COMBUSTION PROPERTIES AND THERMAL DECOMPOSITION KINETICS OF FLAME RETARDANT SILK FABRICS TREATED BY PHYTIC ACID AND SILICA SOLS

by

Yun-Bo CHEN[a], Chun LIU[a], Shao-Li ZHANG[a], Guo-Qiang CHEN[a] and Tie-Ling XING[a,b]*

[a] National Engineering Laboratory for Modern Silk, College of Textile and Clothing Engineering, Soochow University, Suzhou, China
[b] Jiangsu Huajia Group, Suzhou, China

Original scientific paper
https://doi.org/10.2298/TSCI1804665C

In order to obtain the flame retardant silk fabric, silica sols and phytic acid were prepared and applied to the silk fabrics. Vertical combustion experiment, thermogravimetric analysis, Fourier transform infrared spectra and smoke density test were used to investigate the combustion behavior, thermal property, and kinetics model of silk fabrics before and after flame retardant finish. The results showed that the sol coating on silk fabrics could increase the carbon residue and hinder the spread of flame when burning, and the tensile strength of treated silk was slightly damaged. Furthermore, the kinetics model of silk thermal decomposition conformed to Avrami-Erofeev model.

Key words: *silk, thermal decomposition, flame retardant, phytic acid, sol-gel, silica sol, kinetics model*

Introduction

Silk has been widely used for clothing, furniture, high-grade decoration, automobile and aircraft interiors, and biomaterials due to its non-toxic, biocompatible, biodegradable, soft luster, good hygroscopicity, outstanding mechanical properties and comfortable handle [1, 2]. The limiting oxygen index of cellulose is 18% and silk fiber is about 24% because of the existence of N element in its composition [3]. Compared with cellulose fibers, silk fiber is somewhat non-flammable, however, it still belongs to combustible textiles. With fire proofing consciousness constantly increasing, the requirement for silk fabric with flame retardancy is also becoming more and more stringent. Therefore, it is necessary to improve the flame retardancy of silk fabric.

Sol-gel technology is a wet chemical approach to produce macroscopic and microscopic material from 0-D to 3-D. Sol-gel technique takes the metal alkoxides as precursor, dissolving in organic solvents such as ethanol or ethanol-water binary mixture, and under the action of catalyst, metal alkoxides hydrolytic condensate to sol [4]. Under the correct condition, sol is very stable, and the metal elements can be arbitrarily doped to obtain various properties of the composite sol system. Due to its many advantages including simple and cleaning process, low cost, more effective and less chemicals consumption, sol-gel technology has become an important emerging technology in the fabric finishing industry [5].

* Corresponding author, e-mail: xingtieling@suda.edu.cn

As we know, phosphorus and nitrogen are the most important elements among flame retardants [5]. In recent years, halogen-free flame retardant has been widely used in flame retardant fibers because of its low mammalian toxicity, high-flame retardant efficiency and less corrosive products during combustion [6, 7]. The silica hydrogel, phosphorus-nitrogen (P-N) based compounds could catalyze the dehydration and carbonization of matrix, reduce a large number of combustible gases and improve the combustibility of the materials through forming a protective char layer [8-10].

In this work, we have successfully prepared a new sol-gel layer via the chemical reaction of phytic acid (PA), which is the major storage in cereal grains, beans, and oil seeds, in order to obtain a new and effective P-N flame retardant which has a synergistic effect for silk fabric.

Experimental

Preparation of flame retardant silk fabric

Silica sols were synthesized using (3-trimethoxysilylpropyl) diethylenetriamine (TRIAMO) as precursor by sol-gel technique. Sodium chloride and distilled water were mixed to obtained a soluble mixture in a three neck flask, and then the precursor dropped into the flask, stirring at room temperature for two hours (precursor: water: ethanol: sodium chloride molar ratio = 1:50:5:2). After the reaction finished, 10 mol/L hydrochloric acid was used to adjust the pH to 7. Then silk fabric was impregnated in the prepared sol at room temperature for 10 min and squeezed through a padder for 90-100% pickup, and cured at 130 °C for 30 minutes.

Phytic acid (0.2 mol/L) was applied in a subsequent step. The TRIAMO treated silk fabric was impregnated in PA for 10 minutes and squeezed through a padder, then cured at 130 °C for 30 minutes.

