Original Article

Phytic acid/silica organic-inorganic hybrid sol system: a novel and durable flame retardant approach for wool fabric

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ABSTRACT

The fabrication of long-lasting flame retardant wool textiles through an eco-friendly scheme is still an urgent task. In the present study, an eco-friendly and innovative hybrid silica sol with core-shell structure was prepared by using phytic acid (PA) as catalyst and dopant for tetraethoxysilane. PA/silica organic-inorganic hybrid sol (PA/silica sol) was then employed to produce durable flame retardant wool fabric using a combined nanoparticle adsorption and pad-dry-cure procedure. The treated wool had enhanced thermal stability and greatly suppressed smoke production capacity. It could still be self-extinguishing after 30 washing cycles. The present approach brought no great negative influence on the handle and mechanical performance of wool fabric. The PA/silica sol network was found to participate in the degradation of the treated wool in the solid phase. The formation of highly inflated char during burning also revealed the flame retarding activity of the PA/silica sol on wool by a condensed charring action.

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1. Introduction

Textiles have found their massive application in many aspects of our lives, and are also known for their easy ignition and high flammability. Wool fiber has a certain level of flame retardant (FR) performance due to its high nitrogen and sulfur content as well as high moisture regain. But once wool fabrics are ignited, flames can spread rapidly in them, hindering their application in aircraft carpets, upholsteries, wall coverings and protective clothing. To improve the FR property of textiles including wool is an important issue for guaranteeing human safety and extending their potential applications. It is recognized that a majority of the regularly used halogen-based and formaldehyde-containing FR products for textiles can have adverse impacts on human health and environment [1,2]. Besides, the Zirpro treatment, the most commercially available FR approach for wool textiles, may cause metal pollution to water environment. In this context, great progresses have been achieved on the exploitation of eco-friendly and effective FR agents [3,4].
Over the past decade, inorganic nanoparticles and nanotechnology have been applied in the field of the functional modification of textile materials for enhanced UV protection, antibacterial, hydrophobic, self-cleaning and FR properties [5–7]. By acting as a thermal insulator, inorganic nanocoatings are capable to absorb the released heat and restrain the generation of volatiles, thus enhancing the heat and fire resistance of textile substrates. To reach this goal, nanoparticle adsorption, sol-gel processing, pad-dry-cure finishing, and layer by layer assembly were used to develop inorganic nanocoatings on the surface of textiles [8]. These “smart” architectures can impart multifunctionality to textiles. However, the poor washing durability of these coatings on textiles is a significant limitation for their potential industrial application [8–10]. The sol-gel technique to prepare inorganic FR system is considered as a “green” approach. But it was found that pure inorganic architectures based on the sol-gel process may be not effective enough to extinguish the flame on textile substrates if they are not combined with organic compounds containing phosphorus and nitrogen to form synergistic or simple joint FR effects [9].

Phytic acid (PA) is a promising plant-derived and phosphorus-rich compound for the FR protection of polymeric materials including textiles. PA also displays appealing feasibility and functionality when applied to different kinds of materials because it contains functional hydroxyl and phosphate groups. PA can be employed to enhance the FR ability of textiles using the layer by layer assembly, which involves the repeated deposition of polyanionic PA and poly-cationic compounds on the fabric surface. In previous reports it was found that the assembled FR coating based on PA and chitosan [11], nitrogen-modified silane hybrid [12] and 3-aminopropyl triethoxysilane [13], as well as chitosan/oxidized sodium alginate [14], enhanced the flame resistance of cotton and polyamide 66 fabrics. The water-insoluble FR additives based on negatively charged PA and oppositely charged compounds (e.g., chitosan and polyethyleneimine) [15,16] as well as metallic phytates [17] and ferric phytate functionalized graphene [18] were also prepared for plastic materials.

Our group employed PA to enhance the flame retardancy of poly(lactic acid) nonwoven [19] as well as wool and wool/silk blend fabrics [20,21] via pad-dry-cure and exhaustion processes, respectively. The feasibility of the application of PA to wool and silk fibers lies in the electrostatic attractions between them. Nevertheless, the resulting FR effect had poor resistance to washing owing to the high solubility of PA in water. To address this issue, an organic-inorganic synergistic FR approach based on PA and titanium oxide nanoparticles was applied to silk and wool fabrics by the use of 1,2,3,4-butanetetracarboxylic acid to fix titanium oxide on protein fibers [22,23].

