

Performance of Flame Retardancy Silk Modified with Water-Soluble Vinyl Phosphoamide

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ABSTRACT: In this article, a water-soluble flame retardant monomer dimethyl(methacryloyloxyethyl)phosphoramidate (DMMEPN) was synthesized and applied onto silk fabric via graft copolymerization technique initiated with potassium persulfate (KPS). The results of attenuated total reflection infrared spectroscopy (ATR), scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDS) indicated that DMMEPN was successfully grafted onto silk fiber surface. X-ray diffraction (XRD) patterns showed that grafting process didn't change the crystalline structure of silk fibers and the reaction mainly occurred at the amorphous region of silk fibers. DMMEPN grafted silk fabric exhibited self-extinguish property when ignited with a candle like fire with LOI of 32.38% and could pass vertical flammability test with char length of 42 mm. Thermal gravimetric analysis showed that grafted silk fibers had different thermal decomposition mode with control silk fibers and tended to produce more char after combustion. This article also investigated the physical properties like whiteness index, hygroscopicity, and tensile strength of grafted silk fabrics. The results showed that physical properties had some loss but had no negative effect on final uses. Laundering durability test demonstrated treated silk fabrics still showed flame retardancy after enduring 30 hand wash cycles. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 2335–2341, 2013

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INTRODUCTION

Silk is a kind of fibrous protein containing 18 amino acids. And the main species were cultivated *Bombyx mori* silk and wild Tussah silk. It is an important textile material and highly appreciated for its unique luster, comfortable handle, and special scooping.¹ Silk is widely used in apparel (for its luster and wearing comfortability), domestic furnishings (for its luster and aesthetics), and biomaterials (for its superior compatibility with people's skin).^{2,3} Textiles account for 20% dwelling fires,⁴ and this leads to considerable loss of life and property. To improve public fire safety, flame retardancy treatments should be applied onto textiles. And government already realized the flammability hazard posed by textiles in fires and launched related regulations to improve public fire safety such as S.I.1985 No 2043 Nightwear (safety) Regulations of United Kingdom,⁵ CFR 1610 Standard for the flammability of clothing textiles of United States of America,⁶ and so on.

Phosphorus-based compounds were often used as flame retardants for silk. They acted as a char-forming catalyst and convert the organic fiber structure to a carbonaceous residue and hence decrease flammable volatile.⁷ The reported methods for flame

retardancy modification of silk can be summarized as follows: (i) Nondurable treatment. The used flame retardants were inorganic water-soluble phosphorus compounds like phosphate, ammonium polyphosphate, and so on. Flame retardants were easily removed by water, rain,⁸ and were suitable for applications without fluids contact like wall coverings, wall hangings, curtains, and so on. (ii) Crosslinking method. Flame retardants need binder to improve fixation onto silk fabrics and here binders worked as bridge between flame retardant and silk. N-hydroxymethyl(dimethyl phosphono) propionamide (Pyrovatex CP, Huntsman) was applied onto silk fabric with trimethylolmelamine or hexakis (methoxymethyl) melamine as binder. Treated silk fabrics demonstrated high flame retardancy with LOI above 30% but had formaldehyde release. A formaldehyde-free flame retardancy system to be developed for silk fabric by using hydroxyl-functional organophosphorus oligomer as flame retardant and 1,2,3,4-butanetetracarboxylic acid as binder. Treated silk fabric showed great flame retardancy with LOI of 30% and could endure 15 hand wash cycles but had some loss of luster and soft handle.^{9–11} (iii) Grafting method. Graft copolymerization technology is grafting functional monomer onto silk backbone so as to improve silk's performance like

wrinkle resistance,^{12,13} antibacterial property,¹⁴ flame retardancy,¹⁵ and so on. This kind of method could keep the intrinsic characteristics of silk itself well at the same time of introducing new function. Phosphorus-containing vinyl monomer dimethyl-2-(methacryloyloxyethyl) phosphate (DMMEP) and diethyl-2-(methacryloyloxyethyl) phosphate (DEMEP) were successfully applied onto silk fabrics. Treated silk fabrics demonstrated high level of flame retardancy and good physical properties.^{16,17}

In this article, element nitrogen was introduced to DMMEP and aimed at producing phosphorus–nitrogen synergism flame retardancy effect. The synthesized new water-soluble monomer is named dimethyl(methacryloyloxyethyl)phosphoramidate (DMMEPN, seen in Scheme 1). Structures and properties of treated silk fabric are explored in this article.