Characterization of flame retardant silk fabric

The vertical combustion experiment were measured according to ASTM D6413 by applying a propane flame for 12 seconds at the center of a sample (80 mm × 300 mm) using YG815B fabrics flame-retardant tester (vertical method) calculating the damage length. According to the ISO 5659-2 testing standard, the smoke suppression of the samples analysis was conducted using an NBS smoke density test chamber with max radiant heat of 50 kW/m^2 at 560 ℃ for 600 seconds and three sample layers of 80 mm × 80 mm. The thermal stability of the silk fabric was evaluated by thermogravimetry (TG) analysis with the SDT2960 thermal analyzer (Perkin-Elmer, Waltham, Mass., USA). The temperature was set from 30 ℃ to 700 ℃ at the scan rate of 10 ℃ per minute in nitrogen atmosphere (100 mL/min), and each sample was 4-5 mg. The Fourier transform infrared spectra of the samples were measured on a Nicolet5700 FT-IR spectrometer (Thermo Fisher Scientific Inc., Waltham, Mass., USA) using KBr pellets and the results were collected from 120 scans. The breaking strength of silk fabric was tested by a Lioyd's tensile tester (Illinois Tool Works Inc., High Wycombe, Buckinghamshire, UK) according to ISO 13934-1-2013.

Kinetics model

The kinetics models were used to further study the combustion characteristics of silk fabrics before and after flame retardant finish. The reaction eq. (1) was usually used to express the thermal decomposition of solid phase reaction.

$$A(s) \rightarrow B(s) + C(g) \tag{1}$$

The equation of the reaction rate is listed:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = Kf(\alpha) \tag{2}$$

$$G(\alpha) = kt \tag{3}$$

Substituting the Arrhenius formula $K = A\exp(-E/\mathrm{R}T)$ into (2), the eq. (4) is obtained:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A\exp\left(-\frac{E}{\mathrm{R}T}\right) f(\alpha) \tag{4}$$

where t is the time, α – the extent of the reaction, T – the absolute temperature, $\mathrm{d}\alpha/\mathrm{d}t$ – the rate of conversion, E – the apparent activation energy, $f(\alpha)$ – the reaction model, and R = 8.314 kJ/molK.

For the heterogeneous solid phase reactions at constant heating rate, temperature increasing rate could be described as $\beta = \mathrm{d}T/\mathrm{d}t$, eq. (5) could be obtained according to eq. (4):

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A}{\beta}\exp\left(-\frac{E}{\mathrm{R}T}\right) f(\alpha) \tag{5}$$

taking the logarithm of eq. (5), Achar equation could be gained [11]:

$$\ln\frac{\mathrm{d}\alpha}{f(\alpha)\mathrm{d}T} = \ln\frac{A}{\beta} - \frac{E}{\mathrm{R}T} \tag{6}$$

integrating $f(\alpha) = (1-\alpha)^n$ and eq. (5) leads to the integral conversion function, and the Coats-Redfern eq. (7) was obtained [12]:

$$\ln\frac{G(\alpha)}{T^2} = \ln\left(\frac{A\mathrm{R}}{\beta E}\right) - \frac{E}{\mathrm{R}T} \tag{7}$$

By plotting $1/T$ *vs.* $\ln[G(\alpha)]/T^2$ and processing linear-regression analysis, the relevant of thermal decomposition kinetics equation could be obtained through the slope and intercept of curves. Widely used dynamics function of thermal decomposition and $G(\alpha)$ are shown in tab. 1 [12].

Results and discussion

Flame retardant properties analysis

The untreated silk, silk fabric treated by TRIAMO PA. The TRIAMO/PA were marked as SILK (a), TRIAMO-SILK (b), PA-SILK (c), and TRIAMO/PA-SILK (d), respectively. The flame retardancy of the silk fabrics was analyzed through vertical burning test. The result of damage length from vertical combustion experiment is shown in tab. 2 and fig. 1. Obviously, the damaged length of untreated silk fabric is 24.9 cm and treated silk fabrics declined sharply. This indicated that single phosphorus and nitrogen elements were able to improve the flame retardancy of silk fabrics, and P-N synergistic effect could effectively improve the flame retardancy of silk fabric.