Furthermore, a phosphorus-rich organic-inorganic silica sol was developed using PA and tetraethoxysilane (TEOS). The application of such hybrid sol by a pad-dry-cure process showed efficient FR ability on silk fabrics but suffered from poor washing resistance [24]. It was also true for wool fabrics according to our preliminary experiments. On the other hand, if the modified hybrid sols with silane cross-linkers [24] were applied to wool fabrics, they could just offer a limitedly improved washing resistance, and moreover posed a significant influence on the physical performances (especially softness) of the fabrics. Indeed, in the case that the sol-gel systems are applied to textile materials, the achievement of the good washing resistance of the FR function with less influence on the softness of textiles is a great challenge [9]. In general, the hybrid silica sol applied to wool fabrics has poor washing durability due to the fact that the cuticle layer on the surface of wool fiber is an obstacle for nanoparticles to penetrate into fiber interior because of its tight structure, resulting in the surface attachment of nanoparticles. It was reported that the accessibility of nanoparticles into wool fiber could be enhanced by raising the immersion temperature, which increases the swelling extent of wool fiber [25]. Considering this point, in the present study, the PA doped hybrid silica sol (PA/silica sol) was applied to wool fabric by a nanoparticle adsorption process followed by a pad-dry-cure procedure. By doing so, the ability of the hybrid sol particles to penetrate into wool fiber interior was enhanced, and accordingly the durability of the functional wool fabric was significantly improved. In the present study, the FR efficiency of PA/silica sol and its washing resistance on wool fabric were investigated, the smoke generation ability and thermal resistance of the treated wool fabrics were estimated, and the chemical composition of the burned wool and the action of the PA/silica sol in improving the FR performance of wool were also discussed.

2. Materials and methods

2.1. Materials

The woven wool fabric (125 g/m²) was obtained from Shanghai Textile Industry Institute of Technical Supervision, China. Phytic acid (70 wt% in water) was bought from Chengdu Ai Keda Chemical Technology Co. Ltd., China. Tetraethoxysilane (TEOS) and ethanol were supplied by Sinopharm Chemical Reagent Co. Ltd., China. The wool textile detergent was bought from Shanghai Zhengzhang Laundering and Dyeing Co. Ltd., China.

2.2. Preparation of PA/silica sol

The hybrid sols were prepared as follows: the mixture consisting of different dosages of TEOS (0.01, 0.02, 0.03, 0.06 and 0.09 mol) and ethanol (the molar ratio of ethanol:TEOS was 2:1) was dropwise added into PA solution (0.01 mol) in a total volume of 100 mL under stirring; the dropping process was finished within 1 h. Afterward, the mixture was stirred at 70 °C for 3 h.

2.3. Preparation of PA/silica sol treated wool

Firstly, wool fabrics (4 g) were soaked in the hybrid sols (100 mL) at 90 °C for 30 min under stirring. After the completion of soaking, the samples were removed and passed through a padder. The padded samples were then pre-dried at 80 °C for 3 min and cured at 160 °C for 3 min. At last, the samples were rinsed in deionized water and air-dried. In the result and discussion section, Wool-1, Wool-2 and Wool-3 samples denote the fabrics...
were treated with the hybrid sol solutions which were prepared by 0.1 mol/L PA as well as 0.1, 0.3 and 0.6 mol/L TEOS, respectively.

2.4. Measurements and characterizations

The surface images of silica particles were captured by the Hitachi HT7700 transmission electron microscope (TEM). The surface morphologies of the wool fabrics and their chars were observed using the Hitachi TM3030 tabletop scanning electron microscope (SEM). The attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra were collected from the Thermo Scientific Nicolet iS50 FT-IR spectrometer. For the treated fabrics, the whiteness index, bending length, and flexural rigidity were determined following the previously described methods [24]. The thermal stability was determined using the Perkin-Elmer Diamond TG/DTA SII thermal analyzer. The content of P and Si was tested by the inductively coupled plasma optical emission spectrometer following the already described method [24]. The pyrolysis combustion flow calorimetry (PCFC) and smoke generation tests were performed according to ASTM D7309 (Method A) and ISO 5659.2, respectively; the smoke release parameters were obtained under the radiant flux of 25 kW/m². The limiting oxygen index (LOI) test was conducted according to GB/T 5454-1997. The vertical burning test was performed according to GB/T 5455-2014; the burning behavior of the fabrics was classified according to GB/T 17591-2006. The washing resistance was evaluated by repeated washing where each washing cycle was set at 40 °C for 10 min using 2 g/L commercial detergent.

