FLAME-RETARDANT AND CREASE-PROOFING FINISHING OF COTTON FABRICS VIA IN-SITU CO-POLYMERIZATION OF ETHYLENE PHYTIC ACID AND ITACONIC ACID, PART I
Fabrication Process

by

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Ethylene phytic acid and unsaturated itaconic acid could be copolymerized in-situ and cross-linked on the cotton fabrics to enhance flame-retardant and crease-proofing properties. Natural phytic acid was modified with glycidyl methacrylate and characterized by IR, ^{1}H NMR, and TG. The IR indicated that new characteristic absorption peaks appear near 1720 c/m, 1470 c/m, 1380 c/m, and 1002 c/m for the molar ratios phytic acid: glycidyl methacrylate of 1:3 or 1:6, the peaks correspond to the bending vibration of C=O, C–H, CH_3, and C=O–O respectively in the glycidyl methacrylate. The ^{1}H NMR results further confirmed the reaction between glycidyl methacrylate and phytic acid, and the TG results revealed the thermal properties of phytic acid.

Key words: *flame-retardant finishing, ethylene phytic acid, cotton fabrics*

Introduction

Natural cotton fiber is famous for its excellent wearing performance, such as strong moisture absorption, soft hand feel, and comfortable wearing. Flammability and wrinkle are also two important factors in the textile field. With the development of science and technology, the flame retardant finishing technology of textiles has been gradually improved, but a better performance of flame retardant textiles is still much needed. Some problems caused by traditional flame retardants, such as toxicity, low efficiency, formaldehyde emission hazard, have attracted more and more attention. At present, n-hydroxymethyl-3-dimethoxyphosphoryl propionamide (pyrovatex CP), tetrahydroxymethyl phosphine chloride (THPC) and their improved products are widely used as durable flame retardants for cotton in the market. Although this kind of flame retardants does not have the problems of large smoke volume and release of irritating toxic gases, it has the problem of formaldehyde release [1]. Therefore, it has become a new direction to develop new environmental flame retardants with high efficiency, low smoke, low toxicity, low formaldehyde or no formaldehyde and excellent durability. With the development and utilization of various new flame retardants, environmental friendly flame retardant finishing technology and flame retardant mechanism have gradually become one of the research focuses and hot spots in textile dyeing and finishing industry.

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Phytic acid (PA), also known as inositol hexaphosphate, is an organic phosphorus additive with rich raw materials, environment friendliness, and good biocompatibility, and it is widely used as antioxidant, preservative, and flame retardant in food, medicine, metal processing, textile, and other industries because of its high phosphorus content (28.16%) [2, 3]. In recent years, its applications were extended to the textile flame retardant finishing. In Laufer [4] first applied phytic acid and chitosan to the flame-retardant finishing of cotton fabric through the layer by layer self-assembly technology. The 30BLs phytic acid (the main storage form of phosphorus in grains, beans and oilseeds) and chitosan (obtained from crustacean shells) can prevent the flame propagation of cotton fabric and reduce the maximum heat release rate by 50%. In Zhang *et al.* [5] first prepared chitosan and phytic acid polymer (PEC) through electrostatic interaction to form white powder, which was then melt blended with ethylene vinyl acetate copolymer (EVA) at high temperature, and finally cooled to form film. When the PEC concentration is 20%, the carbon slag of the doped film is 12 times of that of the undoped film, and the carbon slag is relatively compact, and the heat release rate and total heat release amount are greatly reduced. Costes *et al.* [6] used sodium phytate, aluminum phytate and iron phytate to melt and co-mix with polylactic acid to form films respectively, and studied the flame retardancy. The results showed that the flame retardant grade of PLA film doped with phytate was above V-2, and with aluminum phytate was superior to that of the other two phytates, and the residue was 15 times of the original sample, but the degree of polymerization of PLA was affected by phytate. Subsequently, Costes *et al.* [7] selected lignin, phytic acid and polylactic acid to melt blend, and studied the flame retardancy of lignin and phytic acid doped polylactic acid film. The heat release rate was reduced to 44%, the flame retardant grade reached V-2, and the elongation increased from 3.1% to 12.6%.