EXPERIMENTAL

Materials and Reagents

Degummed and bleached silk fabrics (plain woven, 36 g/m²) were purchased from Suzhou HuaSi Silk Printing & Dyeing Co., Ltd. Phosphorusoxychloride, methacryloyl chloride, absolute methanol, absolute etheranhydrous, triethylamine (TEA), methylene dichloride, and potassium persulfate (KPS) were purchased from Shanghai Qiangshun chemical reagent company, China. Monoethanol amine was purchased from Suzhou LianSheng chemical company. TEA was dried by CaH₂ overnight and distilled under reduced pressure before use. Other chemicals were used as received.

Synthesis of DMMEPN

- i. 6.40 g (0.1 mol) of absolute methanol mixed with 20.20 g (0.1 mol) of TEA was added dropwise under nitrogen to a mixture of 15.33 g (0.1 mol) of phosphorusoxychloride and 100 g of absolute etheranhydrous at 0–5°C. After completion of the addition, the mixture was still stirred for 4–6 h also at 0–5°C. Then the reacted solution was filtrated and distilled under 50°C/0.1 mmHg. Dimethyl chlorophosphate was obtained.
- ii. 14.44 g (0.1 mol) of dimethyl chlorophosphate was slowly dropped into the mixture containing 6.10 g (0.1 mol) of ethanolamine, 10.10 g (0.1 mol) of TEA, and 100.00 g of methylene dichloride under nitrogen. The temperature was controlled to 0–5°C. After completion of the addition, the mixture was warmed to room temperature and stirred for 2 h. The precipitated TEA hydrochloride was removed by filtration. The filtrate was then put into a three round bottom flask and cooled to 0–5°C, to this solution 10.10 g (0.1 mol) of TEA was slowly added dropwise under an atmosphere of nitrogen. After that a solution of methacryloyl chloride (10.45 g, 0.1 mol) in 100 g methylene dichloride was added dropwise to the mixture. The reaction mixture was then allowed to attain room temperature and stirred overnight. The precipitates

were filtered off and washed with some methylene dichloride. The solvent was evaporated and the residue was distilled under suitable temperature.

- iii. the final product was high viscous yellow liquid, yield: 54%; ¹H NMR (CDCl₃, ppm) δ: 1.28 (t, ³J_{HH} = 7.0 Hz, 6H, –OCH₃), 1.88 (3H, –CH₃), 3.06 (2H, CH₂N), 3.4~3.7 (3H, OCH₂, NH), 5.54 (dd, J = 1.7 Hz, J = 10.5 Hz, 1H, =CH₂ *cis*), 6.08 (dd, J = 1.7 Hz, J = 17.3 Hz, 1H, =CH₂ *trans*); ¹³CNMR (CDCl₃, ppm) δ: 17.66 (–CH₃), 39.62 (CH₂N), 52.43 (POCH₃), 64.34 (OCH₂), 125.35(=C–), 135.55 (CH₂=), 166.66 (–C=O); ³¹P NMR (CDCl₃, ppm) δ: 11.54 (P–O). IR (cm^{–1}) 3392 (NH), 1716 (C=O), 1637 (C=C), 1237 (P=O), 1172, 1039, and 836 (P–O–C).

Preparation of Silk-g-pDMMEPN

The silk fabric (1 g) was immersed into a reaction mixture containing DMMEPN 0.5 g, 0.8 g, 1 g (the DMMEPN concentration was then 50%, 80%, and 100% on the weight of fabric), KPS 3% on the weight of DMMEPN, that is, 0.015 g, 0.024 g, 0.03 g, and 30 mL deionized water in a 100 mL Erlenmeyer flask, the pH value of the solution was adjusted to 3.5. Then the flask was sealed with a rubber-stopper and put into water bath under oscillating at 90°C for 60 min. Then the sample was rinsed with methanol in a soxhlet extractor for 3 h then followed by water, and finally dried at room temperature under vacuum to a constant weight. The weight gain was calculated as follows:

$$\text{Weight gain (\%)} = \frac{W_2 - W_1}{W_1} \times 100 \quad (1)$$

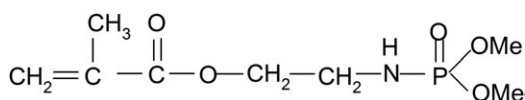
where W_2 and W_1 are the weight of grafted and original silk fabric, respectively.

