(REFEREED RESEARCH)

SIMULTANEOUS DYEING AND FLAME RETARDANT FINISHING OF WOOL FABRIC WITH ACID METAL COMPLEX DYES AND PHYTIC ACID

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ABSTRACT

A potential flame retardant phytic acid (PA) was applied to wool fabric together with acid metal complex dyes in order to prepare coloured and flame retardant textile materials, and the dyeing properties of the dyes and the flame retardant effect of PA on wool fabric were studied. The treated wool fabrics exhibited much higher flame retardancy than pure wool fabric according to limiting oxygen index and vertical burning tests. The thermal stability of wool fabrics was assessed by thermogravimetric analysis, and the results demonstrated that the flame retardant mechanism of the treated wool fabrics involves a significant condensed-phase activity. Despite the competitive effect of the adsorption between PA and the dyes on wool, it is feasible to apply PA and acid metal complex dyes to wool in one bath.

Keywords: Wool, Flame retardant, Phytic acid, Dyeing, Thermal stability

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1. INTRODUCTION

Wool is popular in apparel, industrial applications and interior textiles due to its good comfort, absorbency, anti-static, colouration and warmth retention properties as well as a high degree of inherent non-flammability (1). However, some special products such as seat coverings in cars and buses, aircraft furnishings and blankets, and military textiles need additional treatment to impart higher flame-resistance to them (2, 3).

Phosphorus-containing cellulosic flame retardants, halogen compounds, zirconium and titanium metal complexes and sulphur containing flame-retardants have been applied to the flame retardant treatments of wool textiles (4). As many halogenated products are carcinogenic or produce highly toxic and corrosive gases with great amounts of smoke in combustion, they have been legally banned. The Zirpro treatment, which is based on the exhaustion of negatively charged zirconium and titanium complexes onto positively charged wool under acid conditions, has become the most commonly used flame retardant process (5, 6). However, the heavy metal ions of zirconium/titanium existing in both Zirpro-treated wool textiles and effluent discharges could cause environmental issues. They should be gradually replaced by environmentally friendlier flame retardants. In this study, a bio-based phosphorus-containing phytic acid (PA) (Figure 1) as an eco-friendly agent was used to enhance the flame retardancy of wool fabric.

PA is extracted from beans, cereals, oilseeds and organic soils (7, 8). It has been successfully used as antioxidant, anticancer agent, biosensor, cation exchange resin and nanomaterial because of its special inositol hexaphosphate structure (8). PA contains 28 wt% phosphorus based upon molecular weight, and is promising as one of possible and effective flame retardant materials. Recently, PA as a nontoxic naturally occurring and phosphorus-containing compound has provoked people's interest in the flame retardant finishing of textiles, and found its application in the flame retardant modification of cellulosic materials (cotton fabric and paper) via different methods (7, 8).

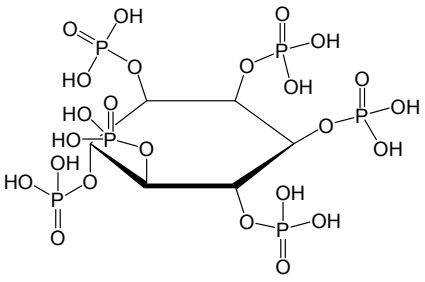

Figure. 1 Chemical structure of phytic acid.

PA contains six negatively charged phosphate carboxyl groups and has a strong tendency to interact ionically with positively charged metal ions or proteins (9).This means it is possible that PA can be bound to wool fibre (natural protein fibre) by virtue of the electrostatic interaction between the positively amino groups in wool and the negatively phosphate groups in PA. This is similar to the mechanism of the acid dyeing of wool fibre. It was reported that the Zirpro treatment could also be applied to wool during the dyeing processing (6). These backgrounds have aroused our interest to understand the feasibility of the combined application of PA and dyes to the processing of wool fibre. Because the simultaneous dyeing and functional finishing of textiles can offer economical and environmental benefits, this study attempted to apply PA and acid metal complex dyes together to wool fibre to prepare coloured and flame retardant textile materials by an exhaustion technique. To the best of our knowledge, this is the first attempt to use PA as a dyeing additive for conferring flame retardancy to wool fabric.

