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The potential of ferric pyrophosphate for influencing the thermal degradation of cotton fabrics

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Abstract Ferric pyrophosphate (FePP) was used as additive to study its synergistic effect of thermal degradation on cotton fabrics. The microscale combustion calorimetry (MCC), thermogravimetric analysis (TG), Raman spectroscopy and Real Time Fourier transform infrared spectroscopy (RT-FTIR) were utilized to evaluate the synergistic effects of FePP on cotton/DIA. The MCC results revealed that cotton/DIA/FePP generated less combustion heat during heating than that of cotton/DIA. TG results showed that presence of FePP improved the thermal stability of materials. The Raman spectroscopy test showed that FePP can ameliorate the structural organization level of the carbon and the graphitization degree of the char. RT-FTIR data revealed the mechanism of the influence of FePP, which can catalyze the break of the flame retardant as well as promote the char forming.

Keywords Cotton fabrics · Ferric pyrophosphate · Thermal degradation · Coating

Introduction

The phenomenon of synergism on thermal degradation was a focus today. Many researchers have investigated the effect of additives on thermal decomposition. Nie et al. [1] investigated the synergistic effect of the nickel phosphates and ion-incorporated nickel phosphates with intumescent flame retardants in a PP matrix. The results showed that both of them can obviously improve the flame retardant behavior of IFR systems. Zhang et al. [2] examined synergistic effect of nanoflaky manganese phosphate on thermal degradation and flame retardant properties of intumescent flame retardant polypropylene system. It was reported that nanoflaky manganese phosphate can take a positive effect on the flame retardancy. Davies et al. investigated the thermal analysis of a series of metal ion–ammonium polyphosphate (APP) combinations [3]. The results were that metal ion-doped APP in the presence of cellulose not only indicates a further sensitisation of cellulose decomposition but also improved flame retardancy.

In our previous report, cotton fabrics were treated by the silica coating containing phosphorus (DIA) via sol–gel process [4]. As we know, sol–gel finishing based on silane precursors was a good alternative to organic networks, enabling the uniform dispersion and embedment particles. Mahltig B investigated the combination of silica sol and dyes on textiles [5]. The results demonstrated that the application together with the silica sol or the aftertreatment of dyed textile with silica sol lead to significant improvement of leaching fastness. Therefore, in this study, sol–gel finishing method was used to embed the particles in the coating.

Ferric pyrophosphate (FePP) has bee used as a nutritional additive for milk powder, baby food, and other general food. Moreover, it has been industrialized and inexpensive. So in this work, FePP was used as the additive to study its potential effect for thermal degradation on cotton fabrics. The combustion properties were evaluated through microscale combustion calorimetry (MCC) experiment. In addition, TG, Real Time FTIR, and TG-FTIR were used to investigate the thermal degradation process of the materials. SEM and Raman diffusion

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measurements were utilized to investigate the surface morphology as well as the structure of residual char.

Experiment

Materials

DIA has been synthesized in the laboratory previously. FePP was bought from Xuzhou Haicheng Food Additive Co. Ltd. (Xuzhou, China). Plain-weave cotton fabrics were from the market with an areal density of 156 g m^{-2}.

Preparation of samples

Cotton fabrics were pre-treated in an 18% NaOH solution and thoroughly rinsed with distilled water then air-dried at room temperature. 9.88 g DIA was dissolved in 40 ml ethanol then 2.2 ml H_2O was added while stirring. Diluted hydrochloric acid was put into it to promote hydrolysis with the pH value around 3. The whole reaction went on about 5 h. After the treatment of hydrolysis, FePP that took 1 wt% (FePP1), 2 wt% (FePP2) of DIA was added, respectively, dispersing with stirring and ultrasonic. The pre-treated cotton fabrics were dipped in, then they were took out and squeezed. After that they were laid at room temperature for 1 h and were put in oven at 80 °C for 2 min and 130 °C for 1 min. Finally, Samples were rinsed with distilled water for 30 s to remove excessive HCl and particles and dried at 80 °C.

