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Effect of modified organic–inorganic hybrid materials on thermal properties of cotton fabrics

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Abstract Phosphorus-modified siloxanes monomer DOPO-IPDI-AMEO (DIA) was synthesized and characterized by ^{1}H nuclear magnetic resonance (H NMR), ^{31}P NMR, and Fourier transform infrared spectra (FTIR). It hydrolyzed and grew an organic–inorganic hybrid coating on the surface of cotton fabrics via sol–gel process. The conversion of gel reaction was characterized by solid-state ^{29}Si NMR. The effect of the modified organic–inorganic hybrid materials on thermal properties of cotton fabrics was investigated by thermogravimetric (TG) analysis, real time Fourier transform infrared (RT-FTIR), and microscale combustion calorimetry (MCC) experiments. In addition, thermogravimetry-Fourier transform infrared spectra (TG-FTIR) were used to investigate the released degradation products. The characterization information represented that DIA has been prepared successfully. Also the conversion of gel reaction was fairly high. The TG data showed that char residues increased with the addition of the DIA coating. While the peak heat release rate (PHRR) decreased with the presence of the coating in MCC test. Moreover, the flammable degradation products dropped obviously, which can be observed from the data of TG-FTIR.

Keywords Thermal properties · Sol–gel · Organic–inorganic hybrid coating · Cotton fabrics

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Introduction

Organic–inorganic hybrid materials have gained much attention, which is because that they combine advantages of organic and inorganic materials. Many reports focus on fabrics treated with hybrid materials. Satoh et al. [1] studied the novel fluorinated inorganic–organic finishing materials for nylon carpeting. Mahltig et al. [2] investigated the optimized UV protecting coatings by combination of organic and inorganic UV absorbers. Generally speaking, the hybrid materials play an important role in fabrics processing. It should be noted that the oxide layers in inorganic part of hybrid materials are stable against heat, which can lower the combustibility of materials. Hribernik et al. [3] examined the flame retardant activity of SiO_2-coated regenerated cotton fabrics. They found that silica layer acts as a thermal insulator, shifting the temperature at which cellulose started to degrade to higher values. Also application of SiO_2–TiO_2 or SiO_2–Al_2O_3 nanosols [4] to textile filters can impart heat resistance up to temperatures of 300 °C. Nevertheless, the effect of physical obstruction on thermal stability for samples was limited. It will take both physical and chemical effects on thermal stability for the underling materials, if other flame resistant elements are induced in, such as phosphorus and boron. Cireli et al. [5] investigated the flame retardancy properties of fabrics treated with phosphorous (P)-doped SiO_2 thin films developed by sol–gel technique. The results showed that treating with phosphorous exhibited a better thermal stability.

Cotton is widely used in every corner of our world. However, it is easily attacked by flame and readily induces fire disasters. Therefore, it is important to lessen the flammability of the material. In this article, we took organic–inorganic hybrid materials via sol–gel method to lower the flammability of fabrics. Phosphorus-modified organic–

inorganic hybrid coating was prepared and coated on the surface of cotton fabrics. The purpose of this research was to investigate the influence of the hybrid coating on thermal properties of cotton fabrics. The characteristics were evaluated through TG, TG-FTIR, and MCC experiments.

Experiment

Materials

9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) from Zhejiang Wansheng Chemical Cor. (China) was recrystallized from tetrahydrofuran (THF) before use. Γ-Aminopropyl triethoxysilane (AMEO) was received from Nanjing Shuguang Chemical Group Cor. (China). Dichloromethane, triethylamine, and Isophorone diisocyanate (IPDI) were provided by the First Reagent Co. of Shanghai, China. Plain-weave cotton fabrics were from the market with an areal density of 156 g m^{-2}.

Synthesis of DIA

IPDI (11.12 g) and Dichloromethane (100 mL) were added into a three-necked flask (250 mL) with a dropping funnel and a mechanical stirrer. The flask was put in ice water. N_2 gas was aspirated for 10 min to eliminate residual moisture. AMEO (5.0 g) was added slowly at 0 °C for about 2 h, and the reaction mixture was stirred for another 2–3 h at room temperature. Then DOPO (10.80 g), triethylamine (0.2 g), and another dichloromethane (50 mL) were placed into the above mixture. The reaction occurred at room temperature and lasted for 8 h [6]. Finally, a transparent solid product in light pink was obtained after dichloromethane and triethylamine were evaporated by a rotary evaporator. The reaction equation was shown in Scheme 1.