Characterization and Measurements

The infrared spectra of silk were recorded on a Nicolet5700 FTIR equipped with a single reflection ATR system and the results were the average of 120 scans. Char residue were measured as follows: weight silk fabric W_1 and put into muffin oven at 600°C for 10 min, and weight the char W_2 , the char residue was calculated as eq. (2):

$$\text{Char residue (\%)} = \frac{W_2}{W_1} \times 100 \quad (2)$$

The surface of the grafted and control silk and morphology of char residue collected from muffin oven were examined after gold coating, with a Hitachi S-4700 scanning electron microscope (SEM) at acceleration voltage of 15 kV. Energy dispersive X-ray spectroscopy (EDS) was used to examine the chemical composition of the surface of silk fabrics. Thermal gravimetric analysis was carried out from 40°C to 600°C on a 2960 SDT 290 TA instrument with heating rate of 10°C/min under the nitrogen atmosphere with flux 100 mL/min, and each sample was controlled to 5~7 mg in primary weight. X-ray diffraction (XRD) patterns were obtained at a scanning rate of 1°/min with a D/Max-IIIC X-ray diffract meter. The voltage and current of the X-ray source were 40 kV and 30 mA, respectively. LOI was



Scheme 1. Structure of DMMEPN.

measured according to ASTM D 2863 on a Fire Testing Technology Oxygen Index Instrument. Char length was measured according to ASTM Standard Method D6413-99. In addition, in order to investigate the durability of flame retardancy the washing fastness of grafted fabrics was also tested according to the following laundering procedure: the treated silk fabric was subjected to a specified number of hand washing (HW) cycles according to AATCC Test Method 124-1996 (Appearance of Fabric after Repeated Home Laundering: 8.2.1 Hand Wash and 8.3.2 Line Dry) using "AATCC Detergent 1993" as a reference detergent. The temperature of water was approximately 41°C. Tensile properties of grafted silk fabrics were measured. The fabric tensile strength was measured according to ASTM Standard Method D 5035-95 with an Instron 4482 tester. The whiteness of silk fabric was measured using WSD III whiteness instrument, and the result was the average of eight measurements. Moisture regain was evaluated in the standard conditions at 20°C and 65% relative humidity (ISO 2060: determination of moisture content and moisture regain of textile-oven-drying method, 1994).

RESULTS AND DISCUSSION

Attenuated Total Reflectance-Fourier Transform Infrared

Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) analysis was used to demonstrate the presence of chemicals grafted on the fiber surface.^{18,19} The reaction between DMMEPN and silk was free radical initiated copolymerization and the structure of final FR silk shown as Scheme 2. Figure 1 showed the ATR spectra of control silk (a) and FR silk (b).

Compared with control silk, FR silk appeared additional peaks at about 1716 cm^{-1} , which attributed to the carbonyl stretching vibration of the flame retardant. The stronger peak of FR silk at 1273 cm^{-1} was because of the stretching vibration of P=O. The stretching vibration of P—O—C resulted in a band at 1164 cm^{-1} . The band at 989 cm^{-1} and the broadband of 1056 cm^{-1} corresponded to the overlapped stretching vibration of P—O—C and C—O—C and the stretching vibration of P—O, respectively. At about 3510 cm^{-1} , it is for the stretching vibration of N—H of the DMMEPN.²⁰ It was obvious that DEMEPN was grafted onto silk fabrics. The peaks at 1269 cm^{-1} and 1228 cm^{-1} (Figure 1(a)) were associated with amide III.^{21,22} The peaks at 1232 cm^{-1} and 1269 cm^{-1} were the characteristic peaks of β sheet and random-coil conformation, respectively. The peak broadened but not weakened, which means grafting