Characterization

Thermalgravimetric (TG) analysis was performed on DT-50 (Shimadzu, Japan). The heating rate was set as 20 °C min^{-1} (air atmosphere, flow rate of 150 ml min^{-1}). Thermogravimetry-Fourier Transform Infrared instrument consists of analyzer (TGA-Q5000, TA Co., USA) coupled with Fourier transform spectrometer (Nicolet 6700) and the transfer line. The investigations were carried out under nitrogen atmosphere at a flow rate of 35.0 mL min^{-1} for TG, with heating rate of 20 °C min^{-1}. Govmark MCC-2 microscale combustion calorimetry was used to determine the flammability characteristics of treated-cotton fabrics according to ASTM D 7309-07. Scanning electron microscopy (SEM) studies were performed on the char residue using a Hitachi X650 scanning electron microscope. Raman spectroscopy (RS) measurements were carried out at room temperature with a SPEX-1403 laser Raman spectrometer (SPEX Co, USA) with excitation provided in back-scattering geometry by a 514.5 nm argon laser line. Real time Fourier transform infrared method (RT-FTIR) was used to study the thermo-oxidative degradation of the cured film. The temperature of the oven was raised at a heating rate of about 10 °C min^{-1}.

Results and discussion

MCC test

Figure 1 was the heat release rate (HRR) curves of cotton fabrics, cotton/DIA and cotton/DIA/FePP. The corresponding combustion data were presented in Table 1. It was found that there were three peaks for each treated cotton fabrics with or without FePP but one peak for untreated cotton fabrics. Presence of FePP had an impact on the change of the curves. With the addition of FePP, the value of PHRR decreased obviously, reducing to 107.5 w g^{-1}. The same was happened to THR. Addition of FePP made the value of THR decline to 3.2 kJ g^{-1}. Generally speaking, the values of HRR and THR for samples with FePP were both lower than those without FePP. It can be explained that FePP catalyzed the formation of a protective char, which can protect the underlying materials from further burning and reduce its heat release.

Thermogravimetric analysis

TG curves of cotton fabrics treated with DIA and FePP were shown in Fig. 2. The related data are listed in

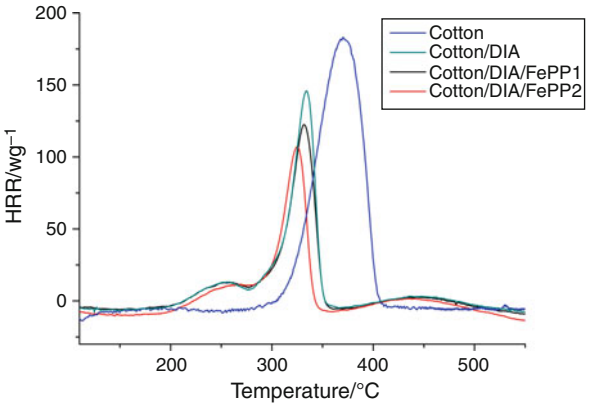

Fig. 1 HRR curves of samples

Table 1 Part data recorded in MCC experiments

Samples	THR/kJ g^{-1}	PHRR/w g^{-1}
Cotton	8.8	182.1
Cotton/DIA	5.3	146.1
Cotton/DIA/FePP1	4.2	121.5
Cotton/DIA/FePP2	3.2	107.5

PHRR Peak heat release rate, *THR* total heat of combustion

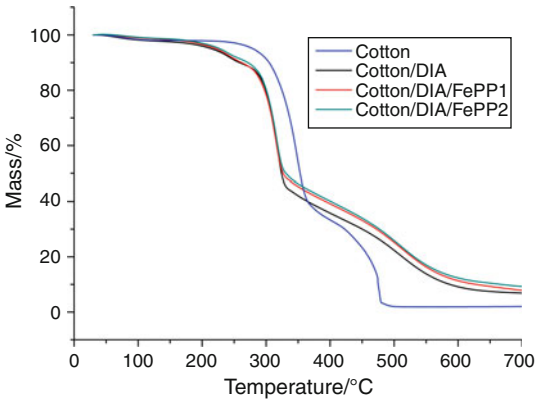

Fig. 2 TG curves of samples

Table 2 Thermal properties and the flame retardancy of samples

Samples	$T_{60\%}$/°C	Char residue at 700 °C/wt%
Cotton	317.1	1.8
Cotton/DIA	365.4	6.9
Cotton/DIA/FePP1	392.6	7.8
Cotton/DIA/FePP2	401.3	9.3