Xu *et al.* [8] used sodium phytate and chitosan as assembly units to finish silk fabrics. When 20 layers were assembled, the limiting oxygen index (LOI) was 30%, and after 20 times of washing, the LOI of silk fabric remained about 27%, which can extinguish itself in case of fire. Tang's group also successfully applied phytic acid to PLA knitted fabric [9], wool [10], and silk [11]. The cotton fabrics had serious damage under acidic condition due to the strong acidity of phytic acid; the application of phytic acid was mainly focused on the flame-retardant finishing of protein fiber, not the cotton fabric.

With the enhancement of people's awareness of environmental protection, more and more people are seeking green and environmental protection flame retardant. Phytic acid, as a natural phosphating with high phosphorus content, has been gradually applied to textiles. But there are few researches on phytic acid flame retardant, and the problems of the poor washability, yellowing and poor hand feeling of the fabrics were not solved yet. Therefore, the research on the flame retardant performance, durability and flame retardant mechanism of phytic acid has become the main direction, and it also provides new ideas for flame retardant finishing of textile materials.

Itaconic acid (IA) is an unsaturated carboxylic acid that contains two carboxyl groups and one vinyl group. The IA can be used in the crease-proofing finishing of cotton fabrics. Li *et al.* [12] used malay-acid (MA) and IA to finish cotton fabrics by in-situ copolymerization and cross-linking in the presence of initiator and catalyst to obtain wrinkle-resistant fabrics. The system is suitable for the crease-proofing finishing of colored cotton fabrics, which is basically the same as that of butane tetracarboxylic acid.

This topic focuses mainly on the current flame retardant smoke, toxicity, formaldehyde release, durability and other issues. Therefore, the natural and high phosphorus content phytic acid was selected as ecological flame retardant for textile applications. Vinyl phytic acid and itaconic acid were used as comonomers to carry out in-situ polymerization and cross-linking reaction on the cotton fabric. In this experiment, the ring-opening reaction of natural PA and glycidyl methacrylate (GMA) was used to make the structure of phytic acid containing double bond groups.

Experimental

Materials

Bleached cotton fabric (density: 100 g/m^2, original weave) was obtained from a local market. Toluene, acetone, methanol, and sodium hydroxide (NaOH) were provided by Sinopharm Chemical Reagent Co., Ltd., GMA, phytic acid (PA, 70 w.t%), and other reagents were all supplied by Aladdin Reagent Co., Ltd. (Shanghai, China). All of the reagents were analytically pure.

Preparation of GPA

The GPA was prepared *via* open-ring esterification. In brief, 0.02 moL 70% phytic acid solution (PA) and 80 mL of acetone were added into a 250 mL beaker. Monomer glycidyl methacrylate (GMA, molar ratio PA: GMA = 1:1, 1:2, 1:3, 1:6) and p-hydroxyanisole inhibitor (3000 ppm of GMA monomer) were mixed and slowly dropped into the phytic acid solution within one hour, the solution was stirred continuously for 5 hours at 65 ℃. At the end of the reaction, the solvent was removed by vacuum distillation to obtain a brown viscous solution. Toluene was added to remove the unreacted GMA. Figure 1 shows the reaction mechanism. White powders were obtained by precipitation with 1 mol/L sodium methoxide solution which was filtered and washed with methanol three times, and then dried in a vacuum at 50 ℃ for 24 hours. According to the mass change before and after the reaction, the conversions were all about 72%. The powders were marked as GPA, 2GPA, 3GPA and 6GPA, respectively, for different molar ratios (PA: GMA = 1:1, 1:2, 1:3, 1:6).

