FLAME RETARDANCY AND ULTRAVIOLET RESISTANCE OF SILK FABRIC COATED BY GRAPHENE OXIDE

by

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Silk fabrics were coated by graphene oxide hydrosol in order to improve its flame retardancy and ultraviolet resistance. In addition, montmorillonoid was doped into the graphene oxide hydrosol to further improve the flame retardancy of silk fabrics. The flame retardancy and ultraviolet resistance were mainly characterized by limiting oxygen index, vertical flame test, smoke density test, and ultraviolet protection factor. The synergistic effect of graphene oxide and montmorillonoid on the thermal stabilization property of the treated silk fabrics was also investigated. The results show that the treated silk fabrics have excellent flame retardancy, thermal stability, smoke suppression, and ultraviolet resistance simultaneously.

Key words: *silk fabric, flame retardancy, graphene oxide, ultraviolet resistance, smoke density*

Introduction

Silk, as a natural fiber with good air permeability, hygroscopicity, and superb wearing comfortableness, has been extensively applied in clothes and household textiles, and it is considered as an ideal material for making wearable electronics and flexible sensor [1, 2]. However, silk belongs to flammable fabric, and it can be easily ignited by flame, which confines its further application. Furthermore, this shortcoming of silk may induce fire disaster and cause huge losses to people [3]. Meanwhile, the human's skin exposure to the ultraviolet (UV) Sun radiation may cause some serious consequences like melanin deposition, skin drying, pain, and wrinkle. However, UV resistance of natural silk fabric is too low to meet the anti-UV standard for protecting people's skin [4]. Therefore, it is significant to improve the flame retardancy and UV resistance of silk fabric in some specific application fields.

Graphene, as a new 2-D laminar carbon material, has attracted a great deal of attention recently for its' excellent electric conductivity, thermal stability, and UV resistance properties [5-7]. Furthermore, graphene oxide (GO) is a derivative of graphene, which has varieties of functional groups on the basal planes like hydroxyl, epoxide functional groups, and carboxyl. The GO, as a novel environmental friendly flame retardant, has no toxicity and zero halogen, and has been used in some flame retardant fields [8]. At present, there are two reported methods of applying the flame retardancy of graphene to textiles finish: one is layer-

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by-layer assembly technology, through which the GO and other flame retardants could be finished onto the fabric surface [9]. The other method is doping method, that is to say, GO doped with flame retardant nanoparticles to finish textiles [10]. But those two methods both can not make the flame retardancy of graphene work most effectively.

In this work, a facile coating method was used to treat silk fabrics with flame retardant GO hydrosol. Moreover, in order to further improve the flame retardancy of silk fabric, different quantity of montmorillonoid (MMT) was added into the GO hydrosol. The flame retardancy and UV resistance property of the treated silk fabrics were investigated, the synergistic effect between GO and MMT on the thermal stabilization property of the treated silk fabrics was also investigated.

Experimental

Synthesis of GO hydrosol

The GO was synthesized from graphite powder by the improved Hummer's method [11]. A 9:1 mixture of concentrated H_2SO_4/H_3PO_4 (135:15 mL) was added into a 1000 mL of flask containing 3 g of graphite powder, then 21 g $KMnO_4$ was added into the mixture with quickly stirring. The reaction system was maintained at 0 ℃ in the ice water bath for 30 minutes. The reaction was then heated to 50 ℃ and stirred for 10 hours. Finally, the reaction was cooled to room temperature and 450 mL deionized water with 6 mL H_2O_2 (30%) was added to stop the oxidation process. The product was then washed in succession with 200 mL of water, 200 mL of 30% HCl, and 200 mL of ethanol, for each wash, than the product was centrifuged at 10000 rpm for 10 minutes. The remained product was then added with enough deionized water and dialyzed for 3 days. The final product, GO hydrosol, was obtained.

Preparation of GO coated silk fabrics

Different quantity of MMT was added into the GO hydrosol, polyvinyl alcohol (PVA) was also added into the GO hydrosol as thickener. Then five different mass ratios of the GO-PVA-MMT (90:10:0, 85:10:5, 80:10:10, 75:10:15, and 70:10:20) flame retardant coatings were prepared to coat five silk fabrics using a sample coating machine. The prepared silk fabrics with different flame retardant coatings were designated as silk-1, silk-2, silk-3, silk-4, silk-5, respectively.

Measurements

The flammability of the samples was determined by limiting oxygen index (LOI) according to ASTM D2863 on a FTT 0002 oxygen index instrument (FTT, Derby, UK). The LOI refers to the minimum concentration of oxygen in a mixture of oxygen and nitrogen which will just support flaming combustion over a length of 40 mm at 23 ± 2 ℃.

The thermal stability of the samples was carried out with YG8158 fabric flame-retardance tester (Ningbo Textile Instrument Factory, Ningbo, China) according to the ISO 6941:2003 testing standard. The samples were vertical suspended in the chamber, with 3 cm high flame burning it for 12 seconds, the damage length of the samples was measured by a ruler.