Table 1. No difference was observed between samples with FePP and those without FePP at the beginning of thermal decomposition. However, after 300 °C, samples with FePP possess more thermal stability than those without FePP. The $T_{60\%}$ (temperature of 60% mass loss) increased from 365.4 to 401.6 °C with the rise of FePP, which can be seen from Table 2. Similarly, with the increase of FePP, the char residues at 700 °C enhanced gradually from 6.9 to 9.3 wt%. The results can be explained that FePP, transition-metal compound, a Lewis acid, was believed to act as a promoter of crosslinking, encouraging the formation of a char [6].

Evolved gas analysis

TG-FTIR is a useful tool to analyze the gas product during the thermal degradation to investigate the effect of flame retardant on cotton fabrics.

Figure 3 presented the main absorbance of pyrolysis products for cotton fabrics, cotton/DIA and cotton/DIA/FePP2: H_2O (3564 cm^{-1}), Carbonyl compounds (1745 cm^{-1}), Hydrocarbons (2814 cm^{-1}) and CH_3OH (1100 cm^{-1}). The data obtained from different samples can be compared quantitatively due to the intensity is replaced by the relative intensity to deduct the influence of weight.

From the figure of the change for H_2O absorption intensity in different time, it can be observed that DIA lowered the time of the presence of peak. However, FePP delayed the appearance of H_2O peak for about 5 min comparing with the one from cotton/DIA, which indicated that FePP could increase the temperature of the presence for the peak. It was important that the appearance of the peak for cotton/DIA/FePP2 was not only later than the peak for cotton/DIA, but also after the one for cotton fabrics. It implied that addition of FePP retarded the thermal degradation of materials effectively. Simultaneously, addition of FePP made the intensity of H_2O absorption stronger than the sample without FePP. It was because that FePP catalyzed the process of dehydration, which was positive for the char forming.

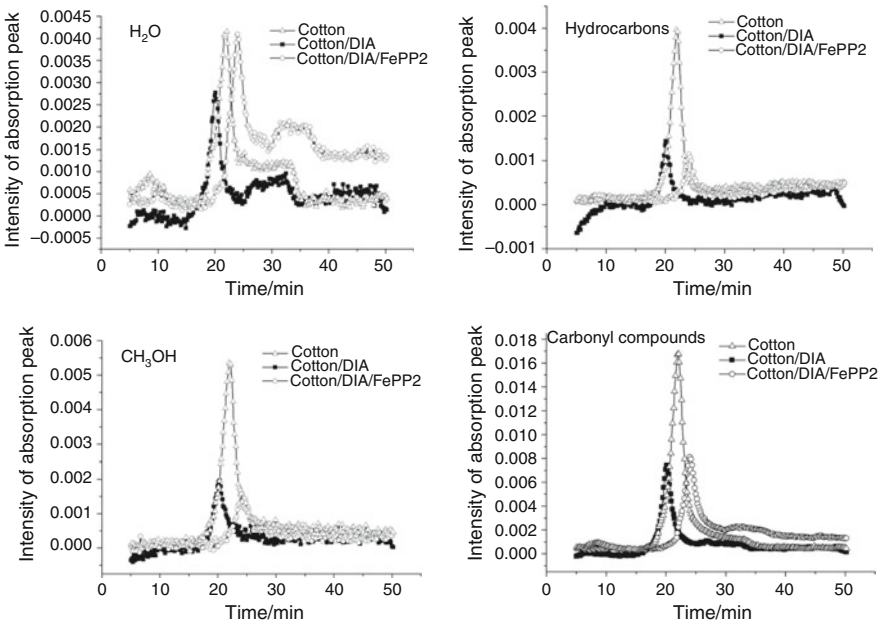

Fig. 3 FTIR spectra of gasses released from thermal decomposition of samples

Other released products such as hydrocarbons, carbonyl compounds and CH_3OH shared the similar trend with H_2O absorption. FePP postponed the present of the released peak for all of the investigative products. It can be explained that addition of FePP suspended the process of thermal degradation, implying that FePP can improve the thermal stability of the sample. This may be due to the cross-link formation by complexing or to high molecular weight molecules of complexes [7].

