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Original Article

High flame retardant performance of SiO_2-TiO_2 sol coated on polyester/cotton fabrics

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Abstract: SiO_2 and TiO_2 sols were successfully synthesized by using sodium silicate and titanium chloride as Si and Ti sources. SiO_2-TiO_2 sol coated polyester/cotton fabric was fabricated by deep-coating method and using SiO_2, TiO_2 sols as coating materials. SiO_2-TiO_2 coated fabric were characterized by XRD, FTIR, TGA, SEM and EDX. From SEM image, it showed the SiO_2, TiO_2 particles of 20-30 nm which well deposited on fabric surface. TGA result revealed the significant improvement of thermal resistance and stability of SiO_2-TiO_2 coated fabric as compared to those of uncoated fabric. Flame retardant performance of SiO_2-TiO_2 coated fabrics was much better than that of uncoated fabric. Thus, SiO_2-TiO_2 coated fabric SiO_2-TiO_2 content of 26wt% showed the UL-94 classification of V-0 and LOI value of 30.3 were obtained. Moreover, mechanical property (tear strength) of SiO_2-TiO_2 coated fabrics were also improved.

Keywords: nano silica, titanium dioxide, polyester/cotton fabrics, flame retardant

1. Introduction

Polyester/cotton fabric is a blend of polyester and cotton and it is widely used in the textile industry. The quality of blended fabric is improved by the combination of the comfort and ventilation of cotton yarn with high strength of polyester [1,2]. However, polyester / cotton fabric is flammable and it cannot be used as flame retardancy materials. Therefore, many efforts on flame retardancy improvements have been devoted [3,4]. Materials of coating can be of organic or inorganic nature. Halogen-based flame retardants materials have been shown to be one of the most effective materials to reduce the risk of fire, but the downside is the release of toxic and corrosive gases during combustion

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[5,6]. Phosphorus and nitrogen based materials are preferably chosen as flame retardants because of their eco-friendly by-products, low toxicity. However, their poor flame retardant performance and low thermal stability were noted [7,8]. Flame retardants of inorganic nature such as nanosilica, nano alumino-silica, nano clay are often used to cover the fabric surface to create an insulating and fireproof protective layer and simultaneously, the physico-mechanical properties can be improved. Among inorganic flame retardants, nano silica and nano titanium dioxide have received a great interest because these materials are environmentally friendly, non-toxic and highly effective in slowing or resisting fire [9-12]. El-Shafei et al. [13] modified the fabric with nano TiO_2 sol gel from titanium isopropoxide and the fire resistance of the TiO_2 modified fabric is significantly improved (LOI increased from 17.4% to 23%). Fei et al. [14] modified fabric with nano silica synthesized from TEOS and the significant enhance of flame retardancy (LOI value from 19.0 to 23.0) is reported. Liu et al. [15] reported that fabric coated with silica nano by using the sources of organic silicon TEOS and trimethylsilane and showed that the thermal stability was considerably improved. Most fabrics used for coating are cotton fabrics. Nano silica coating on polyester/cotton fabric is much more difficult due to its high smooths and low adhesion ability. In this study, we report the synthesis of SiO_2, TiO_2 sols using sodium silicate and titanium chlorides as sources of Si and Ti. Polyester/cotton fabric was coated with SiO_2-TiO_2 sols by deep-coating method. Thermal resistance, flame retardancy and mechanical property (tear strength) were tested and evaluated.

2. Experiments

Chemicals and materials: Sodium silicate 20 wt% was from company Sigma, $TiCl_4$ (purity of 99%, sigma company), KOH (purity 85%, Merck company), ion exchange (*AMBERLITE*™ IR 120 from Down Chemical company), H_2O_2 (31 wt% from Aldrich company), NH_4OH (30 wt% from Sigma company). Polyester/cotton fabric (trade mark-Lacoste, 35% polyester-65 %cotton, 115 g/cm^2) is provided by the textile Dong Xuan-Vietnam company.

2.1. Synthesis of silica sol

Silica sol was synthesized by ion exchange method using Amberlite as ion exchange resin and sodium silicate (liquid glass) as source of silicon [11].

