	ppm
3	Si	251.611	21200	ppm

Table 3
Absorption time of cotton fabrics

Sample	Time (s)
Untreated sample	3602
S_1	1
S_2	1
S_3	1

Table 4
Char content of the samples

Sample	Size (cm)	W_1 (g)	W_2 (g)	Char yield (%)
Untreated cotton (no washing)	3×3.2	0.197	0.01	5.076
S_1 (no washing)	3×3.2	0.439	0.389	88.610
S_2 (no washing)	3×3.2	0.233	0.151	67.713
S_3 (no washing)	3×3.2	0.248	0.245	98.790
Untreated cotton (after washing)	3×3.2	0.298	0.002	0.671
S_1 (after washing)	3×3.2	0.425	0.324	76.235
S_2 (after washing)	3×3.2	0.217	0.134	61.751
S_3 (after washing)	3×3.2	0.229	0.018	7.860

Char content of fabrics

The char yield of both unwashed and washed samples (washed once) was calculated and reported in Table 4. By calculating the amount of ash remaining in the fabrics before and after washing, it was observed that the percentage of ash in the fabrics impregnated with silica nanoparticles was higher than that in the raw fabric. This demonstrates that the silica nanoparticles impart a slow ignition and flame-retardant property to the fabric. Sample 3 exhibited the highest percentage of ash, indicating it had the most significant flame retardant properties. The order of flame retardant properties, based on the comparison of unwashed samples, is the following: Sample 3 > Sample 1 > Sample 2.

Notably, Sample 1 showed the longest complete burning time compared to the other samples. After the samples were washed once, Sample 1 still retained a high percentage of ash, while Sample 3 had the lowest. After washing, the flame retardant properties of all the samples decreased, Sample 3 showing the most significant reduction in flame resistance. The comparison between unwashed and once-washed samples indicated that the flame-retardant performance of Sample 3 was reduced significantly after washing. However, the silica nanoparticle-treated fabrics exhibited a relatively higher percentage of ash than untreated cotton, confirming that the incorporation of SiO_2 nanoparticles improves the flame-retardant properties of cotton fabrics.

Effects of silica nanoparticles on the mechanical properties of cotton fabric

The changes in the mechanical properties of nano-silica–loaded cotton fabrics were evaluated, specifically, the tensile strength, tearing strength and crease recovery angle, were tested and compared with those of untreated cotton fabric.

Table 5
Tensile strength of treated and untreated cotton fabrics

Sample	Tensile strength (N)							
	Warp direction				Weft direction			
	Breaking load (N)	CV%	Extension (mm)	CV%	Breaking load (N)	CV%	Extension (mm)	CV%
S1	344.96	5.2	15.5	5.3	197.372	6.5	24.6	6.3
S2	534.1	4.3	20.7	4.4	356.72	5.1	36.5	5.6
S3	525.2	6.7	19.9	5.9	372.3	5.6	38.2	5.3
Untreated	507.98	3.1	19.5	3.7	344.2	4.2	30.4	4.6

Tensile strength

The results presented in Table 5 show that the incorporation of silica nanoparticles into the fiber structure leads to an improvement in the load-bearing capacity of the fibers, regardless of the application method. However, samples treated in an acidic environment exhibited a reduction in mechanical properties compared to untreated fabric due to the susceptibility of cotton fibers to acid. Overall, the mechanical performance of fabrics treated with silica nanoparticles was enhanced.

Tearing strength

The tearing strength of nano-silica treated cotton fabrics was evaluated using the Elmendorf method. As shown in Table 5, the incorporation of silica nanoparticles generally improved the tearing resistance of the fabrics compared to untreated cotton. Similarly to the tensile strength results, fabrics treated under acidic conditions exhibited slightly lower tearing strength, which can be attributed to the weakening effect of the acid on cotton fibers. Overall, the nano-silica treatment enhanced the fabric’s resistance to tearing.