3. Results and discussion

3.1. Preparation and application of the PA/silica sol

Fig. 1 shows the TEM micrograph of the PA/silica. The synthesized PA/silica particles with core-shell structure were generally spherical in shape and had an average size of about 350 nm. Besides, the prepared PA/silica sol had a high condensation degree as PA served as the acid catalyst for the hydrolysis of TEOS [24].

According to our preliminary experiments, the wool fabrics treated with the PA/silica sol through the pad-dry-cure process had poor washing durability due to the surface barrier effect of wool fiber for the penetration of chemicals. Thus, in this work, the nanoparticle adsorption-assisted pad-dry-cure procedure was employed for the FR modification of wool fabrics with the PA/silica sol to develop long-lasting FR effect. As shown in Table S1, such treatment exerted a negative impact on the whiteness of wool fabric but had little influence on the handle and mechanical performance of wool fabric.

3.2. ATR-FTIR and morphology of the treated wool

As shown in Fig. 2, the characteristic peaks of the untreated wool were observed at 1628 (amide I) and 1514 cm⁻¹ (amide II)
For the spectra of the treated wool samples, the new signals appeared at 1160 and 953 cm\(^{-1}\), which should be assigned to the stretching vibration of P=O and P–O of PA [27,28]. Besides, the overlapped Si-O-Si and O=P=C stretching vibration of the PA/silica sols appeared at 1050 cm\(^{-1}\) [28,29].

As shown in Fig. 3, the PA/silica sol treatment brought some changes in the surface morphology of wool fiber. The deposition of FR compounds on the fiber surface was observed for Wool-1 sample, and more continuous coatings and improved surface coverage of the coatings were found for Wool-2 and Wool-3 samples, which is in correspondence with the higher weight gain of the two samples.

3.3. Thermal analysis of the treated wool

Fig. 4 shows the thermogravimetric (TG) and derivative TG (DTG) curves of the PA/silica sol and wool fabrics in air. Three degradation stages were evidently detected for the untreated wool. The early stage (stage I) below 150 °C, giving rise to a weight loss of about 8 % (Table S2), was induced by the water evaporation, which is in coincidence with the high moisture regain of wool fiber [20]. The second and third stages (stage II and stage III) occurred in the range of 220–425 and 450–650 °C, leading to a weight loss of about 47.6 and 44.4 %, respectively. These two stages are the main decomposition steps. Stage II mainly refers to the gradual destruction of the wool fiber integrity by the heating process, during which the hydrogen and disulfide bonds are fractured, the polypeptide chains are ruptured and the main structures are split and melted [30,31]. Stage III involves the oxidative reaction of the residual organic substrates. The release of pyrolysis gases mainly causes the weight loss of wool substrates, and there is almost no char residue left at 650 °C.
As shown in Fig. 4, the PA/silica sol almost showed a linear weight loss with increasing temperature. Although the PA/silica sol displayed lower thermal stability than wool below 300 °C, the introduction of PA/silica sol increased the thermal degradation temperature of wool and postponed the degradation process of wool. Moreover, the PA/silica sol reduced the decomposition rate of the treated wool (observed from DTG curves), leading to a reduced weight loss and an increased residue weight at the end of each decomposition stage. In addition, the obvious difference of TG curves between the samples before and after the treatment occurred at 250 °C, and such difference increased with increasing heating temperature. The residue weight of the wool samples at 150, 425 and 650 °C (Table S2) offered the comparable evidence for this phenomenon. Clearly, the PA/silica sol mainly disturbs the thermal decomposition of wool at stage II.

The calculated TG curves of the treated wool were obtained based on the simple additive contribution of wool and PA/silica sol system, and the difference between the experimental and calculated TG curves was used to evaluate the interactions between wool and PA/silica sol system during heating [32]. Taking Wool-3 as a sample, the experimental curve showed much higher thermal stability and char residues than the calculated one (Fig. 4). The weight gain of the Wool-3 sample was about 15.8 %. However, compared to 11.2 % char residue for the calculated Wool-3, the experimental Wool-3 sample had a high char residue of 25.7 % at 650 °C (Table S2). These results suggest that certain interactions rather than the simple additive interaction between wool and PA/silica sol occur during heating. The PA/silica sol system can change the thermal degradation pathway of wool and promote the char formation of wool. Moreover, the growing dosage of silica component as a function of increasing TEOS dosage contributes to the further elevated thermal stability of wool. The combination of phosphorus and silicon components could induce the formation of more complicated and thermal stable char, which has good resistance to oxidation, thus the treated wool yields a high amount of char residue at 650 °C. Besides, the treated wool also showed greater thermal stability compared with the untreated wool in nitrogen (Fig. S1).