The process of synthesizing sol silica consists of the following steps: Step 1: Dissolution of sodium silicate in distilled water. Step 2: Na^+ ion exchange by using ion exchange resin (*AMBERLITE*™ IR 120). Step 3: Adjusting pH value of 8.5-9.0 by KOH addition to form the $Si(OH)_4$ slurry. Step 4: Stirring the mixture until to get the homogeneous sols.

2.2. Synthesis of titanium dioxide sol

Titanium dioxide sol was synthesized by using titanium tetrachloride ($TiCl_4$) as Ti soured and H_2O_2 as an oxidizing agent. The synthesis procedure of TiO_2 sol was described in [reference 16], consisting four following steps: Step 1: Titanium tetrachloride ($TiCl_4$) was slowly added to the cold distilled water container in an ice batch under strong stirring for 30 minutes until to get a clear solution. NH_4OH solution was then added to the solution to precipitate the $Ti(OH)_4$ slurry. Step 2: $Ti(OH)_4$ hydroxide slurry was washed with distillated water several times to remove Cl^-. Step 3: $Ti(OH)_4$ slurry was oxidized by adding H_2O_2 (30 wt%) to obtain the titanium peroxide (Ti-OOH). Step 4: Titanium peroxide was heated at 90 ^oC for 8h under stirring condition and then cooled down to room temperature. SiO_2-TiO_2 sol solution was prepared by mixing SiO_2 sol solution (10 wt% SiO_2) and TiO_2 sol solution (2 wt% TiO_2) under stirring condition.

This SiO_2-TiO_2 sol solution was used for coating polyester/cotton fabric.

2.3. SiO_2-TiO_2 sol coating on polyester/cotton fabric

Polyester/cotton fabric (35 % polyester, 65% Cotton) was cut in small pieces of 60 x 40 mm size. Polyester/cotton fabric piece was deepened in a container with 50 ml SiO_2-TiO_2 sol solution (10 wt% SiO_2 and 2 wt% TiO_2) for 2 minutes and then ultrasonically treated for 5 minutes. The SiO_2-TiO_2 coated fabric was dried at 80 ^oC for 30 minutes in an oven. This sample was denoted as S_1 (one time coating sample). Fabric after 3, 5 and 7 times coating were denoted as S_3, S_5 and S_7.

2.4. Characterization of SiO_2-TiO_2 coated fabrics

The X-ray diffraction (XRD) measurements were performed on a D8 Advance diffractometer (Bruker, Germany) using CuK_α as radiation source, $\lambda = 0.154\ 06$ nm, a range of $2\theta = 10°– 80°$. The morphology of the samples was examined on scanning electron microscopy (SEM, JEOL JSM 6500F). The FT-IR spectra of the samples were recorded by the KBr pellet method (JACOS 4700). EDX of samples were measured using JEOL JED-2300 spectrometer. Thermal analyses were conducted from room temperature to 600◦C under air atmosphere using LABSYS evo TG-DTA 1600. UL-94 classification and limiting oxygen index (LOI) were determined according the standards ASTM D2863, BS ISO4589-2.

3. Results and discussion

3.1. Structure characterization of SiO_2-TiO_2 coated fabric

XRD pattern of polyester/cotton fabric (fig 1a) showed the peaks at 2θ of 22.66^o and 25.44^o which corresponded to string segments of small crystal structure of polyester/cotton fabric [17-19]. In the XRD patterns of SiO_2-TiO_2 coated fabrics, the intensity of the peaks at 2θ of 22.66^o and 25.44^o decreased with increasing the SiO_2-TiO_2 content. This clearly indicated the coverage of SiO_2 and TiO_2 particles on polyester/cotton fabrics. Typical peaks of SiO_2 and TiO_2 phase were not detected since these particles were amorphous [20].