Crease recovery angle

The crease recovery angle of the fabrics increased after the nano-silica treatment, indicating improved dimensional stability and resilience. The effect was more pronounced in samples treated under alkali conditions, while acidic treatment showed a marginal reduction in recovery angle, compared to the untreated cotton. These results suggest that silica nanoparticles contribute to enhanced fabric recovery from folding stress (Fig. 7).

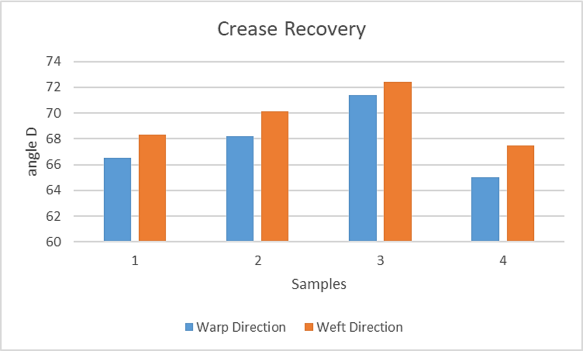

Figure 7: Crease recovery results for Samples 1-3 and the control (4)

CONCLUSION

In this study, the sol-gel method was employed to synthesize silica nanoparticles, which were then impregnated into cotton fabrics. The nanoparticles were synthesized simultaneously using tetraethylorthosilicate (TEOS) and liquid sodium silicate as precursors, while controlling the pH. Various characterization techniques, including X-ray diffraction (XRD), scanning electron microscopy (SEM), inductively coupled plasma

(ICP), water drop tests, and char yield tests, were used to identify and confirm the presence of the nanoparticles on the surface of the textiles and to assess their effect on the properties of cotton fabrics.

XRD analysis revealed that the nanoparticles in Samples 1 and 2 had an amorphous structure, while Sample 3 exhibited a tetragonal crystalline structure. SEM imaging showed that the nanoparticles were spherical in shape, with no significant difference in size between the samples, despite the variation in precursors. The catalyst (acidic or basic) influenced the formation and agglomeration of the nanoparticles, with acidic catalysts leading to larger agglomerates, while basic catalysts caused the particles to remain separated.

ICP analysis demonstrated that the nanoparticles remained on the fabric even after washing, indicating good stability. The water drop test confirmed that all the samples exhibited superhydrophilic properties, with significantly reduced water absorption times compared to the untreated fabric. The char yield test indicated that the silica nanoparticles enhanced the flame-retardant properties of the cotton fabrics, with Sample 3 exhibiting the highest flame resistance. However, washing the samples reduced their flame-retardant performance.

Overall, the study demonstrates that the impregnation of cotton fabrics with silica nanoparticles enhances their flame-retardant and hydrophilic properties. Additionally, the stability of the nanoparticles against washing is influenced by the precursor concentration and the catalyst type. The sol-gel method proves to be an effective approach for preparing silica nanoparticle-treated fabrics with improved functional properties. It can be concluded that the use of SiO_2 nanoparticles not only improves the hydrophilicity and durability of fabrics to washing, but also enhances their functional properties, making them more resistant to wear and degradation during multiple washes. The changes in the mechanical properties (*i.e.* tensile strength, tearing strength, and crease recovery angle) of nano-silica treated cotton fabrics were evaluated, and compared with those of untreated cotton fabric. Overall, the mechanical performance of fabrics treated with silica nanoparticles was enhanced.

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REFERENCES

[1] W. Stöber, A. Fink and S. Bohn, *J. Colloid Interface Sci.*, **26**, 62 (1968), https://doi.org/10.1016/0021-9797(68)90272-5

[2] X. Ding, K. Yu, Y. Jiang, H. Bala, H. Zhang *et al.*, *Mater. Lett.*, **58**, 3618 (2004), https://doi.org/10.1016/j.matlet.2004.07.008

[3] M. S. Morey, J. D. Bryan, S. Schwarz and G. D. Stucky, *Chem. Mater.*, **12**, 3453 (2000), https://doi.org/10.1021/cm001001t

[4] Y. L. Lam, C. W. Kan and C. W. M. Yuen, *Fiber Polym.*, **15**, 1880 (2014), https://doi.org/10.1007/s12221-014-1880-6