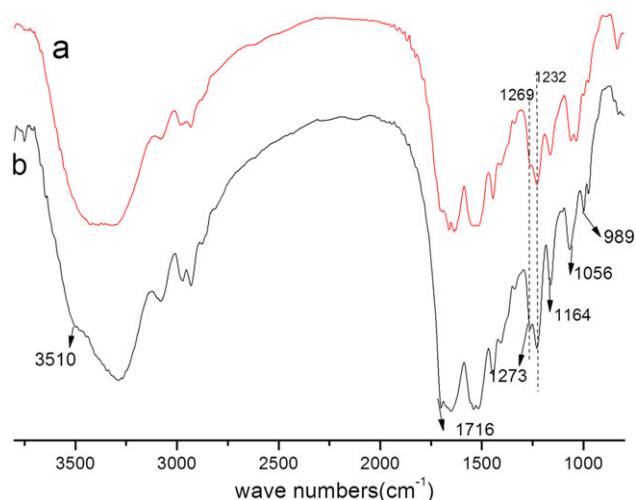


Figure 1. ATR spectra of control silk (a) and FR silk (b, weight gain 24.22%). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

mainly happened in the random-coil amorphous area of silk fiber, and the main conformation and crystalline structure were not destroyed during graft copolymerization.

SEM and EDS

Figure 2 showed the surface morphology and surface chemical composition of silk fibers of control (a) and DMMEPN-treated FR silk (b). From the SEM images, one could see that control silk fiber was smooth whereas DMMEPN silk fiber was coarse and there was chemical deposit on its surface. Furthermore, EDS spectrum showed that the chemical composition of FR silk was C, N, O, P, and the element content was different from control silk fabric. This was strong evidence that DMMEPN was successfully grafted onto the surface of silk fabric.

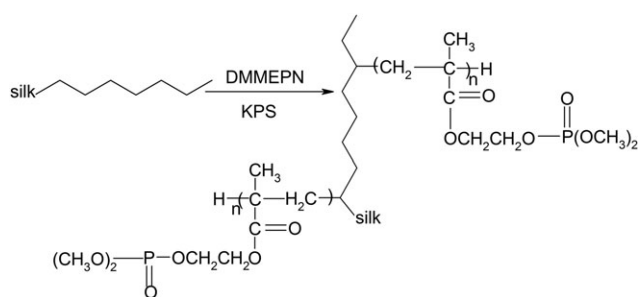
X-ray Diffraction

XRD intensity was examined to ascertain whether there were structural changes in the crystalline region of silk fabric after being treated with DMMEPN (Figure 3). FR silk showed a major X-ray diffraction peak at 20.5°, corresponding to the highly ordered β -folded crystalline structure of silk fibers.²³ Control silk fabric had the similar pattern curves with FR silk, which showed that grafting did not alter the major crystalline structure of silk fibers, which is identified with the results of ATR-FTIR.

Thermalgravimetric

TG analysis was one of the most effective tools to evaluate the thermal stability and thermal decomposition behavior of materials. Figure 4 showed the TG curves of control silk (a) and FR silk (b, weight gain 24.22%). Corresponding DTG curves could provide the data of decomposition stages and temperatures where maximum weight loss occurred. Thermal decomposition data collected from Figure 4 were listed in Table I.

Figure 4 showed that FR silk appeared at two significant areas of weight loss. Weight loss at $T_{\text{max}} = 238^\circ\text{C}$ corresponding to the decomposition of polyDMMEPN linkage and 307°C for the decomposition of the silk itself. Control silk had only one



Scheme 2. Graft copolymerization of DMMEPN and silk.