SEM micrograph

Figure 4 was the SEM photographs of cotton fabrics treated with DIA and FePP. Figure 4a showed that the coating was on the surface of the cotton fabric, and FePP particles were embedded in the coating. The residual char of cotton/DIA and cotton/DIA/FePP2 was obtained after their combustion in the air. Figure 4b and c presented the SEM photographs of above residual char. Char without FePP presented a smooth surface, which can be observed from b. Nevertheless, many particles were on the surface of char for cotton/DIA/FePP2, just as c and d showed to us. It may be owing to the residual products after the combustion of additives. Furthermore, it also can be observed that particles dispersed uniformly on the surface of the char indicating that FePP particles dispersed well in the coating.

Structure of the char

Raman spectroscopy is a useful tool for the characterization of carbonaceous material. Fig. 5 showed the Raman curves of cotton/DIA/FePP2 and cotton/DIA. Both of the curves had two peaks at 1596 and 1364 cm^{-1}, which were the characteristic of pregraphitic structures. The first peak can be assigned to the E2g vibrational mode, while the second one represents defects in the structure [8]. Obviously, the intensity of peak with FePP was stronger than that without FePP, which meant that FePP improved the structural organization level of the carbon [9]. Other two pictures showed the curve fitting of Raman spectroscopy of cotton/DIA and cotton/DIA/FePP2. Relative intensity ratio between 1596 and 1364 cm^{-1} was inversely proportional

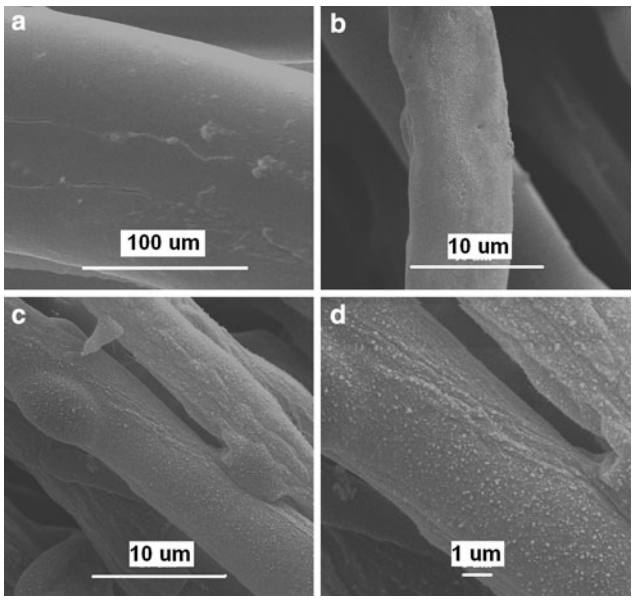

Fig. 4 SEM micrographs. **a** Sample before combustion. **b** Char of cotton/DIA. **c** Char of cotton/DIA/FePP2, 10 um. **d** Char of cotton/DIA/FePP2, 1 μm)