[5] C. K. Poon and C. W. Kan, *Fiber Polym.*, **17**, 380 (2016), https://doi.org/10.1007/s12221-016-5809-0

[6] M. O. Coppens, J. Sun and T. Maschmeyer, *Catal. Today*, **69**, 331 (2001), https://doi.org/10.1016/S0920-5861(01)00386-8

[7] D. Zahao, P. Yang, Q. Huo, B. F. Chemelka and G. D. Stucky, *Curr. Opin. Solid State Mater. Sci.*, **3**, 111 (1998), https://doi.org/10.1016/S1359-0286(98)80073-9

[8] J. Y. Ying, C. P. Mehnert and M. S. Wong, *Angew. Chem. Int. Ed.*, **38**, 56 (1999), https://doi.org/10.1002/(SICI)1521-3773(19990115)38:1/2<56::AID-ANIE56>3.0.CO;2-E

[9] H. P. Lin and C. Y. Mou, *Acc. Chem. Res.*, **35**, 927 (2002), https://doi.org/10.1021/ar000074f

[10] K. Okada, A. Shimai, T. Takei, S. Hayashi, A. Yasumori *et al.*, *Micropor. Mesopor. Mater.*, **21**, 289 (1998), https://doi.org/10.1016/S1387-1811(98)00015-8

[11] B. Lee, Y. Kim, H. Lee and J. Yi, *Micropor. Mesopor. Mater.*, **50**, 77 (2001), https://doi.org/10.1016/S1387-1811(01)00437-1

[12] F. He, R. X. Zhuo, L. J. Liu, D. B. Jin, J. Feng *et al.*, *React. Funct. Polym.*, **47**, 153 (2001), https://doi.org/10.1016/S1381-5148(01)00027-X

[13] J. F. Chen, H. M. Ding, J. X. Wang and L. Shao, *Biomaterials*, **25**, 723 (2004), https://doi.org/10.1016/S0142-9612(03)00566-0

[14] Z. Zhang, S. Dai, X. Fan, D. A. Blom, S. J. Pennycook *et al.*, *J. Phys. Chem. B.*, **105**, 6755 (2001), https://doi.org/10.1021/jp010541q

[15] A. Jain, S. Rogojevic, S. Ponoth, N. Agarwal, I. Matthew *et al.*, *Thin Solid Films*, **398-399**, 513 (2001), https://doi.org/10.1016/S0040-6090(01)01311-6

[16] H. D. Jang, *Powder Technol.*, **119**, 102 (2001), https://doi:10.1016/S0032-5910(00)00407-1

[17] W. Zhu, Y. Han and L. An, *Micropor. Mesopor. Mater.*, **84**, 69 (2005), https://doi.org/10.1016/j.micromeso.2005.04.020

[18] H. Fang, M. Zhang, W. H. Shi and T. L. Wan, *J. Non-Cryst. Solids.*, **352**, 2279 (2006), https://doi.org/10.1016/j.jnoncrysol.2006.02.057

[19] H. Van de Van, M. Vermeersch, A. Matheeussen, J. Vandervoort, W. Weyenberg *et al.*, *Int. J. Pharm.*, **420**, 122 (2011), https://doi:10.1016/j.ijpharm.2011.08.016

[20] O. Renault, A. V. Tadeev, G. Delabouglise and M. Labeau, *Sens. Actuat. B: Chem.*, **59**, 260 (1999), https://doi.org/10.1016/S0925-4005(99)00231-2

[21] C. J. Brinker and G. W. Scherer, “Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing”, Academic Press, San Diego, 2013

[22] J. Hyeon-Lee and J. G. Beaucage, *Chem. Mater.*, **9**, 2400 (1997), https://doi.org/10.1021/cm9703482

[23] Sh. Shahidi, H. Mohammadbagherloo, S. Elahi, S. Dalalsharifi and R. Mongkholrattanasit, *Key Eng. Mater.*, **891**, 37 (2021), https://doi.org/10.4028/www.scientific.net/KEM.891.37