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FLAME RETARDANCY IMPROVEMENT OF MODIFIED COTTON FABRIC BY NANOSILICA SOL COATING

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Abstract. Cotton fabric was coated by silica sol at different times using dip-coating method. Nanosilica coated fabrics were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM), Energy dispersive X-Ray spectroscopy (EDX), and Thermal gravimetric analysis (TGA). From SEM result, it showed that fabric surface was coated by nanosilica particles of 20 - 30 nm size. Nanosilica coated fabrics showed the improvement not only in flame retardancy (LOI increased from 18.4 to 30.8) but also in tear strength. Tear strength increased from 23 N/mm (cotton fabric) to 29.9 N/mm (fabric coated nanosilica at 3 times).

Keywords: nanosilica, cotton fabric, flame retardancy.

Classification numbers: 2.4.4, 2.9.4, 2.5.3.

1. INTRODUCTION

Cotton fabrics are widely used in the textile, household and industrial products such as clothing, towels, sheets etc. [1]. Cotton products have the advantage of being environmentally friendly, their mechanical properties are very good and their biodegradability is high [2, 3]. But the major drawback of cotton is its flammability with a low limiting oxygen index (LOI) of 18.4 %), therefore, the application of cotton in fire protection suits, military and aviation industries is limited [4 - 6]. Efforts to improve the fire resistance of cotton fabric have become one of the most interests of researchers. Flame-retardant cotton fabrics include four main groups: inorganic, organic halogens, organic phosphorus, and nitrogen-based materials [7, 8]. Halogen-based flame retardants have been shown to be one of the most effective ways to reduce the risk of fire, but the downside is the release of halogenated and corrosive gases during combustion [9, 10]. Phosphorus and nitrogen substances are also used for halogen-free flame retardants because of their eco-friendly by-products, and low toxicity; however, their poor flame retardant performance and poor thermal stability [11, 12] are noted. Flame retardants of inorganic nature such as nanosilica, nano alumino - silica, and nano clay are often used to cover the fabric surface

to create an insulating and fireproof protective layer and also improve the mechanical properties. Among effective inorganic flame retardants, nanosilica is of interest to research and develop because this material is environmentally friendly, non-toxic and of low cost [13 - 18].

Recently, Fei You *et al*. [19] modified fabric with nanosilica synthesized from TEOS (tetraethylorthsilicate) and showed that the fire resistance of the fabric is significantly improved (LOI index increased from 19.0 to 23.0 %). Chun Liu *et al*. [20] fabricated nanosilica fabric from organic silicon sources (TEOS and trimethylsilane) and demonstrated the enhanced thermal stability. Nanosilica is usually synthesized from organic silicon sources such as tetraorthoethyl silicate (TEOS), alkyl silane. However, due to their high cost, the use of nanosilica on a large scale is limited and difficult to compete in the market.

In this study, we synthesized silica sol by ion exchange from sodium silicate. Silica sol solution is used for coating the surface of cotton fabrics [21, 22]. Effect of nanosilica content (through number of coating times) on fire resistance (UL-94, LOI) and mechanical properties of the materials are investigated and evaluated.

2. MATERIALS AND METHODS

2.1. Chemicals, material

Sodium silicate (liquid glass) with density of 1.4 - 1.42; SiO_2 content of 27 % (Merck); 85 % potassium hydroxide (Merck), AmberliteTM IR120 ion exchange resin (Dow chemical), and cotton fabric (115 g/m^2) (Viet Nam) were used.

2.2. Synthesis of silica sol

Silica sol was synthesized by ion exchange method using resin Amberlite as ion exchanger and sodium silicate as the source of silicon. The process of synthesizing sol silica consists of the following steps [14, 15]:

Step 1: Creating a sodium silicate solution by diluting liquid glass with distilled water.

Step 2: Exchanging Na^+ ion with H^+ ion of Amberlite (ion exchange resin).

Step 3: Pouring KOH solution slowly into the mixture and adjust pH to 8 - 10 to create silicon acid (active form - newly formed).

Step 4: Continuing stirring the mixture to form a solution of 3 - 4 nm hydrosol silica suspension (at pH = 8.5 - 9).

2.3. Nanosilica coated cotton fabrics

Cut the cotton fabrics into pieces of 60 × 40 mm. Dip a cotton piece in 50 ml of 10 % silica sol solution and treat for 2 minutes in ultrasonic bath. The nano silicate coated cotton piece was dried at 80 °C for 30 minutes. For obtaining nanosilica coated cotton pieces with different SiO_2 content, cotton piece was dip-coated in several times (Nanosilica coated pieces after 1, 3, 5 and 7 coating times).