Table 1. Common thermal decomposition mechanism function

No.	Function	Reaction model	$G(\alpha)$
1	Mampel power law		$\alpha^{1/4}$
2	Mampel power law		$\alpha^{1/3}$
3	Mampel power law		$\alpha^{1/2}$
4	Mampel power law		α
5	Parabola law	1-D diffusion	α^2
6	Valensi	2-D diffusion	$[-\ln(1-\alpha)]^{-2}$
7	Ginstling-Broushtein	3-D diffusion	$(1-2\alpha/3)-(1-\alpha)^{2/3}$
8	Avrami-Erofeev	$n = 2$	$[-\ln(1-\alpha)]^{1/2}$
9	Avrami-Erofeev	$n = 3$	$[-\ln(1-\alpha)]^{2/3}$
10	Avrami-Erofeev	$n = 4$	$[-\ln(1-\alpha)]^{3/4}$
11	Phas boundary reaction	contraction cylinder	$1-(1-\alpha)^{1/2}$
12	Phas boundary reaction	contracting sphere	$1-(1-\alpha)^{1/3}$
13	Chemical reaction	$n = 1$	$[-\ln(1-)\alpha]^{-1}$
14	Chemical reaction	$n = 1.5$	$2[\ln(1-\alpha)^{-1/2}-1]$
15	Chemical reaction	$n = 2$	$\ln(1-\alpha)^{-1}-1$

Table 2. The damage length of silk fabrics

Sample	Damaged length [cm]
SILK (a)	24.9
TRIAMO-SILK (b)	12.3
PA-SILK (c)	13.0
TRIAMO/PA-SILK (d)	11.8

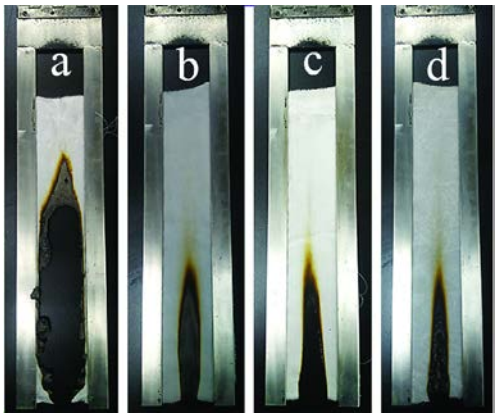

Figure 1. Damage length of wool fabric in vertical combustion experiment

The FT-IR characterization

The chemical structure of samples was characterized by FT-IR spectra and shown in fig. 2. The peaks around 3130 per cm is assigned to the characteristic absorption bands of –OH stretching vibration, and the characteristic absorption peak at 2955 per cm is attributed to –CH stretching vibration of the silk fabric. The spectra of the silk treated with TRIAMO (b) shows a Si–O–C stretching vibration at 1110 per cm, and the sample treated by PA (c) and TRIAMO/PA (d) both appear a P = O stretching vibration at 1080 per cm and Si–O–C stretching vibration is invisible due to the overlap with P = O stretching vibration.

Thermal stability

The TG analysis is widely used for analyzing the thermal stability of fibers, and it represent for the decomposition behaviors of the fibers at all kinds of temperatures [13].

The results of thermal stability of the samples are shown in fig. 3 and the relative thermal gravimetric data are listed in tab. 3.

The figure shows that before 230 ℃ the weight of samples have a light loss due to the loss of adsorption water. The initial decomposition temperature of untreated silk (a) is 240 ℃, and after that the weight loss increases quickly with the increase of temperature at 250-300 ℃, and the maximum decomposition rate occurred. Moreover, when the temperature reached 600 ℃, the final residue was 31.3%. The silk fabric treated only by TRIAMO silica sol decomposed at 240 ℃, and the maximum decomposition rate occurred at 250-320 ℃. The mass loss declined down when the temperature was higher than 500 ℃, and the weight residue of the sample was 33.7% at 600 ℃. While the mass loss of samples (c) and (d) happened at around 250 ℃, indicating that the thermal decomposition temperature of the treated silk fabric increased. After 450 ℃, the weight loss rate of the sample became stable and the final weight residue was 45.4% and 48.9% at 600 ℃, respectively. It can be seen that the treated silk (d) exhibited a higher weight loss at low temperature, and lower weight loss at high temperature. The results showed that the fabric surface forming the residue at burning which hindered the further combustion of silk fabric, indicating obvious improvement in thermal performance of TRIAMO/PA treated silk fabrics.