### 3.4. Smoke density analysis of the treated wool

The potential fire risk of the treated wool under irradiative heat flux was evaluated using the smoke density test. Fig. 5 shows the specific optical density (Ds) curves of the wool samples. Table 1 reports the corresponding parameters: the maximum Ds value (Dmax) and the time to reach Dmax.

Smoke in a fire accident is quite detrimental to victims because the particles in smoke interfere with eyesight, and carbon monoxide induces hypoxia and coma [33]. The suppression of smoke release is one of the top priorities of FR protection. During the smoke density test, heavy smoke was detected for the untreated fabric. However, the treated wool fabrics displayed remarkably depressed smoke release in the whole combustion process; the smoke release saturation of Wool-1, Wool-2 and Wool-3 dropped to 26.9, 22.2 and 19.2, respectively from 93.7 of the untreated wool. The low smoke release suggests the low combustion intensity and fire risks of the treated wool fabrics.

### 3.5. Flammability and durability of the treated wool

The untreated wool fabric was lit easily in the vertical burning test, and the flame destroyed the whole sample within the ignition time (12 s), yielding a full char length of 30 cm. Besides, the untreated wool had no afterflame and afterglow time as it was completely burned out. However, the treated wool showed good char formation ability during burning, displaying a different burning behavior compared with the untreated one. The bottom substrate touching the fire swelled quickly during burning, and produced a bulgy char (Fig. 6). The inflated char...
was able to withstand the open fire and protect the upper substrate. As a result, the treated wool fabrics extinguished once the ignition source was removed, and they had no afterflame and afterglow phenomena. As shown in Fig. 7, the treated wool showed a remarkable reduction in char length, and reached the B1 rating (char length < 15 cm) in the vertical burning test. The improved flame retardancy of the coated wool can be attributed to the protective role of the PA/silica sol coating that favors the char formation of wool instead of producing volatile organic compounds which can support the combustion.

In the LOI test, the treated wool also showed enhanced charring ability and remarkably improved FR ability. As shown in Fig. 7, the weight gain and LOI values of the treated wool increased with increasing TEOS concentration. When treated with 0.1 mol/L PA, the wool fabric had a weight gain of 11.8%, and its LOI increased to 31.6 from 23.6% of the untreated one. The addition of TEOS further raised the weight gain and LOI of the treated wool; by increasing TEOS dosage from 0 to 0.3 mol/L, the LOI increased from 31.6–36.8%, indicating an effective joint FR action of silicon and phosphorus. Further addition of TEOS gave rise to little increase in the weight gain and LOI value of wool fabric.

For the treated fabrics, the Si content increased obviously and the P content had little change by increasing TEOS dosages (Table 2), revealing that the gradually improved flame retardancy of the treated wool should be ascribed to the increased Si content. In conclusion, the PA/silica sol works efficiently in conversing organic matters to intumescent char and heightening the FR ability of wool fabric.

The FR ability and washing resistance of the samples prepared via the traditional pad-dry-cure procedure (Wool-3-traditional) and the combined nanoparticle adsorption and pad-dry-cure procedure (Wool-3) were compared. As shown in Fig. 8, both Wool-3-traditional and Wool-3 displayed low char length and high LOI values, meaning their good flame retardancy. Furthermore, the Wool-3 displayed better FR ability, revealing that the PA/silica sol can impart higher FR efficiency to wool when applied using the nanoparticle adsorption-assisted pad-dry-cure procedure.

In addition, with increasing washings, Wool-3-traditional and Wool-3 showed reduced FR performance, and the former displayed a higher reduction in FR ability. Wool-3-traditional attained a char length of 15.3 cm and could not reach the class B1 standard after 20 washing cycles. However, Wool-3 still possessed a low char length, which was shorter than 11 cm, and met B1 standard after 30 washing cycles; besides, the washed Wool-3 had an LOI of 31.0%, which was much higher than 26.8% of the washed Wool-3-traditional after 30 cycles of washing. As a whole, the PA/silica sol showed excellent efficiency and durability on wool fabric when applied by the combined nanoparticle adsorption and pad-dry-cure process. It should be ascribed to the increased swelling ability of wool fiber during the nanoparticle adsorption step at a high immersing temperature (90°C), which results in the better diffusion ability of the FR agents in wool fiber.