2.4. Characterization

The X-ray diffraction (XRD) measurements were performed on a D8 Advance diffractometer (Bruker, Germany) using CuK_α as radiation source, $\lambda = 0.15406$ nm, in a range of $2\theta = 10°– 80°$. The morphology of samples was examined on scanning electron microscopy (SEM) using JEOL JSM 6500F equipment. The Fourier Transform Infrared spectroscopy (FTIR)

spectra of the samples were measured by the KBr pellet method (JACOS 4700). Energy Dispersive X-Ray spectroscopy **(**EDX) spectra of samples were measured using JEOL JED-2300 spectrometer.

The fire resistance of silica sol was analyzed by means of LOI determined by the following standards: ASTM D2863, BS ISO4589-2, and mechanical properties (tear strength) was determined based on TCVN 1597.

3. RESULTS AND DISCUSSION

3.1. FTIR spectra

FTIR spectra of cotton fabric (M) and silica coated cotton fabric at 1, 3, 5 and 7 coating times are presented in Figure 1.

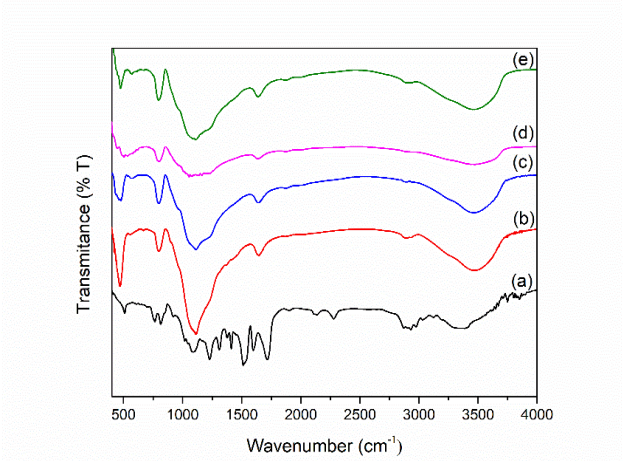

Figure 1. FTIR spectra of cotton fabric (a) and silica coated cotton fabric at 1 (b), 3 (c), 5 (d) and 7 coating times (e).

In the FTIR spectra, the band appears at 3472 cm^{-1} is assigned to the Si-O-H group of nano SiO_2 and the band at 3390 cm^{-1} is attributed to the vibration of C-OH group of cotton fabric (cellulose) [18]. The band appearing at 1646 cm^{-1} is attributed to the fluctuation vibration of group C = O. After coating a sol silica layer on fabric surface, the bands at 802 - 795 cm^{-1} and 473-467 cm^{-1} appearances are assigned to asymmetric and symmetric vibrations of Si-O-Si group, respectively.

3.2. XRD patterns

In the XRD pattern of cotton fabric (Figure 2), the diffraction peak appears at 2θ of 20.5^o (corresponding to d = 0.43 nm), which is attributed to the small crystal structure and partial arrangement of cotton string segments. With increasing nanosilica layers deposited on cotton fabric surface, the intensity of this peak decreased. This indicated the intercalation of nanosilica particles within fabric layers. No typical peaks of nanosilica structure were observed, indicating that nanosilica existed as amorphous phase.

3.3. EDX analysis

To determine the chemical composition of cotton fabric and silica sol coated fabrics, we performed the EDX analysis. EDX spectra of cotton fabric and nanosilica coated fabrics are shown in Figure 3. Chemical composition of fabric and silica coated fabrics are given in Table 1. As seen in Table 1, O and N amount sharply decreased with increasing nanosilica coating times while Si amount increased from 0 to 38.44%. It is noted that after nanosilica coating at 1 and 3 times, Si content is greatly increased and then slightly increased after nanosilica coating at 5 and 7 times. This can be explained that the silica coating at 3 times is almost saturated and the further silica coating increased the amount at low extent.

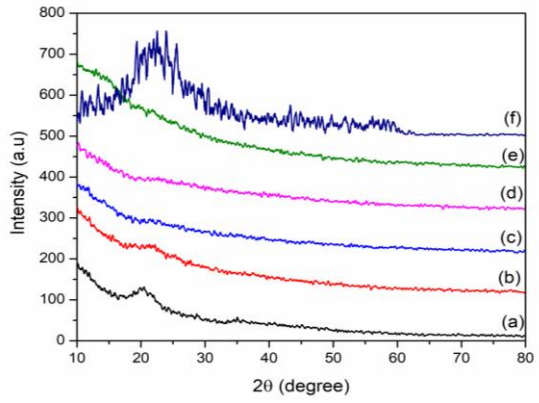

Figure 2. XRD patterns of fabric (a) and silica coated fabrics at 1 (b), 3 (c), 5 (d) and 7 coating times (e), nanosilica (f).