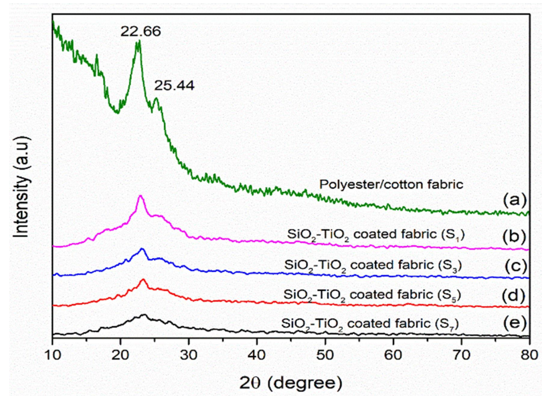

Fig. 1: XRD patterns of polyester/cotton fabric (a) and SiO_2-TiO_2 coated fabrics (b-e)

FTIR spectra of polyester/cotton fabric and SiO_2-TiO_2 coated fabrics were presented in figure 2. The FTIR spectrum of polyester/cotton fabric (fig 2.a) showed the band at 3430 cm^{-1} is attributed to the vibration of C-OH of fabrics (cellulose) [21,22]. Bands at 1690 -1700 cm^{-1} and 730 cm^{-1} are corresponded to the vibrations of C=O and C-C bonds in fabric structure [22,23]. In the FTIR spectra of SiO_2-TiO_2 coated fabrics (figure2, b-e), a new band appeared at 3490-3500 cm^{-1} which assigned to the vibrations of Si-OH, Ti-OH groups [24,25]. Also, new bands at 780 cm^{-1}, 480 cm^{-1} appeared which attributed to vibrations of Si-O-Si, Ti-O-Ti, Si-O, Ti-O groups of SiO_2, TiO_2 structure. Moreover, disappearing of bands at 3430 cm^{-1}, 1730 cm^{-1} and 700 cm^{-1} which are characteristic for fabric structure indicated the coverage of SiO_2, TiO_2 particles on the polyester/cotton fabric surface [26,27]. As presented in figure 3A, weight loss diagram of polyester/cotton fabric showed 3 stages: at the first stage (50 - 200 ^oC), weight loss of 10 wt% was observed.

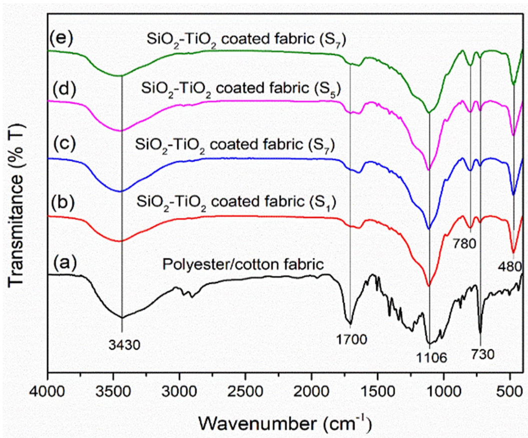

Fig. 2: FTIR spectra of polyester/cotton fabric (a) and SiO_2-TiO_2 coated fabric (b-e)

This weight loss is due to the water desorption. At the second stage (250 - 350 °C), weight loss of 50 wt% is noted. This is due to the partial decomposition of fabric. At the third stage (350 - 500 °C), weight loss was 38 wt%. The weight loss in this region is due to the further decomposition of fabrics. As seen in the derivative thermogravimetry of polyester/cotton fabric (Fig 3B), the decomposition occurred at T_{max} of 330 - 430 °C and 480 °C. The behavior of weight loss for SiO_2-TiO_2 coated fabrics was different from that of polyester/cotton fabric. Thus, in the temperature range from 50 °C to 300 °C, weight loss of 1.5-2% was observed. In the range from 350 °C to 550 °C, weight loss of SiO_2-TiO_2 coated fabric (S_1-S_7) was 65 wt%, 50 wt%, 41 wt% and 38 wt%, respectively. From this result, it clearly indicated that SiO_2-TiO_2 coating reduced the weight loss of fabric. Thus, SiO_2-TiO_2 coated fabric (7 coating times) showed the weight loss of 38% which was 2.5 times less than that of polyester/cotton fabric (98 wt%). Moreover, the decomposition of SiO_2-TiO_2 coated fabrics needed higher temperature (see fig 3B).