2. EXPERIMENTAL

***Materials*:** The scoured, woven wool fabric (warp and weft thread, 156 dtex×2) was purchased from Shanghai Textile Industry Institute of Technical Supervision. Phytic acid (70% aqueous solution) of analytical reagent grade was obtained from Chengdu Ai Keda Chemical Technology Co. Ltd., China. Everset Yellow M-2R, Everset Red M-G and Everset Navy M-R (1:2 metal complex dyes) were supplied by Everlight Chemical Industrial Co. Ltd., Taiwan.

***Dyeing and finishing experiments*:** All the dyeing and finishing experiments were carried out in the sealed and conical flasks immersed in a universal dyeing machine under laboratory conditions. The liquor ratio was 50:1. Considering that the pH of dye solutions was low, the dyeing treatments were carried out at 90 ^{o}C in order to prohibit fibre damage. The dyeing procedure was as follows: the fabrics were immersed in the solutions at 30 ^{o}C, and subsequently the solutions were heated to 90 ^{o}C at a rate of 2 ^{o}C/min and the treatment continued for 60 min; at the end of the processing, the wool fabrics were washed in tap water and then dried in the open air.

To assess the effect of dye concentration on the dyeing properties of trichromatic dyes, wool fabrics were treated with a series of dye solutions of various concentrations (0-8% omf) in the absence and presence of 120% omf PA. For the study of PA concentration dependence of the dyeing properties of trichromatic dyes and the flammability of the treated fabrics, wool fabrics were treated with a series of PA solutions of various concentrations (0-200% omf) in the absence and presence of 5% omf dyes. The pH values of all the dye solutions were adjusted to 1.2 using dilute sulfuric acid and sodium hydroxide. All the dyes mentioned above were used to investigate the dyeing properties of the dyes together with PA, and Red M-G was used along with PA to study the flame retardancy and thermal behaviors of the treated wool fabrics.

***Measurements*:** The absorption spectra and the absorbance of dye/PA mixture solutions were measured using a Shimadzu UV-1800 UV-vis spectrophotometer. The maximum absorptions of Yellow M-2R, Red M-G and Navy M-R solutions were observed at 410, 485 and 571 nm, respectively. PA solutions had no absorbance above 400 nm. The exhaustion of dyes on wool fibres was calculated by the difference in the initial and final concentrations of dyes in solution. The apparent colour depth (K/S) was measured using a HunterLab UltraScan PRO reflectance spectrophotometer (illuminant D65; 10^{o} standard observer); the maximum absorption wavelengths of the fabrics dyed with Yellow M-2R, Red M-G and Navy M-R were 440, 510 and 600 nm, respectively. The limiting oxygen index (LOI) measurement was conducted using the FTT0080 oxygen index apparatus (Fire Testing Technology Ltd., UK) according to ASTM Standard Method D2863. The vertical burning test was carried out on the YG815B automatic vertical flammability cabinet (Ningbo Textile Instrument Factory, China) according to ASTM Standard Method D6413. The thermogravimetric (TG) analysis was performed using the Diamond TG/DTA SII thermal analyzer (Perkin-Elmer, USA) from 30 to 600 ^{o}C at the scan rate of 10 ^{o}C/min under a flow of air (20 mL/min).