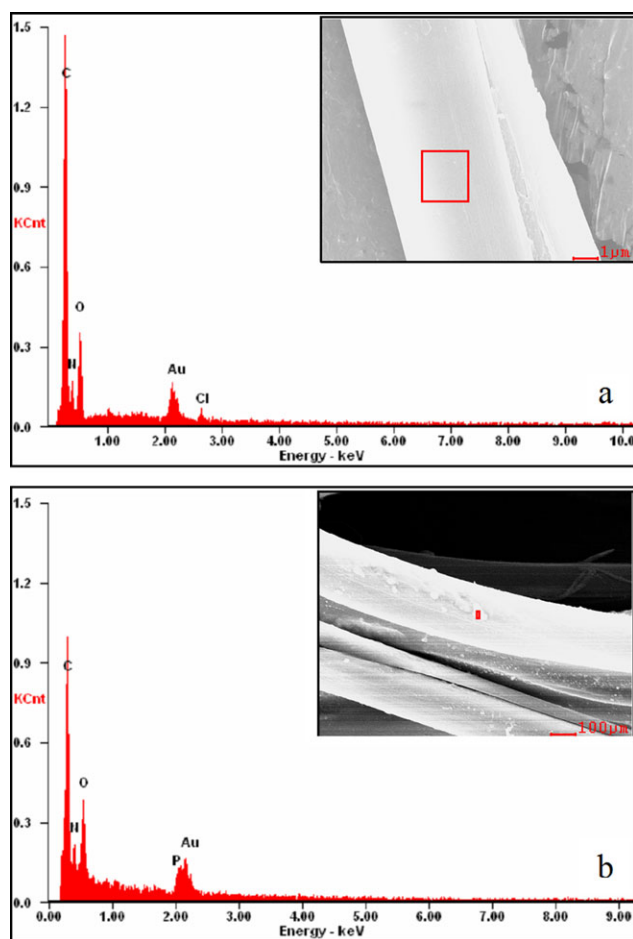


Figure 2. SEM and EDS of control silk (a) and FR silk (b, weight gain 24.22%). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

significant weight loss area at $T_{\max} = 327^{\circ}\text{C}$. The onset decomposition temperature at weight loss of 11% of FR silk shifted to a lower temperature with 10°C decrease. It could be explained

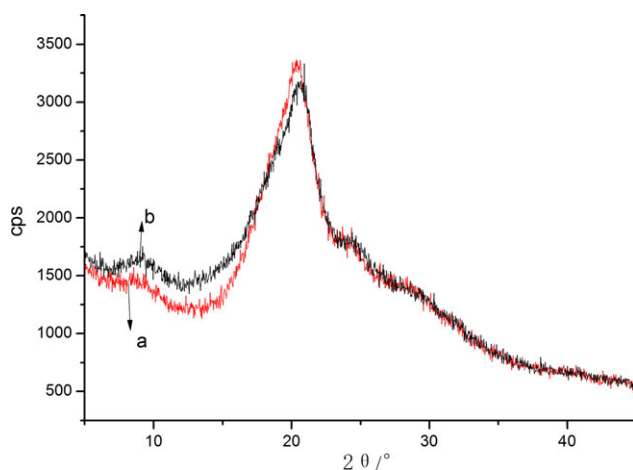


Figure 3. XRD patterns of control silk fabric (a) and FR silk (b, weight gain 24.22%). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

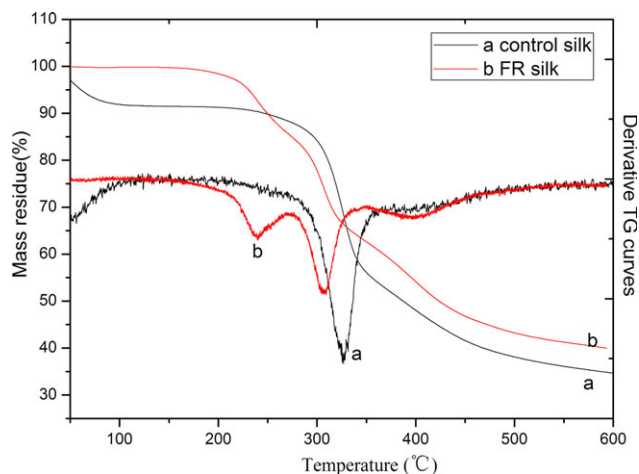


Figure 4. TG curves of control silk (a) and FR silk (b, weight gain 24.22%) in nitrogen atmosphere. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

that polyDMMEPN on the silk surface had a lower decomposition temperature than the silk itself.²⁴ Decomposed flame retardant interfere with the burning process by catalyzing the dehydration of silk and form more nonflammable char, and the char was more stable than that of control silk, so at the end of decomposition at 600°C it showed higher residue char percentage.