FTIR (KBr, cm^{-1}): 2971 (C−H), 1650 (N−H), 1200 (P=O), 1102 (Si−O−C),

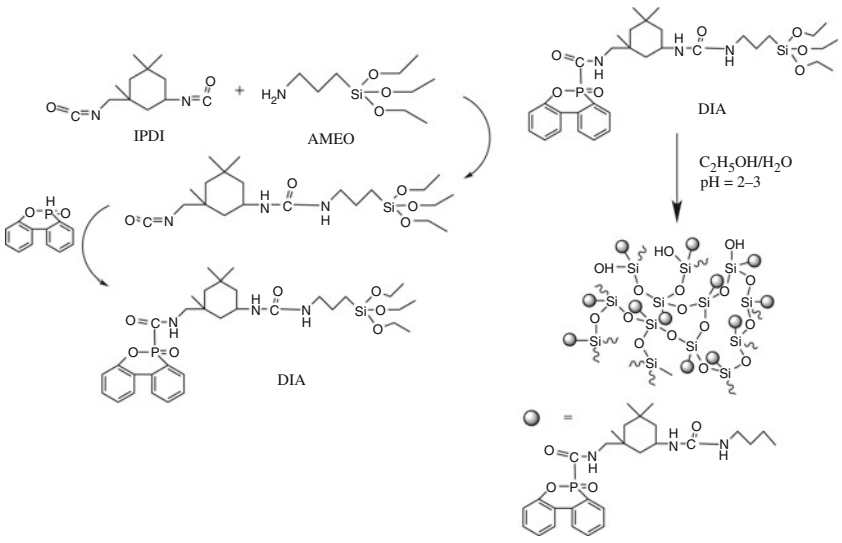
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 0.61 (Si–CH_2–), 0.90 (–CH_3, IPDI), 1.02 (–C–CH_2–C–), 1.21 (–O–C-CH_3), 1.47–2.09 (–N–C–CH_2–), 2.87–3.12 (–N–CH_2–), 3.68 (–CH–), 3.80 (–OCH_2–), 7.0–8.2 (aromatic H), 7.28 ($CDCl_3$).

Preparation of samples

Cotton fabrics were pre-treated in an 18 wt% NaOH solution and thoroughly rinsed with distilled water before they were 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 used to promote hydrolysis with the pH value around 3. The whole reaction went on about 5 h. After the hydrolysis, pretreated cotton fabrics were dipped in, taken out, and squeezed before they were laid at room temperature for 1 h. Then they were dried in an oven at 80 °C for 2 min and 130 °C for 1 min. At last, samples were rinsed with distilled water to remove excessive hydrochloric acid and dried at 80 °C. The process was shown in Scheme 1.

Characterization

FTIR spectroscopy (EQUINOX55, Bruker Co., Germany) was employed to characterize DIA. NMR measurement of DIA was conducted on Avance 300 spectrometer (Bruker Biospin, Switzerland, frequency) using $CDCl_3$ as the solvent. Solid-state ^{29}Si NMR was characterized by Bruker AVANCE III (400 WB: ^{29}Si 79.50 MHz). Thermogravimetric (TG) analysis was performed on TGAQ5000 (TA Co., USA). The heating rate was set as 20 °C min^{-1} (air



Scheme 1 Preparation and hydrolyzation of DIA

atmosphere). The TG-FTIR instrument consists of analyzer (TGA-Q5000, TA Co., USA) coupled with Fourier transform spectrometer (Nicolet6700) 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 in 20 °C min^{-1}. Govmark MCC-2 microscale combustion calorimetry (MCC) was used to determine the flammability characteristics of treated cotton fabrics according to ASTM D 7309-07. About 5-mg specimens were thermally decomposed in an oxygenated environment at a constant heating rate of 1 K s^{-1}.