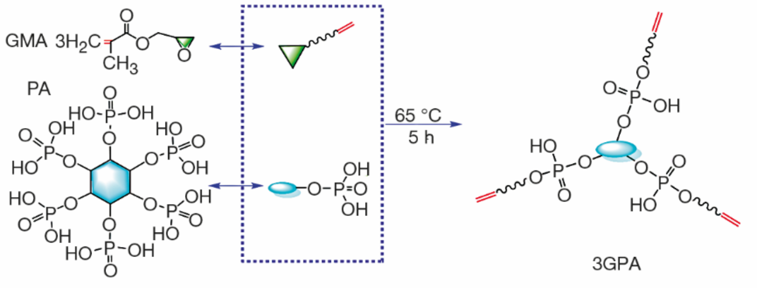

Figure 1. Reaction mechanism of PA and GMA

Reaction mechanism of GPA

Epoxy group is a ternary ring composed of two carbon atoms and one oxygen atom. The two carbon atoms and one oxygen atom are in the same plane, which makes the epoxy group resonate. The electronegativity of oxygen is larger than that of carbon, which leads to electrostatic polarization and increases the density of electron cloud around oxygen atom. Therefore, two reactive active centers are formed on epoxy group: oxygen atom with high density and carbon atom with low density of electron cloud. The density distribution of electron cloud on epoxy ring plays an important role in the reaction mechanism of nGPA. When the electrophilic reagent is approached, the oxygen atom is attacked. While when the nucleophilic reagent is approached, the carbon atom is attacked, as a result, a rapid reaction happens, causing the C–O bond to break and the epoxy group to open. At the same time, the bond angle for the normal case is about 109°, but it is only about 60° in the epoxy group. By comparison, each bond angle flexes inward by about 24° which produces a great tension that is the potential force of the open loop. It is due to the polarization of charge and the large deformation energy of epoxy ring that epoxy group has high reactivity. Protons and electrophilic reagent such as Lewis acid attack oxygen atoms for addition. In this case, the more stable the carbon cations are, the easier for cracking and increasing proportion of abnormal addition products [13].

Characterization

The attenuated total Fourier transform-infrared spectra (ATR-FTIR) were used to analyze the chemical composition of GPA using ATR-FTIR spectrometer (Nicolet Nexus-670, USA). The samples were scanned from 400 c/m to 4000 c/m. Data analysis was carried out using Origin 8.0 software.

The structure of GPA was further analyzed by ^{1}H NMR (Germany Avance III 600 MHz) with deuterated chloroform as reagent.

Fourier transform-infrared spectra (TENSOR27 Germany) were collected under the nitrogen atmosphere at a heating rate of 10 ℃/min and temperature ranging from 20 ℃ to 700 ℃. The wavelength coverage ranged from 600 c/m to 4000 c/m. The samples were cut into power and placed in an aluminum oxide pan. About 10.0 mg of the sample was used in each case.

Results and discussion

The ATR-FTIR analysis

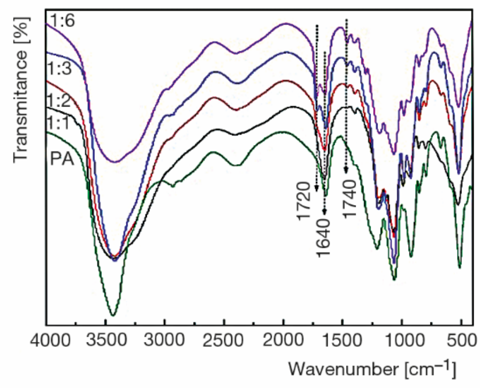

Figure 2. Infrared spectra of the products

The infrared spectra of PA and nGPA (different mol ratios) are shown in fig. 2. The vibration absorption peak of –OH group is near 3300 c/m in the PA curve. The peaks at about 1200 c/m and 1070 c/m correspond to the characteristic absorption peak of P=O and P–O group vibration in PA, respectively. Compared with the infrared spectrum curve of PA, in addition to the characteristic absorption peak of PA, new characteristic absorption peaks appear near 1720 c/m, 1470 c/m, 1380 c/m, and 1002 c/m in the 1:3 or 1:6 ratios of PA : GPA, which correspond to the bending vibration of C=O, CH, CH_3, and C=O–O respectively. The position of the characteristic peak is basically consistent with that of the corresponding group in the molecular structure of glycidyl methacrylate. The vibration absorption peak of unsaturated double bond C=C near 1640 c/m coincides with that of C-H in the phytic acid structure. No characteristic absorption peak of epoxy matrix exists near 815 c/m and 908 c/m [14]. Under strong acidic conditions, the epoxy group opens up the ring and reacts with phosphoric acid group in PA to modify it.