Char Residue and Its Morphology

Figure 5 showed SEM pictures of the char residue formed from control (a) and FR silk (b) after incineration at 600°C for 10 min.

From the morphology of char residue, one could see very different appearance of the two pictures. Figure 5(a) showed more porous, loose, and fragile char of control silk, while the char of Figure 5(b) was more solid, rigid, and surface intact. It could be inferred that the adding of flame retardant DMMEPN could reduce flammable volatile and prone to form more nonflammable char during combustion. So char of control silk had intumescent phenomenon while FR silk char did not.

Flame Retardancy Property

The flame retardancy properties of control and FR silk were listed in Table II. When the concentration of DMMEPN was 50%, 80%, and 100% on the weight of silk fabric, the weight gain of silk fabric could reach 8.43%, 13.09%, and 24.22%, respectively. And the LOI increased with the increasing DMMEPN add on. Only after the addition of 50% DMMEPN, silk fabric could exhibit hard igniting property with a candle-

Table I. Thermal Analysis Data Collected From Figure 4

Samples	T_d at weight loss of 11% ($^{\circ}\text{C}$)	T_{\max}^a ($^{\circ}\text{C}$)	Char residue at 600°C (%)
Control silk	263	327	34
FR silk	253	238, 307	40

Note: From DTG curves.

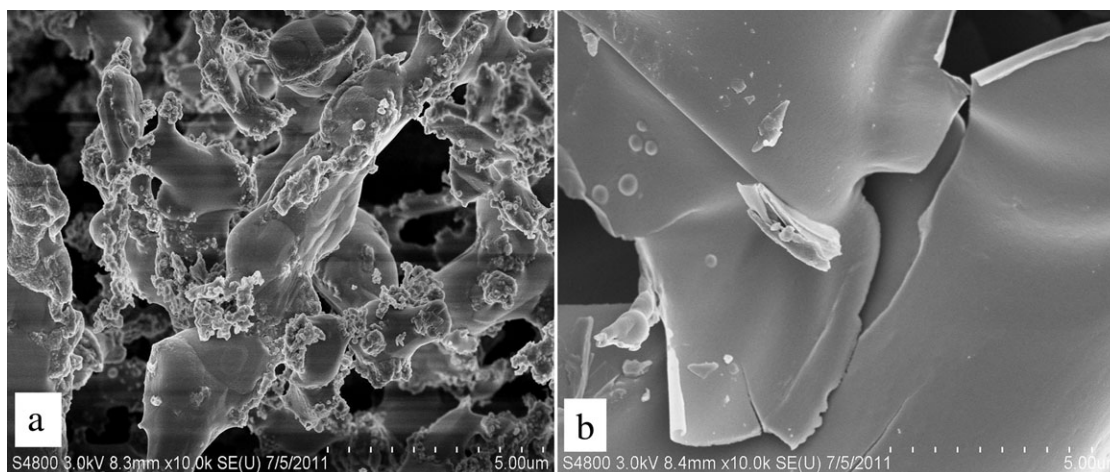


Figure 5. Char residue morphology of control silk (a) and FR silk (b, weight gain 24.22%).

Table II. The Flammability of Control Silk and FR Silk

DMMEPN(P-N) or DMMEP (P) Concentration (%)	Weight gain (%)		LOI (%)		Char length (mm)		Char residue (%)	
	P-N	P	P-N	P	P-N	P	P-N	P
0	0	0	23.21	23.21	BEL	BEL	0.96	0.96
50	8.43	7.5	29.34	26.21	66	120	5.64	1.54
80	13.09	18.8	31.75	29.45	44	68	5.88	3.88
100	24.22	27.2	32.38	30.22	42	50	10.93	5.16

Note: BEL, burn entire length.