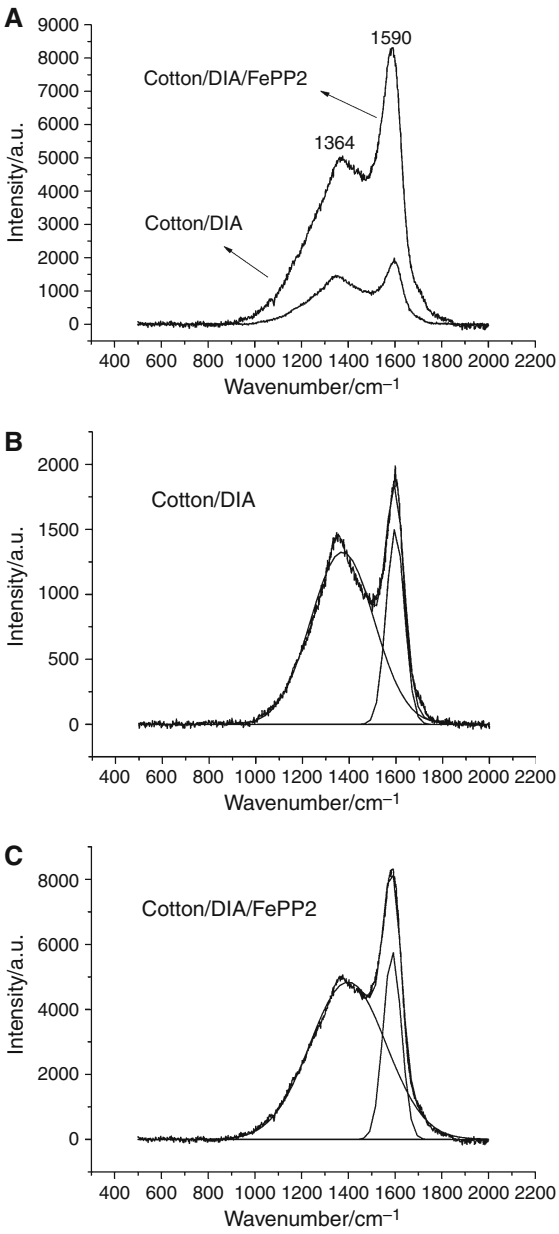

Fig. 5 Raman curves of the char residues of cotton/DIA and cotton/DIA/FePP. **a** Total. **b** Fitted Raman curves of cotton/DIA. **c** Fitted Raman curves of cotton/DIA/FePP2

Table 3 The relative intensity ratio of two peaks around 1596 and 1364 cm^{-1}

Samples	Intensity ratio
Cotton/DIA	$I_{1596/1364} = 0.31$
Cotton/DIA/FePP2	$I_{1601/1397} = 0.40$

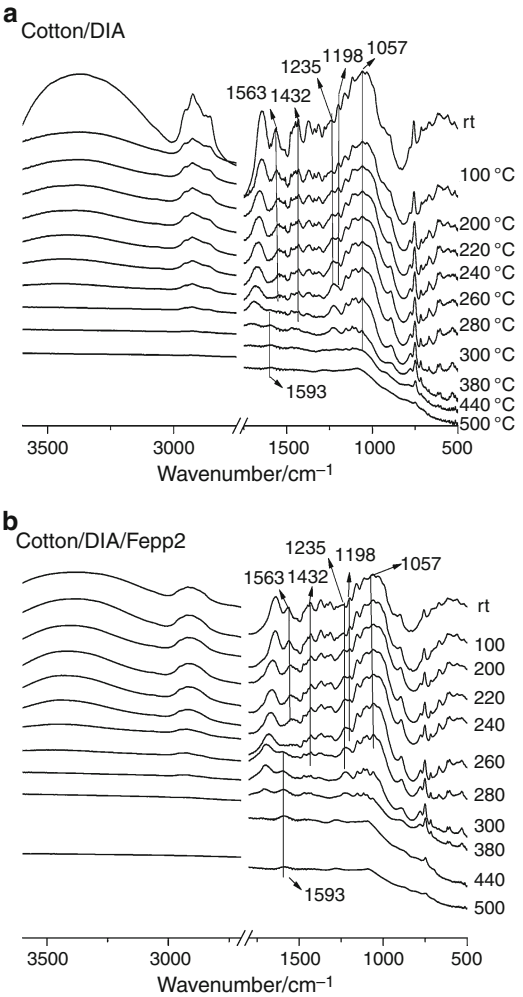

Fig. 6 Real time FTIR spectra for the degradation process of cotton/DIA and cotton/DIA/FePP2

to an in-planemicrocrystalline size and/or an in-plane phonon correlation length obtained from Raman spectroscopy [10]. The related information showed in the Table 3. It can be seen that the sample with FePP had a higher intensity ratio (0.4) than that without FePP (0.31). Bourbigot found that higher protective shield efficiency was related to the smaller size of carbonaceous microstructures [11]. Therefore, FePP led to the char more compact containing smaller carbonaceous microstructures, which caused the reduction of heat release in MCC data.

Thermal degradation analysis of cotton/DIA and cotton/DIA/FePP2

Real time FTIR is used to evaluate the thermal degradation mechanism of cotton/DIA and cotton/DIA/FePP2.