3.2. Morphology and chemical composition

SEM images of polyester/cotton fabric and SiO_2-TiO_2 coated fabric (S_7) were given in figure 4. In figure 4A, polyester/cotton fabric

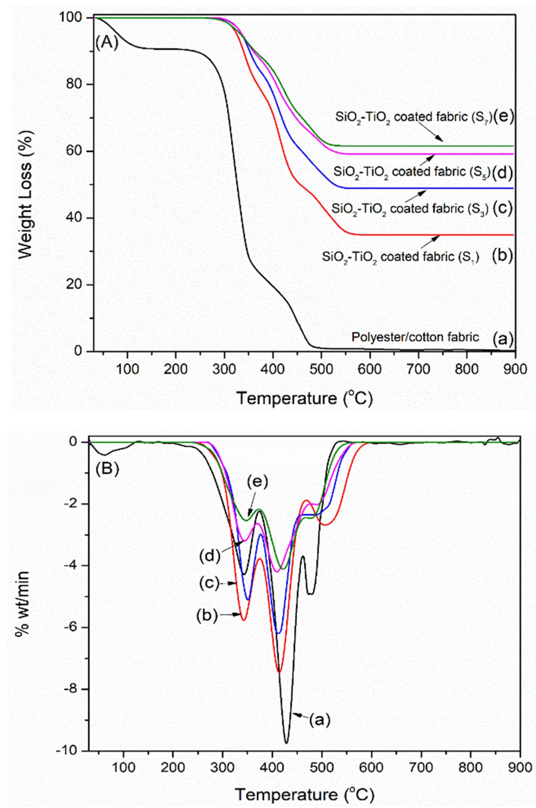

Fig. 3: Weight loss (A) and derivative thermogravimetry (B) of polyester/cotton fabric and SiO_2-TiO_2 coated fabric

showed the heterogeneous structure with the pore system consisted of large pore (100 - 150 nm), medium pore (50-60 nm) and small pore (20 -30 nm). In the SEM image of SiO_2-TiO_2 coated fabric (figure 4B), it can be seen SiO_2, TiO_2 particles of 30-40 nm size which filled up the pore system of polyester/cotton fabric and simultaneously covered the fabric surface.

EDX spectra of polyester/cotton fabric and SiO_2-TiO_2 coated fabric-S_7 were presented in figure 5 and elemental composition was given in table 1.

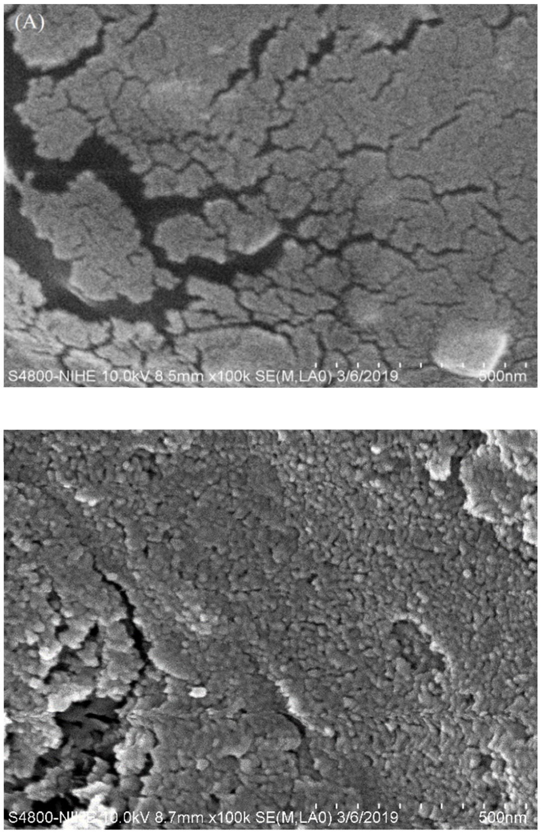

Fig. 4: SEM image (A) polyester/cotton fabric and (B) SiO_2-TiO_2 coated fabric (S_7)