like fire with LOI of 29.34% and could pass the vertical flammability test with char length 66 mm. DMMEPN was more effective in flame retardancy for silk fabric than we previously reported.¹⁷ In previous research, silk fabric was treated with only phosphorus-containing monomer. When DMMEP concentration is 100%, the LOI of silk fabric is 30.22%,¹⁷ whereas LOI is 31.75% for 80% DMMEPN-treated silk fabric. Less DMMEPN add on could produce better flame retardancy property, which showed that the introduction of nitrogen atom could have synergism flame retardancy effect with phosphorus. Table II also showed that with increasing weight gain, treated silk was prone to produce more char residue than DMMEP-

treated silk fabric and control fabric under combustion. This could be the result that P-N bond was more reactive in phosphorylation than P-O bond so that it could decompose more easily and was tend to promote silk produce more char during combustion.²⁵

Table III showed the laundering durability of flame retardancy of treated silk fabrics with different weight gains. After 15 hand wash cycles, silk fabrics still exhibited excellent flame retardancy with LOI above 27% and char length less than 125 mm. But after 30 hand wash cycles, only silk fabric with high weight gain 24.22% could keep good flame retardancy with LOI of 27% and char length of 120 mm. Silk fabrics treated with DMMEPN

Table III. Laundering Durability of Flame Retardancy

Weight gain (%)	1 HW		15 HW		30 HW		50 HW	
	LOI (%)	Char length (mm)	LOI (%)	Char length (mm)	LOI (%)	Char length (mm)	LOI (%)	Char length (mm)
Control	23.21	BEL	23.19	BEL	23.27	BEL	23.24	BEL
8.43	29.34	66	27.17	125	24.44	BEL	23.18	BEL
13.09	31.75	44	27.85	118	25.62	BEL	24.35	BEL
24.22	32.38	42	28.39	105	27.48	120	25.13	BEL

Table IV. Physical Properties of Control and FR Silk Fabrics

Samples	DMMEPN Concentration (%)	Weight gain (%)	Whiteness index	Moisture regain (%)	Tensile strength (CN)	
					Warp	Filling
Control silk	0	0	81.23	9.66	435	350
FR silk	50	8.43	74.30	8.02	420	345
	80	13.09	72.23	7.53	410	338
	100	24.22	71.90	7.38	350	245

could not endure 50 HWs with LOI less than 25.13% and failed to pass vertical flammability test.

Physical Property

Table IV listed whiteness index, moisture regain, and tensile strength of control and FR silk fabrics. From Table IV, one could see that after grafting, the whiteness index slightly decreased, which was mainly because of the oxidation of tyrosine by KPS during grafting copolymerization process.²⁶ Higher DMMEPN add on needed more KPS to be initiator, so the whiteness index decreased with increasing weight gain. Moisture regain could be indicated by the hygroscopicity corresponding to the wearing conformability of silk fabric. Treated silk fabrics had decreased moisture regain compared with control silk fabric, which mainly because covered grafted PDMMEPN on silk surface imparted some hydrophobic property to silk fabric. The decreased moisture regain could not affect the wearing comfortability too much as its moisture regain was equivalent to cotton. Table IV also showed changes in tensile strength of silk fabrics at warp and filling direction at different weight gains. At weight gain below 13.09%, the tensile strength almost remained unchanged as the weight gain increased whereas it sharply decreased at weight gain of 21.22%. The tensile loss is 19.5% at warp direction and 30% at filling direction. The decrease was mainly because DMMEPN entered into the amorphous region of silk fibers and destroyed the Van der Waals interaction between silk molecules.²⁷

CONCLUSIONS

A water-soluble flame retardant monomer DMMEPN was successfully applied onto silk fabric initiated by KPS. Grafted silk fabric exhibited good flame retardancy with high LOI 32.38%, char length 42 mm, and could endure 30 hand wash cycles. The grafting process did not affect the crystalline structure of silk, and copolymerization reaction only occurred at amorphous area of silk. TG and char residue morphology showed the DMMEPN-grafted silk had a very different thermal decomposition mode with control silk. PolyDMMEPN grafted on the silk decomposed first and interfered with the burning process by catalyzing silk to form more stable and nonflammable char during combustion. Synthesized new DMMEPN showed more effective flame retardancy property than DMMEPN previously reported for its P–N synergism effect. Grafted silk fabrics showed slight decrease of whiteness index, hygroscopicity, and tensile strength, which had little negative effect on the final uses.

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