3. RESULTS AND DISCUSSION

***Dyeing properties*:** The dyeing properties expressed by the exhaustion of the dyes and the K/S of the fabrics are depicted in Figures 2 and 3. The K/S of the fabrics increased with increasing dye concentration, but it had little augmentation when the dyes concentration exceeded 6% omf. Figure 2 also reveals that the lower exhaustion was obtained as the concentration of the dyes increased, but the exhaustion of the three dyes was still higher than 90% in the concentration range used, indicating that the dyes have a high utilization rate when applied. The addition of PA lowered the exhaustion of the dyes and the K/S of the fabrics. Figure 3 also shows that both the dye exhaustion and the K/S decreased with increasing PA concentration. This is attributed to the competitive effect between the dyes and PA ions for the positive sites of wool fibre available for the adsorption. PA ions can compete with the dye molecules for the active sites of wool fibre, thus decreasing the exhaustion of the dyes. But the K/S showed little decrease, indicating that the competitive adsorption effect between PA and acid metal complex dyes is acceptable.

***Flame retardancy*:** The flammability of wool fabrics was evaluated using LOI and vertical burning tests. The LOI values and char length of the wool fabrics treated with PA solutions of various concentrations are shown in Figure 4. The LOI values increased with increasing PA concentration. The fabric treated without PA had a low LOI value (24.0%). When the fabric treated together with 120% owf PA and 5% owf Red M-G, it exhibited a remarkably increased LOI value (34.0%). The untreated wool fabric burned completely and had a char length of 30 cm for the vertical burning test. Figure 4 also shows the char length of wool fabrics was greatly reduced by the introduction of PA, and the higher PA concentration, the shorter was the char length. The results above reveal that PA can endow wool fabric with excellent flame retardant performance. The addition of Red M-G reduced the flame retardant efficiency of PA due to the competitive adsorption effect between dye and PA ions which discussed above. But the little adverse effect of Red M-G on the flame retardancy of PA also indicates that it is feasible to apply PA and acid metal complex dyes together to the processing of wool fibre.

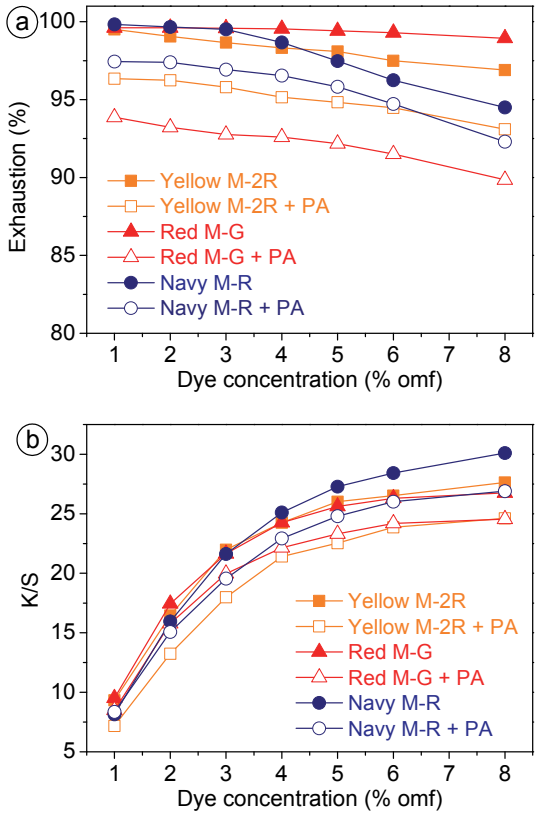

Figure 2. Influence of initial dye concentration on the exhaustion of the dyes (a) and the colour depth of wool (b).

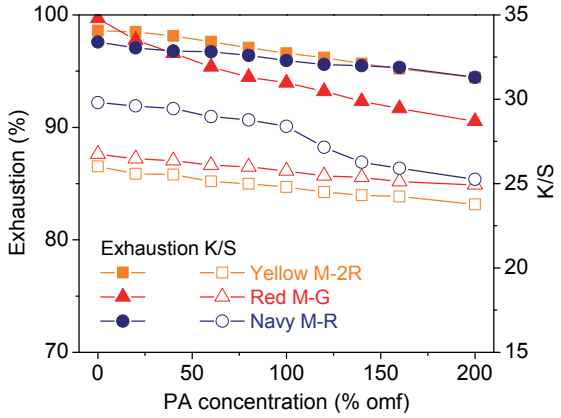

Figure 3. Influence of initial PA concentration on the exhaustion of the dyes and the colour depth of wool.