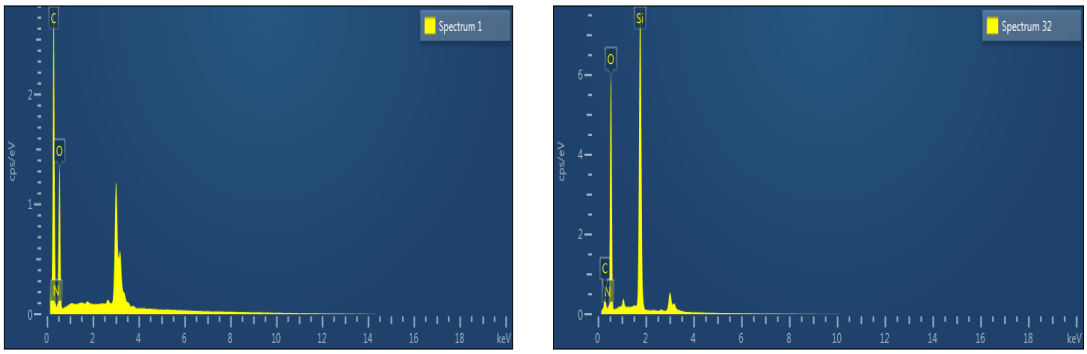

Figure 3. EDX spectra of fabric (M) and silica sol/M material samples.

Table 1. Chemical composition of fabric and nanosilica coated fabrics determined by EDX.

Sample Element	Cotton fabric (M)	M coated nanosilica at one time	M coated nanosilica at 3 times	M coated nanosilica at 5 times	M coated nanosilica at 7 times
O (weight %)	45.88	41.72	43.30	43.78	49.12
C (weight %)	38.37	30.49	17.86	15.69	7.26
N (weight %)	15.75	10.07	6.59	6.48	5.18
Si (weight %)	0.00	17.72	32.25	34.05	38.44

3.4. Thermal gravimetric analysis

To investigate the thermal stability of nanosilica coated fabrics, we performed the thermal gravimetric analysis. Weight loss and thermal differential diagrams are presented in Figure 4.

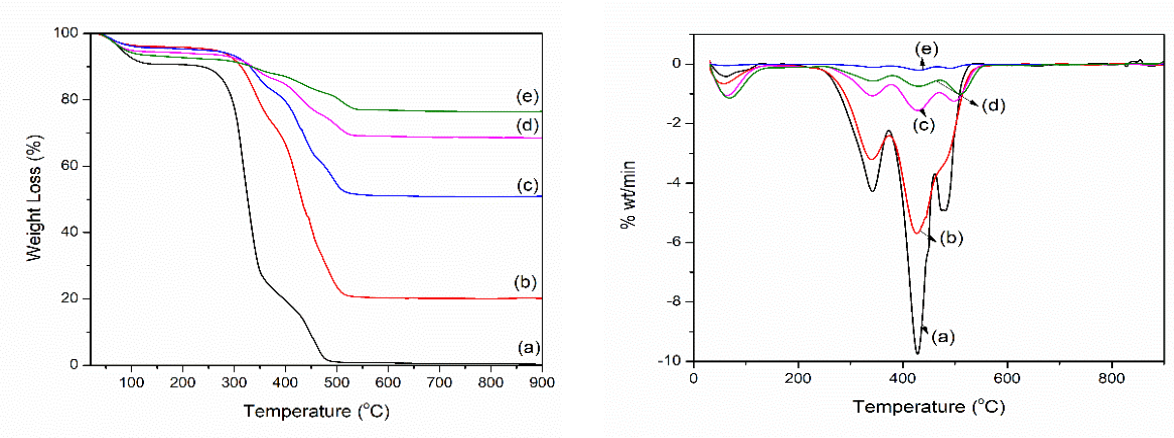

Figure 4. Weight loss of fabric and fabric coated with different silica content (A) and thermal differential diagrams (B) of cotton fabric (a) and silica coated fabric (b-e).

TGA diagrams of cotton fabric showed that the weight loss process consisted of 3 stages: physical H_2O loss at 150 ^oC, chemical H_2O loss at 350 ^oC and exothermic combustion at 450 ^oC. It's observed that weight loss of nanosilica coated fabrics proportionally decreased from 47 % weight (1 time) to 24 % weight (7 times). Note that weight loss of cotton fabric without silica coating is 99 %.