As given in Table 1, C content decreased with increasing SiO_2-TiO_2 coating times while O, Si and Ti content increased with increasing SiO_2-TiO_2 coating times (S_1-S_7). Thus, C content decreased from 51.06 wt% to 20.45 wt%, respectively. O content of S_1, S_3, S_5 and S_7 samples was 28.38%, 33.41%, 38.7% and 45.97 wt%, respectively. N content of S_1, S_3, S_5 and S_7 samples was 14.12%, 12,42%, 10.09% and 7.58%. Si content of S_1, S_3, S_5 and S_7 samples was 5.34%, 11.06%, 18.72% and 23.99%, respectively. Ti content of S_1, S_3, S_5 and S_7 sample was 1.01%, 1.35%, 1.64% and 2.01 wt%, respectively. Interestingly, the ratio of Si/Ti increased with increasing SiO_2-TiO_2 coating times. Normally, this ratio Si/Ti should maintain unchanged since the same concentration of SiO_2-TiO_2 solution (10 wt% SiO_2 and 2 wt% TiO_2) was used. This can be explained on the basis of the competition between SiO_2 and TiO_2 particles since concentration of SiO_2 was 5 times higher than that of TiO_2 which promoted much more SiO_2 deposition on fabric surface than TiO_2 deposition.

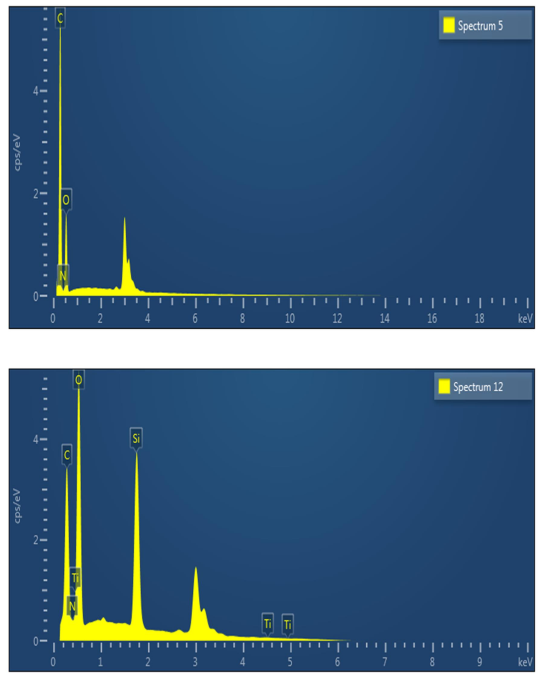

Fig. 5: EDX spectra of polyester/cotton fabric (A) and SiO_2-TiO_2 coated fabric-S_7 (B)

Table 1: Elemental composition of polyester/cotton fabric and SiO_2-TiO_2 coated fabrics

Element, wt.% / Sample	C	O	N	Si	Ti	Si+Ti
Polyeste/cotton fabric	60.24	23.63	16.13	-	-	-
SiO_2-TiO_2 coated fabric (S_1)	51.06	28.38	14.21	5.34	1.01	6.35
SiO_2-TiO_2 coated fabric (S_3)	41.76	33.41	12.42	11.06	1.35	12.41
SiO_2-TiO_2 coated fabric (S_5)	30.85	38.7	10.09	18.72	1.64	20.36
SiO_2-TiO_2 coated fabric (S_7)	20.45	45.97	7.58	23.99	2.01	26.0

3.3. Flame retardancy and mechanical property

UL-94 classification and limiting oxygen index (LOI) of polyester/cotton fabric and SiO_2-TiO_2 coated fabric were listed in the table 2

Table 2: UL-94 classification and limiting oxygen index (LOI) of polyester/cotton fabric and SiO_2-TiO_2 coated fabrics

Sample	UL - 94	LOI (%)
Polyester/cotton fabric	V-2	17.5
SiO_2-TiO_2 coated fabrics (S_1)	V-2	19.0
SiO_2-TiO_2 coated fabrics (S_3)	V-1	23.6
SiO_2-TiO_2 coated fabrics (S_5)	V-1	25.2
SiO_2-TiO_2 coated fabrics (S_7)	V-0	30.3