The ^{1}H NMR analysis

Based on infrared analysis, 3GPA and 6GPA were obtained successfully, therefore, the structure of 3GPA was further characterized based on the infrared spectrum. The ^{1}H NMR spectra ($CDCl_3$, PPM) of PA, GMA, and 3GPA were shown in fig. 3. The ^{1}H NMR results explained again the reaction between GMA and PA [13].

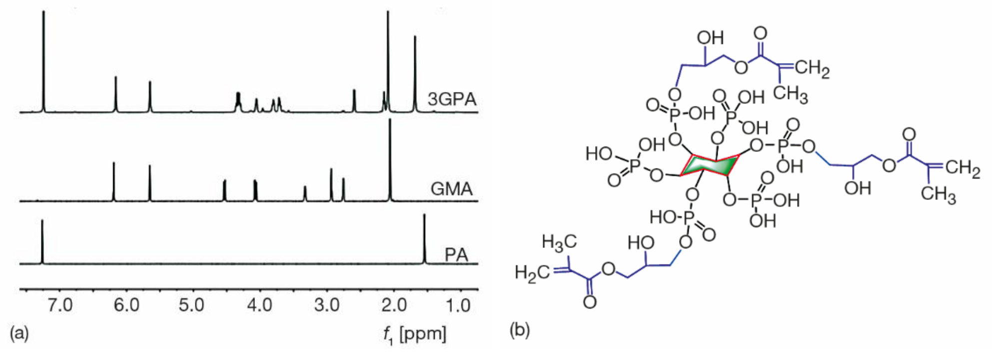

Figure 3. The ^{1}H NMR spectra and structure of GPA

1.54 (CH group on six-membered ring);

4.2 – 4.4 (P-$\underline{\mathbf{OH}}$);

2.45 (-O-$\underline{\mathbf{CH_2}}$-CH(OH)-$CH_2$-O-C(=O)-C($CH_3$)=$CH_2$);

5.59 (-O-CH_2-CH($\underline{\mathbf{OH}}$)-CH_2-O-C(=O)-C(CH_3)=CH_2);

4.1 (-O-CH_2-$\underline{\mathbf{CH}}$(OH)-CH_2-O-C(=O)-C(CH_3)=CH_2);

3.5 – 3.9 (-O-CH_2-CH(OH)-$\underline{\mathbf{CH_2}}$-O-C(=O)-C($CH_3$)=$CH_2$);

1.9 – 2.2 (-O-CH_2-CH(OH)-CH_2-O-C(=O)-C($\underline{\mathbf{CH_3}}$)=$CH_2$);

6.15 (-O-CH_2-CH(OH)-CH_2-O-C(=O) -C(CH_3)=$\mathbf{CH_2}$).

The TG and DTG

The pyrolysis process can be divided into three stages: initial pyrolysis, main pyrolysis, and residue pyrolysis. The initial cracking is the change in physical properties and a little weight loss, which could be related to the amorphous part [15]. The weight loss rate of the main pyrolysis is very fast. The crystallization zone cracked and then decomposed into various combustible gas products. The pyrolysis of residue is mainly dehydration and carbonization.

Figure 4 shows the thermal stability of PA-Na, 2GPA and 3GPA in nitrogen atmosphere. The thermal property parameters obtained from fig. 4 included initial decomposition temperature, T_i, extrapolation initial temperature, T_e, maximum weight loss rate temperature, T_max, and char residue, *CR*. The detailed data are shown in tab. 1. The T_i corresponds to the point at which the TG curve starts to deviate from the baseline. The T_e corresponds to the intersection of the tangent drawn at the temperature point of the maximum weight loss rate, $(\mathrm{d}w/\mathrm{d}T)_\mathrm{max}$, with the extended baseline of the TG curve. The $(\mathrm{d}w/\mathrm{d}T)_\mathrm{max}$ is the intersection of the *X*-axis, which is perpendicular through the peak point in the DTG curve with the TG curve. The extrapolated onset degradation temperature reflects the ease of combustion of the sample. The $T_{\max}$ corresponds to the peak point in the DTG curve.

