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Condensed tannin from *Dioscorea cirrhosa* tuber as an eco-friendly and durable flame retardant for silk textile

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A B S T R A C T

Condensed tannin derived from *Dioscorea cirrhosa* tuber was employed as a novel and eco-friendly flame retardant agent for enhancing the thermal shielding and flame retardant properties of silk textile. A facile adsorption technique of condensed tannin in the weakly acidic condition was able to impart good and durable flame retardancy to silk fabric. In the treatment process, the adsorption, diffusion and deposition of condensed tannin onto silk fiber took place. The flame retardancy was demonstrated by limiting oxygen index, vertical burning and pyrolysis combustion flow calorimetry tests. The treated fabric exhibited the limiting oxygen index above 27% and the char length below 12 cm even after 20 washing cycles. The thermogravimetric analyses of the treated fabric and the morphological studies of the burned fabric residue suggested that a significant condensed-phase mechanism contributed to the improvement in the flame retardancy of silk fabric. In addition to flame retardancy, antibacterial and antioxidant activities were imparted to silk fabric. Such multifunctional properties provided by condensed tannin can expand the application of flame retardant silk. The present research indicates that condensed tannin is a promising alternative to traditional flame retardants for the finishing of silk textile.

1. Introduction

Many textiles are quite flammable and burn well, and about 50% of fire incidents are associated with the burning of textiles in the world according to fire statistics (Rosace et al., 2015). The fire risk caused by flammable textiles can be reduced by the flame retardant (FR) treatment. The FR agents commercially used for textiles include inorganic and organic compounds. Inorganic FR agents such as zirconium and titanium metal complexes are mostly applied to wool textiles, whereas organic FRs can be almost applicable to all textiles, and occupy most of the consumption of FRs. The widely used organic FRs are bromine, chlorine, phosphorus and nitrogen containing compounds. Although these products impart flame retardancy to textiles, some of them are toxic or not eco-friendly. Halogen-based compounds can generate large quantities of toxic gases in the burning process, and have the serious issues of persistence, bioaccumulation and environmental toxicity (De Wit, 2002), leading to the prohibition of their uses in textile industry. Previous studies have shown that small molecule FRs can migrate out of many products during use, and dermal exposure to FRs poses accumulated threat to human health (Blum et al., 1978; Gomes et al., 2016). As the alternatives to halogen-based FRs, organophosphorus agents are widely used. However, the effluent discharge of phosphorus compounds during laundering and use of products leads to water eutrophication (Lee, 1973), and the phosphorus-based FRs bearing methylol groups cause formaldehyde release (Šehić et al., 2016).

The recognition of toxicity and environmental persistence of FR agents stimulates the research efforts toward innovative solutions (Alongi et al., 2014a). It is urgent and necessary to develop more eco-friendly and harmless FR agents for replacing traditional chemicals. In this context, the application of FR agents from natural resources to the processing of textiles has attracted great attention (Basak and Ali, 2016; Malucelli et al., 2014). Some protein-based polymers such as casein, hydrophobin, deoxyribonucleic acid, and whey protein have been used to enhance the FR performance of cotton fabric (Alongi et al., 2013; Alongi et al., 2014b; Bosco et al., 2013; Bosco et al., 2017; Malucelli et al., 2014). Very recently, the plant extracts have been attempted to be used as FR agents (Basak and Ali, 2016; Basak et al., 2015a; Basak et al., 2015b; Cheng et al., 2016; Laufer et al., 2012; Teli et al., 2018). Phytic acid extracted from beans, cereals, and oilseeds has been confirmed to be effective in decreasing the flammability of cotton and wool fabrics due to the presence of 6 phosphate groups in its structure (Cheng et al., 2016; Laufer et al., 2012). Banana pseudostem sap, spinach leaves juice, and coconut shell extract have also found their applications in the FR treatment of cotton and jute fabrics as they contain

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various metal salts (Basak et al., 2015a; Basak et al., 2015b; Teli et al., 2018).

Silk fiber is often used to produce upscale clothing as well as high-grade bedding fabrics, interior decoration cloth, carpets and wall cloth which have requirements for good flame resistance. Currently, the commercial FR treatment of silk textiles can be carried out by using organophosphorus agents (Guan et al., 2009), and zirconium and titanium metal complexes. Herein, a traditional and commercial two-color silk fabric (Gambiered Guangdong silk) characterized by shiny black on the face side and reddish brown on the back side has to be mentioned. The process of this peculiar silk fabric, which is identified as a National Intangible Cultural Heritage, includes repeated coating (soaking and spraying) with the condensed tannin solution from *Dioscorea cirrhosa* tuber, repeated exposure to sunlight on lawn, and mordanting or coating with iron salt-containing mud on the face side (Yang et al., 2018), thus being quite complicated and time-consuming. Very recently, we are surprised to find the good flame retardancy (limiting oxygen index [LOI], 29%) of a Gambiered Guangdong silk fabric (Yang et al., 2018). This arouses our interest in the use of condensed tannin as a novel and eco-friendly flame retardant in the textile field.

Tannins are the non-toxic, cheap and abundant polyphenolic oligomers from the biomass. Among all the tannins (hydrolyzable, complex, and condensed tannins), condensed tannins represent 90% of the world production (Duval et al., 2017). Tannins have high chemical and thermal stability as well as low thermal conductivity owing to their specific aromatic structure (Duval et al., 2017), which make them suitable for the preparation of thermal insulating and FR materials for various applications (Tondi et al., 2009).