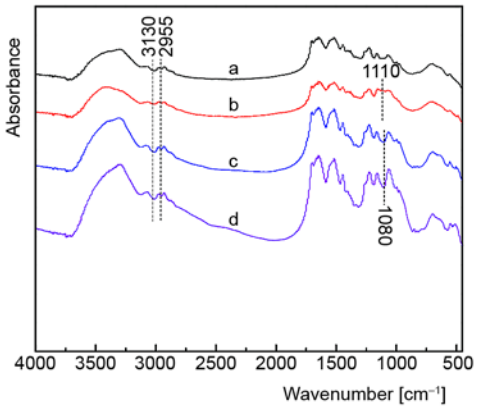

Figure 2. The FT-IR spectra of sample

Table 3. Thermal properties data for treated and untreated silk fabric

Sample	$T_{10\%}$ [°C]	$T_{50\%}$ [°C]	Weight residue at 600 °C [%]
a	258	360	31.3
b	260	389	33.7
c	251	487	45.4
d	247	557	48.9

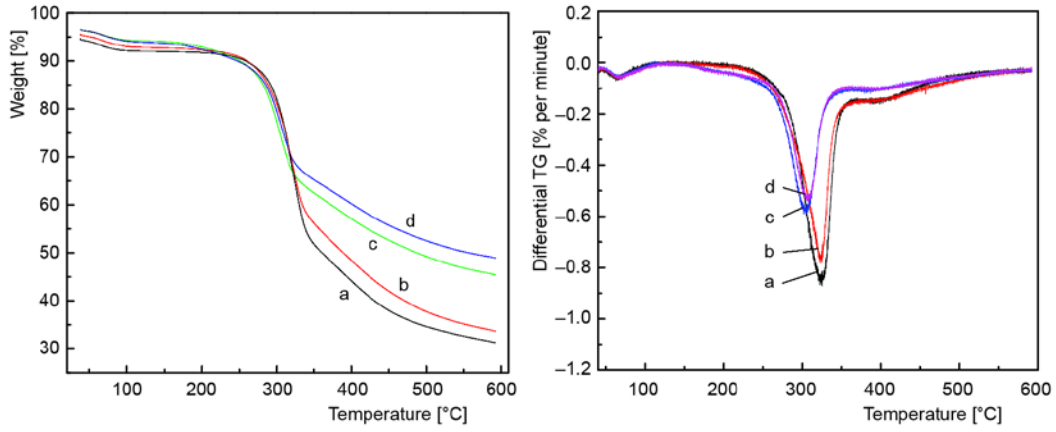

Figure 3. The TG and differencial TG curves of sample under nitrogen

Kinetics analysis

In order to obtain the reaction kinetics function equation that could accord the decomposition process well, five points were selected from the each temperature interval from

40 °C to 600 °C of 15 kinds of dynamics function (tab. 1), and substituting into all kinds of dynamics, subsequently, the same data could be obtained. Using these data for drawing and linear fitting, the values of statistical parameters, R^2, was obtained and the reaction kinetics function equation was got when $R^2 > 0.98$. The calculation result of reaction kinetics function of untreated silk and treated silk by TRIAMO (b) and PA (c) conforms to model 9 and treated silk with TRIAMO/PA (d) conforms to model 8. The statistical parameters R^2 = 0.9925, 0.9929, 0.9835, and 0.988, respectively.

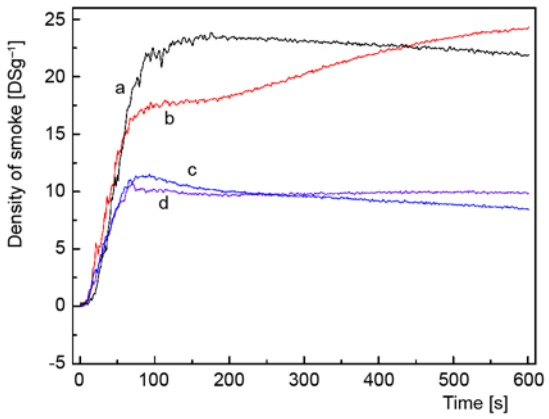

Figure 4. D_s curves of treated and untreated silk fabric

Smoke suppression

The smoke suppression of the sample was analyzed with the maximum smoke density, D_s, released in flameless burning process. The result of the NBS test is shown in fig. 4. It can be seen that maximum smoke density of the untreated silk fabrics reaches 23.84 at the time of 175 seconds, and the treated silk by TRIAMO (b) was 24.24 after 600 seconds, while the treated silk through PA (c) and TRIAMO/PA (d) can only reach 11.36 at 79 seconds and 10.86 at 77 seconds, respectively. It could be concluded that the elements Si, N, and P in the blend coating turns out to further hamper the formation of volatile products during the silk combustion, meanwhile, to form the char on the surface of silk fabric [14].