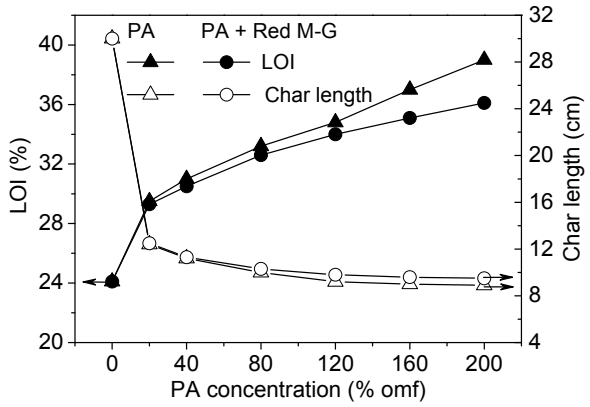

Figure 4. LOI values and char length of the treated wool fabrics.

***Thermal behaviors*:** TG analysis was used to investigate the thermal degradation properties of wool fabrics. The TG curves under air for the untreated and treated wool fabrics as well as PA are shown in Figure 5. As many published reports depicted, three processes take place during the wool pyrolysis progress (10, 11). Compared to wool, PA exhibited higher weight loss at low temperature, and lower weight loss at high temperature. The difference of residual weight between the untreated and treated wool in the 30 to 350 ^{o}C region was small. However, a growing gap for the difference was found above 350 ^{o}C, indicating that PA can change the decomposition behaviors of wool, and increase the thermal stability of wool at high temperature.

Compared to 0.6% char residue for Wool-0 at 600 ^{o}C, the char residues of Wool-40, Wool-80 and Wool-120 were 24.7%, 31.8% and 32.4%, respectively. This implies that the flame retardant mechanism of the treated wool fabric involves a significant condensed-phase activity. Such high char residue for the PA treated wool indicates the good resistance of char to oxidation and high thermal insulation of the char. Also, the char formation can limit the production of combustion gases, inhibit combustion gases from diffusing to the pyrolysis zone, and protect the material surface from heat and air.

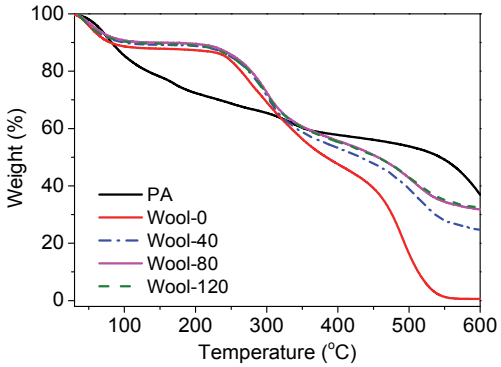

Figure 5. TG curves of PA and wool fabrics under air: Wool-0, Wool-40, Wool-80 and Wool-120 represent the fabrics treated with 0, 40, 80 and 120% owf PA, respectively together with 5% owf Red M-G.

4. CONCLUSIONS

PA, as an environmentally eco-friendlier flame retardant agent than conventional flame retardants, was successfully applied to the dyeing processing of wool fabric along with acid metal complex dyes in one bath, although the competitive adsorption effect occurred between dye and PA ions for the positive sites of wool fibre. The treated wool fabric exhibited good flame retardancy, and the flame retardant properties of the fabric tended to increase with increasing PA concentration. TG analysis revealed that PA could impart wool with good thermal stability and high char residue at high temperature, demonstrating that condensed-phase mechanism is applicable to the flame retardant wool fabric treated by PA.

ACKNOWLEDGEMENTS

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