Figure 6 showed the FTIR spectra of cotton/DIA as well as cotton/DIA/FePP2 at different degradation temperatures. Most of peaks were assigned to different vibrations: 1198 cm^{-1} (P=O), 1235 cm^{-1} (P–O vibration in P–Ph structure), 1432 cm^{-1} (P–C vibration in aliphatic chain), 1057 cm^{-1} (Si–O–Si), 1563 cm^{-1} (N–H stretch), 1593 cm^{-1} (C=C stretch).

No difference represented between cotton/DIA and cotton/DIA/FePP2 at lower temperature. However, with the increase of temperature, the peak at 1563 cm^{-1} for the sample with FePP disappeared abruptly at 260 °C, while it vanished completely at 300 °C for that without FePP. It can be explained that FePP accelerated the break of N–H bond, which meant that the presence of FePP promoted the degradation of the flame retardant. Furthermore, for cotton/DIA/FePP2, the peak at 1593 cm^{-1} appeared at 280 °C, which was 20 °C earlier than that of cotton/DIA. It was because that FePP catalyzed the formation of C=C bond, such as aromatic species that would produce char residues at high temperature. The result was consistent well with TG data which showed that the residual char of cotton/DIA/FePP2 is more than that of cotton/DIA above 300 °C.

Conclusions

The potential of FePP for influencing the thermal degradation of cotton fabrics was remarkable. Presence of FePP can both lower the value of HRR and THR comparing with those without FePP. The gas released analysis showed that FePP delayed the thermal degradation of the materials obviously. Char analysis showed that FePP can improve the structural organization level of the carbon as well as graphitization degree of the char. The RT-FTIR results revealed the mechanism of synergism that FePP catalyzed the break of the molecular chain for the flame retardant. At the same time, FePP promoted the C=C bond forming, which is benefit for the formation of char. From the above results, it can be concluded that FePP improved the thermal stability of cotton fabrics effectively.

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References

1. Nie SB, Song L, Zhan J, Hu Y, Tai QL, Chen LJ. Synergistic effect of novel synergists-transition metal ion-incorporated nickel phosphates with intumescent flame retardants in polypropylene. J Macromol Sci A. 2009;46:554–9.
2. Zhang P, Song L, Lu HD, Hu Y, Xing WY, Ni JX, Wang J. Synergistic effect of nanoflaky manganese phosphate on thermal degradation and flame retardant properties of intumescent flame retardant polypropylene system. Polym Degrad Stab. 2009;94:201–7.
3. Davies PJ, Horrocks AR, Alderson A. The sensitisation of thermal decomposition of ammonium polyphosphate by selected metal ions and their potential for improved cotton fabric flame retardancy. Polym Degrad Stab. 2005;88:114–22.
4. Hu S, Hu Y, Song L, Lu HD. Effect of modified organic–inorganic hybrid materials on thermal properties of cotton fabrics. J Therm Anal Calorim. doi:10.1007/s10973-010-1093-1.
5. Mahltig B, Textor T. Combination of silica sol and dyes on textiles. J Sol-Gel Sci Technol. 2006;39:111–8.
6. Ebdon JR, Guisti L, Hunt BJ, Jones MS. The effects of some transition-metal compounds on the flame retardance of poly(styrene-co-4-vinyl pyridine) and poly(methyl methacrylate-co-4-vinyl pyridine). Polym Degrad Stab. 1998;60:401–7.
7. Hanna AA, Basta AH, El-Saied H, Abadir IF. Thermal properties of cellulose acetate and its complexes with some transition metals. Angew Makromol Chem. 1998;260:1–4.
8. Tamor MA, Vassell WC. Raman fingerprinting of amorphous-carbon films. J Appl Phys. 1994;76:3823–30.
9. Lespade P, Al-Jishi R, Dresselhaus MS. Model for Raman scattering from incompletely graphitized carbons. Carbon. 1982;20:427–31.
10. Tuinstra F, Koenig JL. Raman spectrum of graphite. J Chem Phys. 1970;53:1126–30.
11. Bourbigot S, Le Bras M, Delobel R, Tremillon JM. Synergistic effect of zeolite in an intumescence process. Study of the interactions between the polymer and the additives. J Chem Soc Faraday Trans. 1996;92:3435–44.