The smoke suppression of the samples was carried out with FTT 0064NBS smoke density test chamber according to the ISO 5659-2 testing standard in terms of flameless combustion mode at 560 ℃ for 500 seconds, with the maximum radiant heat of 50 kW/m^2 and one sample layer of 80 × 80 mm^2.

The morphology of the samples was observed by a Hitachi TM3030 desktop scanning electron microscope (SEM) at an acceleration voltage of 3 kV under vacuum condition. The samples were mounted on a conductive adhesive tape and coated with gold before testing.

The UV resistance property of the samples was characterized by ultraviolet protection factor (UPF) according to UV standard 801 on a UV-1000F UV transmittance analyzer (Labsphere Inc., North Sutton, N. H., USA). The samples were transmitted by UVA and UVB.

Results and discussion

Limiting oxygen index analysis

The flame retardancy of the treated and untreated silk fabrics was evaluated by LOI test. It can be seen from fig. 1 that LOI value of the untreated silk fabric is just 24.5%. With the increasing of MMT dosage, LOI value of the treated silk fabrics became higher. Moreover, LOI reached 38.5% when the silk fabric coated by GO hydrosol (silk-1), and LOI reached up to the highest 44.6% when the silk fabric coated by GO hydrosol with MMT doped (silk-5). The results proved that the prepared silk fabrics have fabulous flame retardancy property. Moreover, GO hydrosol with MMT doped can further improve LOI value of the treated silk fabrics, MMT and GO has a good synergistic effect on promoting flame retardancy of the prepared silk fabrics.

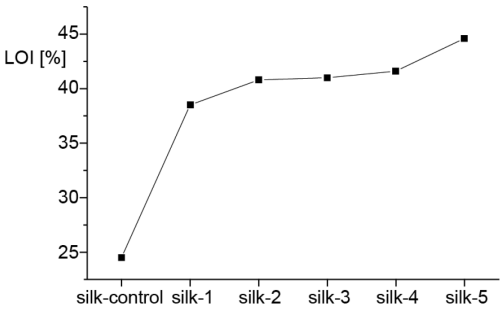

Figure 1. The LOI value curve of the treated and untreated samples

Vertical flame test and thermal stability analysis

In order to investigate the thermal stability of the prepared silk fabrics, the vertical flame test was conducted. The result is showed in tab. 1 and fig. 2. It can be seen that there is a serious damage appeared in the sample silk-control with 22.0 cm of damaged length. In contrast, a slight damage appeared in the sample silk-1 with 11.5 cm of damaged length. Furthermore, sample silk-5 kept its shape as before and its damaged length is only 9.5 cm. The results indicated that GO coating had an effective protection to silk fabric because the GO

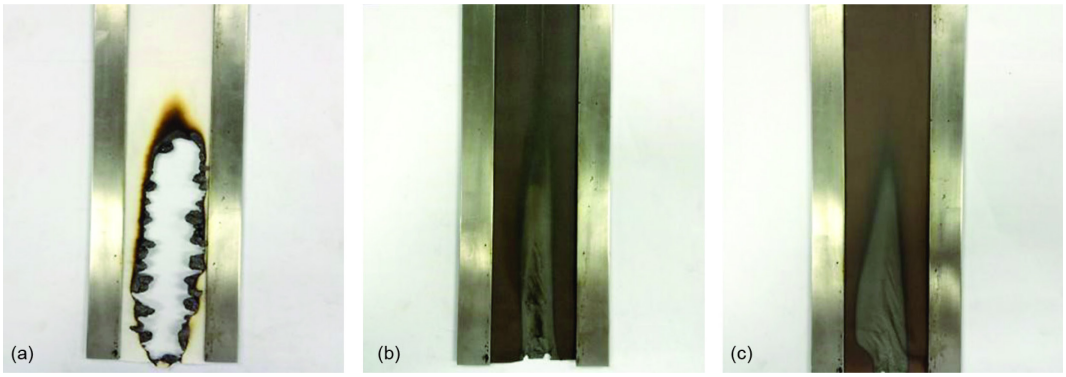

Figure 2. Vertical flame test images of silk-control (a), silk-1 (b), and silk-5 (c)

Table 1. Damaged length of silk samples

Sample	silk-control	silk-1	silk-2	silk-3	silk-4	silk-5
Damaged length [cm]	22.0	11.5	11.0	10.4	10.0	9.5

films deposited on the silk fabric surface can protect the fabric from damaging by the flame, and GO coating can also greatly improve the thermal stability of the silk fabric. In addition, MMT doped in GO hydrosol appropriately could further improve the thermal stability and flame retardancy of silk fabric. When the dosage of MMT doped in the composite hydrosol reached 20%, the synergistic effect between GO and MMT on promoting thermal stability and flame retardancy was the best, which was also consistent with LOI value of the treated samples.

Smoke density test

Smoke density refers to the amount of smoke produced by the material under test conditions. If the material generates great amount of smoke in the fire disaster, evacuating personnel and extinguishing the fire would be more difficult.