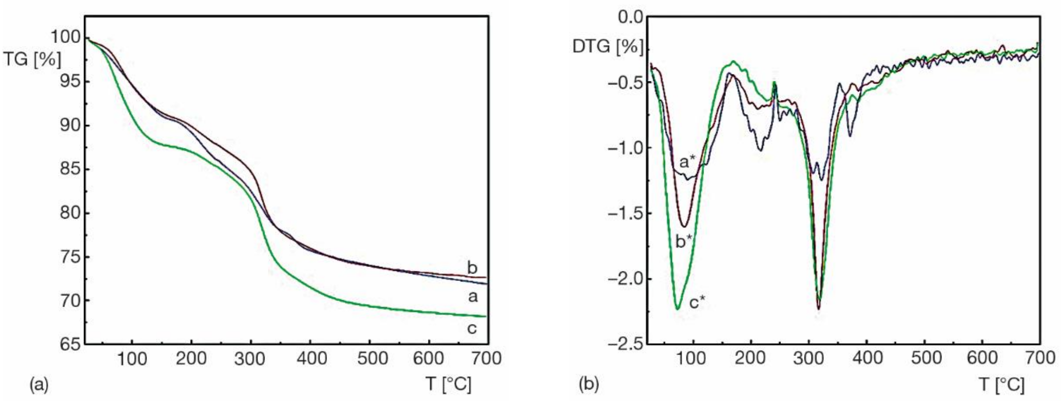

Figure 4. The TG (a) and DTG (b) spectrum of fabrics; (a-c: TG of PA-Na, 2GPA, and 3GPA and a*- c*: DTG of PA-Na, 2GPA, and 3GPA)

The loss during room temperature to 150 °C of PA-Na, 2GPA and 3GPA was due to evaporation of water. The T_i and T_e of three samples were not obvious below 200 °C, due to the lower stability of the P–O–C structure than that of aggregation structure. During combustion, phytic acid, as flame retardant, was decomposed to phosphoric acid derivatives, which promoted carbonization. As a result, the value of T_i decreased, and the CR value achieved to about 70%. As shown in tab. 1, the $T_{\max}$ of samples was above 300 °C, and the CR value was about 70% at 700 °C, which indicated that the grafting reaction of 2GPA and 3GPA had no effect on the thermal properties of PA. Phytic acid was used in flame retardant of cotton fabrics, phosphorus-containing compounds first decomposed and released phosphoric acid when heated. Phosphoric acid polymerized into polyphosphoric acid under certain conditions or reacted with the hydroxyl group at C6 position in the fiber chain to break the pyran ring, thereby accelerating the degradation and dehydration of cotton fabric, promoting the formation of CR. The content of CR was greatly increased. Secondly, the CR covered the surface of the fabric, insulated the internal fiber from oxygen, smothered, and slowed down the thermal decomposition reaction to achieve flame retardancy. Compared the PA, thermal properties of 2GPA and 3GPA basically remain unchanged, and 2GPA and 3GPA contain ethene active groups, which is more conducive to the combination with cotton fabrics.

Table 1. The TG parameters of cotton fabric samples

Cotton fabrics	$T_{\max}$ [°C]	CR at 700 [°C/%]
PA-Na	324	72
2GPA	320	73
3GPA	323	68

Conclusions

In order to obtain the flame retardancy and wrinkle resistance cotton fabrics by *in situ* polymerization and crosslinking with GPA and IA, various kinds of the nGPA were produced with PA and GMA under 65 °C by ring-opening esterification. The IR and ^{1}H NMR indicated that the 3GMA and 6GMA were acquired successfully. The thermal properties are basically consistent with PA and the carbon residue content was about 70%, which thereby effectively inhibits or slows down the combustion degree. This study provides a method for flame-retardant and wrinkle resistant finishing of fabrics, which can be mathematically treated [16-18]. The theoretical analysis will be carried out in Part 2 of this series of publications, where a mathematical model will be established.

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