In the light of the aforementioned developments, and the non-toxic, vegetal and water-soluble characteristics of condensed tannins which are more acceptable than synthetic FRs from the eco-friendliness point of view, in the present work, the condensed tannin extract from *Dioscorea cirrhosa* (DC) tubers was applied to the FR treatment of silk textile by an impregnation technique. The application conditions of DC extract and the flame retardancy of the treated fabrics were discussed. The combustion and thermal behaviors of the treated silk fabrics were assessed by means of LOI and vertical burning tests, pyrolysis combustion flow calorimetry (PCFC) and thermogravimetry (TG). The morphologies of the treated silk fabrics and corresponding burned areas were investigated by scanning electron microscopy (SEM). In addition, the antibacterial and antioxidant activities of the treated silk fabrics were evaluated. In textile industry, although the use of tannins as natural dyes has a long history (Restivo et al., 2014; Smith et al., 2016) and tannins have been proved to be good antibacterial, antioxidant and UV protection agents in recent years (Gupta et al., 2004; Gupta and Laha, 2007; Pisitsak et al., 2016; Rather et al., 2017; Singh et al., 2005), their application as FR agents has not been reported so far. To the best of our knowledge, this is the first attempt to use condensed tannins for imparting flame retardancy to a textile material without the help of other chemicals (e.g., metallic salts and organic FR agents) having FR function.

2. Materials and methods

2.1. Materials

The scoured silk fabric of crepe de Chine with a weight per unit area of 52 g/m^2 was purchased from Suzhou Jiaduoli Silk Apparel Co. Ltd., Suzhou, China. The fresh *Dioscorea cirrhosa* (DC) tubers were bought from the Taobao Shop of Longhui Shanzhuang, China. Citric acid and disodium hydrogen phosphate were of analytical reagent grade, and both of them were purchased from Sinopharm Chemical Reagent Co. Ltd., Shanghai, China. 2,2′-Azino-bis (3-ethylbenzothiazoline-6-sulphonic acid) diammonium salt (ABTS) was bought from Sigma-Aldrich (Shanghai) Trading Co. Ltd.

2.2. Extract of condensed tannin

The peeled DC tubers (300 g) were first sliced into small pieces. Afterwards, the sliced tubers were mixed with distilled water (750 mL), and this mixture was crushed into a pulp by a food shredder. In order to extract condensed tannin, the aforementioned thick liquid was heated in the sealed glass container in a XW–ZDR low-noise oscillated dyeing machine (Jingjiang Xinwang Dyeing and Finishing Machinery Factory, China) at 60 °C for 2 h. Subsequently, the hot liquor was allowed to separate into layers, cooled to room temperature, and filtered with a three-layer polyester cloth. The filtrate liquor was diluted with distilled water to a constant volume of 1 L. The as-prepared reddish brown stock solution was applied to the FR treatment of silk fabric, and its concentration was defined as 300 g/L for the purpose of clear measurement.

2.3. FR treatment

All the FR treatment experiments were carried out in the conical flasks immersed in the XW–ZDR low-noise oscillated dyeing machine. The ratio of the volume of liquor to the weight of fabric was 50:1. The pH values of DC extract were adjusted by McIlvaine buffers (citric acid/disodium hydrogen phosphate). The fabrics were immersed into the DC extract solutions at 30 °C, and subsequently the solutions were heated to the required temperature at a rate of 2 °C/min, and the treatment continued at this temperature for a certain period of time. At the end of treatment, the fabrics were removed, rinsed thoroughly in distilled water and allowed to dry in the open air.

The four factors affecting the FR treatment of silk fabrics using DC extract included pH, temperature, time, and DC extract concentration. To study the effect of pH, eight pH values in the range of 3.38–8.34 were employed, and the other parameters (DC extract 300 g/L, 85 °C, and 90 min) were fixed. To estimate the effect of time, DC extract 300 g/L, pH 4.5 and 85 °C were used, and the silk fabrics were treated for 30–150 min. To evaluate the effect of temperature, six temperatures ranging from 50 to 95 °C were employed, and the other parameters including DC extract 300 g/L, pH 4.5, and 90 min were fixed. To assess the effect of DC extract concentration, five DC extract concentrations ranging from 60 to 300 g/L were used, and the other parameters were pH 4.5, 90 °C and 90 min.

Taking the discussions of the above four factors into consideration, silk fabrics were further treated in the following conditions: 37.5, 75, 150, 225 and 300 g/L DC extract, pH 4.5, 90 °C, and 90 min, and the as-prepared samples were used for the evaluation of FR properties and other functionalities as well as the instrumental analyses.

2.4. Measurements

2.4.1. IR spectrum

The FT-IR spectrum of the air-dried DC extract was determined by the Nicolet 5700 FT-IR spectrometer (Thermo Fisher Scientific Inc., USA) using the KBr pellet method.

2.4.2. Weight gain

The fabrics before and after treatment were equilibrated for 24 h in a standard condition (20 ± 2 °C and relative humidity 65 ± 3%), and then weighed. The weight gain of the treated fabrics was calculated using the following equation:

$$\text{Weight gain}(\%) = 100 \times (W_1 - W_0)/W_0$$

where W_0 and W_1 represent the weight of the fabrics before and after treatment, respectively.

2.4.3. Flammability

The flammability of silk fabrics was assessed by the LOI and vertical burning tests. The LOI values were determined using the ASTM