The smoke suppression situation of treated and untreated silk fabrics is depicted in fig. 3. It can be seen that the silk-control kept the smoke density value of 8.20 (/g) after 150 seconds, in contrast, the sample silk-1 shows fabulous smoke suppression ability. The maximum smoke density value of silk-1 was only 3.09 (/g), which appeared at the time of 154 seconds. Furthermore, the smoke density curve of the sample silk-5 shows that its' smoke suppression ability is stronger than sample silk-1, and its maximum smoke density value is 2.72 (/g). These results indicated that GO hydrosol could efficiently suppress the smoke release of silk fabric under flame burning condition, and the GO films deposited on the silk surface endowed the silk fabric with excellent smoke suppression ability. In addition, the synergistic effect between GO and MMT could further decrease the smoke density value of the silk fabrics. From fig. 3, it also can be seen that curves of the sample silk-1 and silk-5 appear a downward trend obviously after the maximum smoke density peak, and the final smoke density value of the sample silk-5 is only about 1.60 (/g). This result might be attributed to the honeycomb structure consisted of combusted GO films carbon layer upon the silk fabric surface. As a result, the structure could absorb a large amount of smoke and reduce the smoke density value of the treated samples.

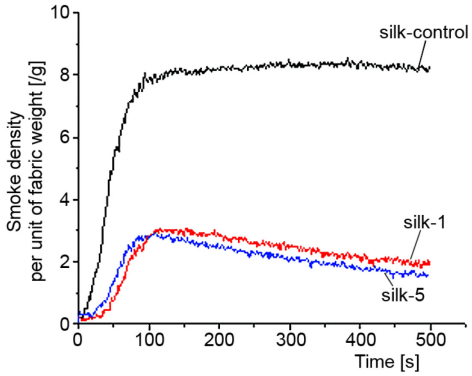

Figure 3. Smoke density curves of silk-control, silk-1, and silk-5

The SEM

The surface morphology of silk samples observed by SEM are showed in fig. 4. Compared fig. 4(b) with 4(a), it can be seen that GO films successfully deposited on the silk fabric surface. These films made silk fabric separate from oxygen just like fire prevention net. Meanwhile, as a carbon material, GO has higher ignition point than silk fabric and its com-

bustion would produce a large amount of CO_2. As we know, the CO_2 can prevent burning efficiently. Besides, compared fig. 4(c) with 4(b), it can be seen that there were so many MMT particles in GO films deposited on the silk fabric surface, indicating that the flame retardant elements Si and Al have been attached to the surface successfully. The two elements would improve the thermal stability of the silk fabrics treated by MMT doped GO hydrosol.

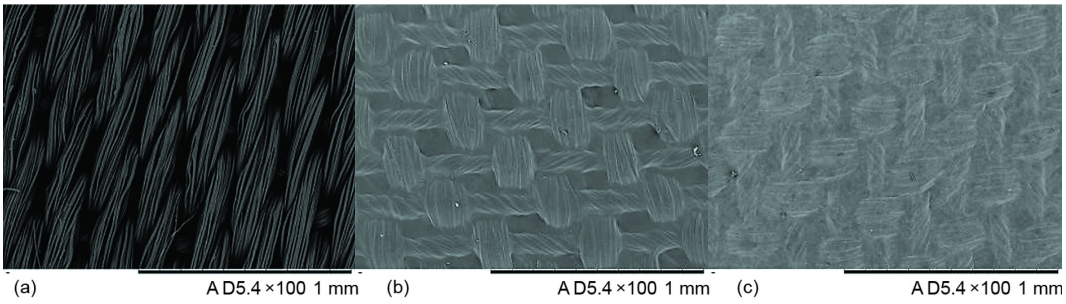

Figure 4. The SEM images of silk-control (a), silk-1 (b), and silk-5 (c)

Ultraviolet resistance analysis

In order to investigate the UV resistance property of the silk fabrics, three UV resistance factors were taken into consideration to measure it, *i. e.* the UPF values, transmittance of UVA, and UVB. The measurement results of these silk fabric samples are shown in fig. 5. It can be seen that the UPF value of sample silk-control is 7, but the UPF value of all the other treated samples reached striking 500. In addition, 28% of UVA and 9% of UVB could transmit the controlled silk fabric, however, the silk coated by GO can block more than 99.9% of UVA and UVB. The results indicated that GO films deposited on the surface provide the silk fabric with excellent UV shielding effect.

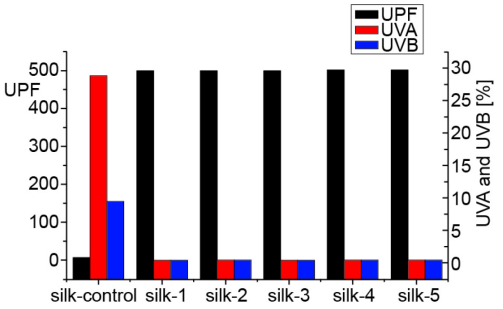

Figure 5. The UPF value and UVA and UVB transmittance of silk samples

Conclusion

In conclusion, silk fabric coated by GO has superb flame retardancy, thermal stability, smoke suppression, and UV resistance properties simultaneously. The GO hydrosol doped with MMT presented a good synergy effect on promoting flame retardancy and thermal stability of silk fabric. This multifunctional silk fabric would have a promising application in the future.

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