As seen in table 2, polyester/cotton fabric and SiO_2-TiO_2 coated fabric-S1 had the UL-94 of V-2 which did not satisfy the quality requirement for flame retardant materials. SiO_2-TiO_2 coated fabrics (S_3 and S_5) showed UL-94 classification of V-1 which satisfied the quality requirement for flame retardant materials. SiO_2-TiO_2 coated fabric-S_7 reached the best quality requirement for flame retardant materials (UL-94 classification of V-0). Polyester/cotton fabric showed the LOI value of 17.5 while the LOI value of SiO_2-TiO_2 coated fabrics was 19.0 (for S_1), 23.6 (for S_3), 25.2 (for S_5) and 30.3 (for S_7), respectively. It is well known that O_2 content in the air is ca. 19 % (v/v). Therefore, polyester/cotton fabric is easily burned in air. SiO_2-TiO_2 coated fabrics (S_3, S_5) with LOI value of 23.6-25.2 are slowly burned in air. SiO_2-TiO_2 coated fabric (S_7) showed the highest LOI value of 30.3 which is unburnable under flame. Thus, the SiO_2 and TiO_2 nanoparticles with the size of 30-50 nm were covered on the surface of the polyester/cotton fabric to help prevent contact between flame and combustible components (polyester/cotton fabric).

Mechanical property of polyester/cotton fabric and SiO_2-TiO_2 coated fabrics

One of the most important physico-mechanical properties of fabric is the tear strength. Tear strength of polyester/cotton fabric and SiO_2-TiO_2 coated fabric was shown in table 3.

Table 3: Tear strength of polyester/cotton fabric SiO_2-TiO_2 coated fabrics

Sample	Tear strength (N/mm)
Polyester/cotton fabric	39.37
SiO_2-TiO_2 coated fabric (S_1)	41.22
SiO_2-TiO_2 coated fabric (S_3)	43.35
SiO_2-TiO_2 coated fabric (S_5)	45.27
SiO_2-TiO_2 coated fabric (S_7)	37.56

As seen in table 3, the increase of tear strength from 39.37 (polyester/cotton fabric) to 45.26 N/mm (SiO_2-TiO_2 coated fabric-S_5) was observed. Further SiO_2-TiO_2 coating (SiO_2-TiO_2 coated fabric-S_7) leaded to decrease the tear strength (37.56 N/mm). This can be explained by the fact that SiO_2-TiO_2 coated fabric with high loading, SiO_2 and TiO_2 particles tended to the agglomeration, making SiO_2-TiO_2 coated fabric become more fragile and consequently decreased the tear strength.

4. Conclusions

From the obtained results, some conclusions could be drawn: SiO_2 and TiO_2 sols were successfully synthesized by using sodium silicate and titanium chloride as Si and Ti sources. SiO_2-TiO_2 sol polyester/cotton fabric was fabricated by deep coating method and using SiO_2-TiO_2 sol as coating materials. SiO_2-TiO_2 coated fabrics with different SiO_2-TiO_2 content were made by repeating the coating times. Polyester/cotton fabric and SiO_2-TiO_2 coated fabrics were characterized by XRD, FTIR, TGA, SEM and EDX. From SEM result, it showed that SiO_2, TiO_2 particles of 20-30 nm filled up the pore system of fabric and well deposited on fabric surface. From TGA analysis of the samples, it revealed the significant improvement of thermal resistance and stability of SiO_2-TiO_2 coated fabrics.

Flame retardancy and mechanical property (tear strength) of polyester/cotton fabric and SiO_2-TiO_2 coated fabric were tested and evaluated. The SiO_2-TiO_2 coated fabric (7 coating times, Si-Ti content of 26 wt%) showed the highest flame retardancy performance. Thus, UL-94 classification of V-0 and LOI value of 30.3 were obtained. Additionally, mechanical property (tear strength) of SiO_2-TiO_2 coated fabrics was also improved.

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