![Fig. 7 – Weight gain, char length and LOI of the wool fabrics treated with the hybrid sol at various TEOS dosages.](image)

![Fig. 8 – Char length (a) and LOI (b) of the treated wool fabrics after repeated washing.](image)
### Table 2 – Si and P content of the wool samples before and after the vertical burning test.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si content (mg/g) Before burning</th>
<th>After burning</th>
<th>P content (mg/g) Before burning</th>
<th>After burning</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Wool-1</td>
<td>1.82</td>
<td>3.65</td>
<td>13.86</td>
<td>27.74</td>
</tr>
<tr>
<td>Wool-2</td>
<td>3.88</td>
<td>7.07</td>
<td>13.97</td>
<td>30.05</td>
</tr>
<tr>
<td>Wool-3</td>
<td>4.41</td>
<td>8.86</td>
<td>14.26</td>
<td>31.19</td>
</tr>
</tbody>
</table>

3.6. **ATR-FTIR and morphology of the char residues**

As observed from the burning tests, the modification with the PA/silica sol changed the burning behavior of wool fabrics. To investigate the burning process of wool and the action of the PA/silica sol, the ATR-FTIR analysis was performed to determine the composition of the residue of the wool samples. For the spectrum (Burned wool) of the untreated wool after burning (Fig. 9), the band of O–H and N–H stretching at around 3276 cm\(^{-1}\) almost disappeared, indicating the production of water and ammonia volatiles during the burning; the bands of CH₂ and CH₃ at 2958 and 2931 cm\(^{-1}\) no longer appeared, implying the generation of hydrocarbon gases; the strong bands of amide I at 1640 cm\(^{-1}\) and amide II at 1516 cm\(^{-1}\) also disappeared, revealing the thermal cracking of the peptide chains; besides, the new bands of C=C stretching at 1590 cm\(^{-1}\) and C–H bending at 760 cm\(^{-1}\) appeared, and the broad band of C–N and C–O stretching at 1228 cm\(^{-1}\) had an increase in intensity, suggesting the formation of aromatic carbonaceous compounds [34–36].

![Fig. 9 – ATR-FTIR spectra of the wool char residues after the vertical burning test.](image1)

![Fig. 10 – SEM micrographs of the char residues after the PCFC test.](image2)
For the spectrum of the Burned Wool-3, the new bands at 1081, 984 and 890 cm\(^{-1}\) are ascribed to the absorption of Si-O-Si, O–P–C and P–O structures [28,29]; the band of C=O stretching at 1228 cm\(^{-1}\) also exhibited increasing intensity, revealing the enhanced char formation induced by the PA/silica sol, and the function of P/Si network in the solid phase. The significantly increased Si and P content (Table 2) of the wool samples after burning also confirms that these elements act in the solid phase. The phosphate groups can catalyze the generation of the insulating char layer with good thermally stability, and the silica network is beneficial to develop the dense protective char layer on the substrate surface to isolate heat and oxygen and thus increase the FR effect.

Fig. 10 shows the SEM images of the char residue from the PCFRC test, which was conducted under irradiative heat flux. For the untreated wool, no fibrous structure was observed in the loose and fragile char residue because of the deficient char formation. However, for the treated wool, the fibrous structure was preserved in the char residue owing to the good charring ability and high thermal stability. The intumescent structures of the char residue are beneficial to the increased FR ability of wool by hampering the substance/energy exchange between the gas and condensed phases. Therefore, the condensed charring mechanism can be drawn for the PA/silica sol treated wool.

4. Conclusions

A phosphorus-rich silica sol was prepared and exploited to improve the FR property of wool textiles by the combined application of the nanoparticle adsorption and pad-dry-cure processing, which offered great potential to increase the FR ability and durability of the PA/silica sol on wool fabric. The efficient catalytic bubbling ability of the PA/silica sol was beneficial to extinguish the wool combustion in a vertical configuration and impede the production of smoke particles. The phosphorus and silicon elements had a joint FR action as phosphorus promoted the generation of bulgy structures and silicon reinforced the developed char. The PA/silica sol was found to interfere with the degradation of wool by a condensed charring action. Besides, the PA/silica sol modification imposed limited influence on the handle and mechanical performance of wool fabric. In conclusion, the efficient and durable FR treatment in the present report represents a prospective candidate in practical application for preparing functional wool textiles.

Conflict of interest

The authors declare no conflicts of interest.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at https://doi.org/10.1016/j.jmrt.2019.11.011.

REFERENCES