Conclusion

In this work, silk fabrics were treated by TRIAMO, PA, and TRIAMO/PA, and good flame retardancy could be obtained. Silk fabric treated by TRIAMO/PA had the best flame retardancy and superior thermal stability.

Acknowledgment

The work is supported by Natural Science Foundation of Jiangsu Province (BK 20151242), the Six Talent Peaks Project of Jiangsu Province (JNHB-066), China Postdoctoral Science Foundation (2016M600437), Jiangsu Planned Projects for Postdoctoral Research Funds (1601025B), Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD) and Qing Lan Project.

Nomenclature

E – apparent activation energy, [kJmol^{-1}]
T – absolute temperature, [K]
t – time, [s]

References

[1] Taddei, P., *et al.*, Intermolecular Interactions between B. Mori Silk Fibroin and Poly(L-lactic Acid) in Electrospun Composite Nanofibrous Scaffolds, *Materials Science and Engineering, 70* (2017), 1, pp. 777-787

[2] Ferrero, F., *et al.*, Silk Grafting with Chitosan and Crosslinking Agents, *Fibers & Polymers*, *11* (2010), 2, pp. 185-192
[3] Zang, Q. H., *et al.*, Flame Retardant Performance of Finishing Silk Fabric with Ammonium Borate Doped Silicon Sol, *Journal of Silk*, *52* (2015), 1, pp. 8-13
[4] Wan, N. W. I., Sol-Gel Technology for Innovative Fabric Finishing-A Review, *Journal of Sol-Gel Science and Technology*, *78* (2016), 5, pp. 698-707
[5] Lecoeur, E., *et al.*, Flame Retardant Formulations for Cotton, *Polymer Degradation and Stability*, *74* (2001), 3, pp. 487-492
[6] Zheng, Z. H., *et al.*, Preparation of a Novel Phosphorus – and Nitrogen-Containing Flame Retardant and its Synergistic Effect in the Intumescent Fame-Retarding Polypropylene System, *Polymer Composites*, *36* (2015), 9, pp. 1606-1619
[7] Aksit, A., *et al.*, Synergistic Effect of Phosphorus, Nitrogen and Silicon on Flame Retardancy Properties of Cotton Fabric Treated by Sol-Gel Process, *International Journal of Clothing Science and Technology*, *28* (2016), 3, pp. 319-327
[8] Yang, Z., *et al.*, A Novel Halogen-Free and Formaldehyde-Free Flame Retardant for Cotton Fabrics, *Fire and Materials*, *36* (2012), 1, pp. 31-39
[9] Liu, Y. L., *et al.*, The Effect of Silicon Sources on the Mechanism of Phosphorussilicon Synergism of Flame Retardation of Epoxy Resins, *Polymer Degradation and Stability*, *90* (2005) 3, pp. 515-522
[10] Wang, X., *et al.*, Intumescent Multilayer Hybrid Coating for Flame Retardant Cotton Fabrics Based on Layer-by-Layer Assembly and Sol-Gel Process, *RSC Advances*, *14* (2015) 5, pp. 10647-10655
[11] Zeng, W. R., *et al.*, The Degradation Kinetic Study of Polystyrene by a Combination of Non-Iso Thermal Differential and Integral Methods, Polymer Materials Science & Engineering, *22* (2006), 5, pp. 162-165
[12] Wu, Y., *et al.*, Thermal Decomposition Kinetics and Flame Retardance of Phosphazene-Containing Epoxy Resin, *Ploymer Materials Science and Engineering*, *32* (2016), 3, pp. 54-58
[13] Bing, L., *et al.*, Synthesis of Novel Intumescent Flame Retardant Containing Phosphorus, Nitrogen and Boron and Its Application in Polyethylene, *Polymer Bulletin*, *72* (2015), 11, pp. 2967-2978
[14] Jenny, A., *et al.*, Thermal and Fire Stability of Cotton Fabrics Coated with Hybrid Phosphorus-Doped Silica Films, *Journal of Thermal Analysis & Calorimetry*, *110* (2012), 3, pp. 1207-1216

Paper submitted: September 12, 2016
Paper revised: September 21, 2017
Paper accepted: September 22, 2017