3.5. SEM images

SEM – images of cotton fabric and nanosilica coated fabric at 7 times are illustrated in Figure 5.

As seen in Figure 5, cotton fabric showed a heterogeneous structure with different pores size from several micro size (µm) to nano size (nm).

After 7 times coating with nanosilica, all pores of cotton fabric were filed up with nanosilica particles of 20-30 nm size.

3.6. Analysis results UL-94 and LOI

Table 2. UL-94 and LOI of cotton fabric and nanosilica coated fabrics.

Sample	UL - 94	LOI (vol%)
M	V-2	18.4
M-1	V-1	25.9
M-3	V-0	30.7
M-5	V-0	31.5
M-7	V-0	32.8

From Table 2, it is noted that LOI value increased with increasing the silica coating times. Thus, LOI of cotton fabric is 19.5 and LOI values of nanosilica coated fabrics at 1, 3, 5 and 7

times are 23.7, 30.7, 31.5 and 32.8, respectively. From this result, it can be concluded that after 3 times of nanosilica coating, nanosilica coated fabric reached the required quality of flame retardant fabrics. Further increase of nanosilica coating is not necessary since LOI value slightly increased only at small extent after 5 and 7 times of nanosilica coating.

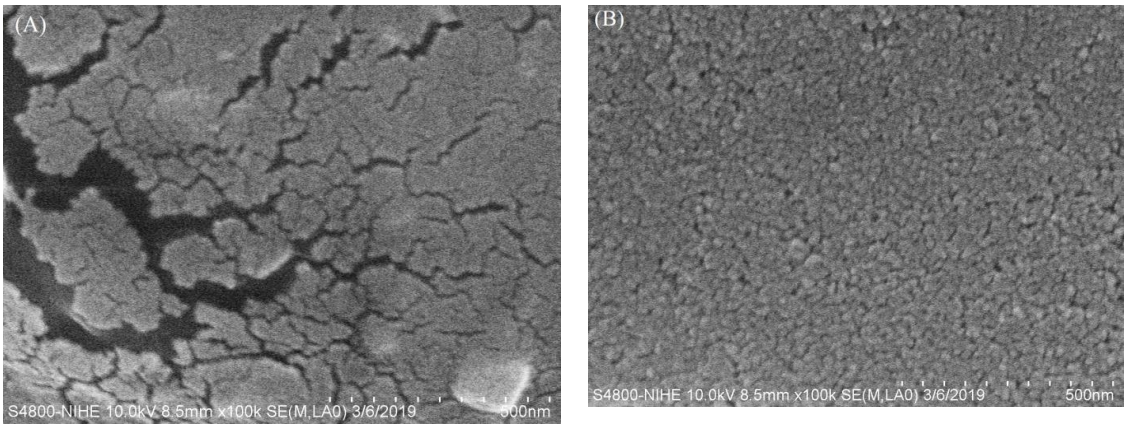

Figure 5. SEM images of fabric (A) and fabric coated nanosilicate at 7 times (B).

3.7. Mechanical properties of materials

Mechanical properties cotton fabric and nanosilica coated fabrics are also investigated. One of the most important properties for fabrics quality is a tear strength. The tear strength of fabric and nanosilica coated fabric are listed in Table 3.

Table 3. Tear strength of fabric and nanosilica coated fabric at 1, 3, 5 and 7 times.

Sample	Tear strength (N/mm)
M	23.52
M-1	30.79
M-3	29.97
M-5	28.46
M-7	26.81

As seen in Table 3, tear strength of cotton fabric increased from 23.52 N/mm to 30.79 N/mm after 3 times of nanosilica coating. Thus, further coating nanosilica layer leaded to agglomeration of nanosilica particles which are easily broken. Further increase of nanosilica coating caused the decrease of tear strength. This result shows that the tear strength of nanosilica coated fabrics is improved.

4. CONCLUSIONS

By coating silica sol with different SiO_2 content on cotton fabrics, the flame retardancy of cotton fabric is improved. LOI value increased from 19.5 to 32.8 %. It is found that cotton fabric with 32 % SiO_2 coating (nanosilica coating at 3 times) reached the required quality of flame retardant fabrics (LOI of 30.2). Nanosilica coated fabrics showed the improvement not only in

the flame retardancy (LOI of 30.8) but also in the tear strength. Tear strength increased from 23.52 N/mm (cotton fabric) to 29.97 N/mm (fabric coated nanosilica at 3 times).

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