Results and discussion

Characterization of DIA and cured DIA

The FTIR spectrum of DIA was shown in Fig. 1a. It can be observed that –C–N=O absorption around 2,270 cm^{-1} has been vanished. In addition, P–H band at 2,384 cm^{-1}, which belonged to DOPO, disappeared as well. They both confirmed the accomplishment of the reaction. ^{1}H NMR spectrum of DIA was represented in Fig. 1b. Ar–H peaks were during 7.0–8.2 ppm. Other peaks have been labeled on. A small peak at 4.3 ppm for Si–OH was resulted from the hydrolysis of Si–OR [6, 7]. Figure 1c showed ^{31}P NMR graph of DIA. Besides the major peak at 13.62 ppm, two other peaks at 5.23 and 17.49 ppm were observed. The small peak at 5.23 ppm was owing to the side reaction that the other C–N=O group of IPDI reacted with DOPO. Another small peak at 17.49 ppm should result from the hydrolysis of DIA, where Si–OR transformed into Si–OH. ^{29}Si NMR of the cured DIA can be observed from Fig. 1d. Silica network with tri-, di-, and mono-substituted siloxane is designated as *T3* (around −62.4 ppm), *T2* (around −56.4 ppm), and *T1* (around −49.1 ppm), respectively. According to Fig. 1d, tri-substituted siloxane T3 was the major microstructure in the coating, suggesting the conversion of gel reaction is fairly high [6]. In sum, DIA has been synthesized successfully and was cured correctly.

Thermogravimetric analysis

TG and DTG curves of cured DIA coating, cotton fabrics, and fabrics coated with cured DIA (DIA/cotton) were shown in Fig. 2, and the related data were listed in Table 1. For hybrid DIA coating, two degradation stages can be observed. The first step around 240 °C can be attributed to the break of group containing phosphorus, while the other phase was owing to the further decomposition of the coating. From the thermogravimetric data, it can be found that DIA/cotton possessed less thermal stability than cotton fabrics at the beginning of thermal decomposition. With the increase of DIA coating content, the onset temperature ($T_{10\%}$, temperature of 10% mass loss) decreased, which was owing to the degradation of DIA coating. The maximum mass loss temperature (T_{max}) showed the similar trend, reducing from 347.6 to 315.9 °C. The result indicated that DIA coating accelerated thermal degradation of cotton fabrics at a low temperature, which may be because of the presence of the organic group containing phosphorus. Specifically, the acid environment from the degradation products accelerated the dehydration of cotton fabrics. At the same time, with the addition of DIA, char residues increased from 1.82 to 9.38 wt% at 700 °C, demonstrating clearly that the coating catalyzed the formation of char. It

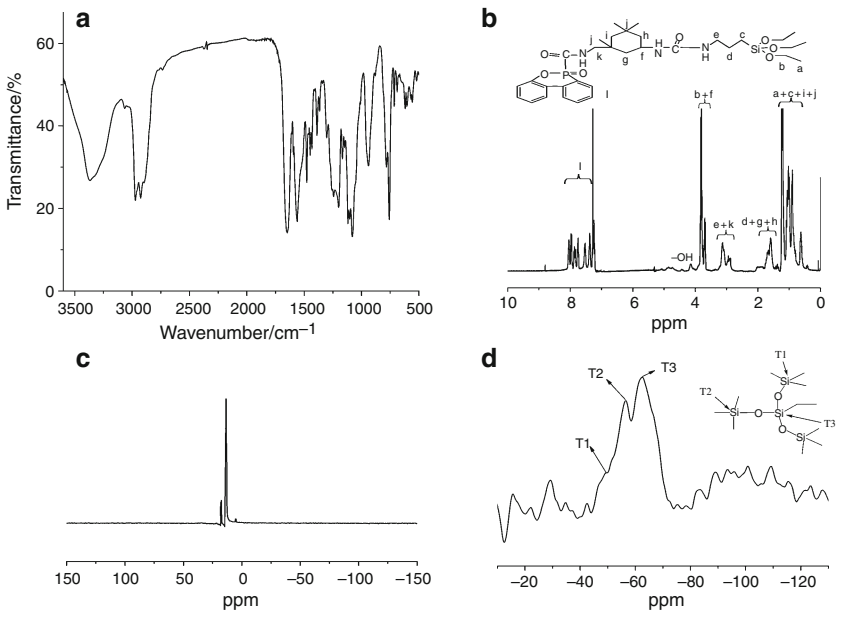


Fig. 1 Characteristic of DIA (**a** FTIR; **b** ^{1}H NMR; **c** ^{31}P NMR; **d** solid-state ^{29}Si NMR)

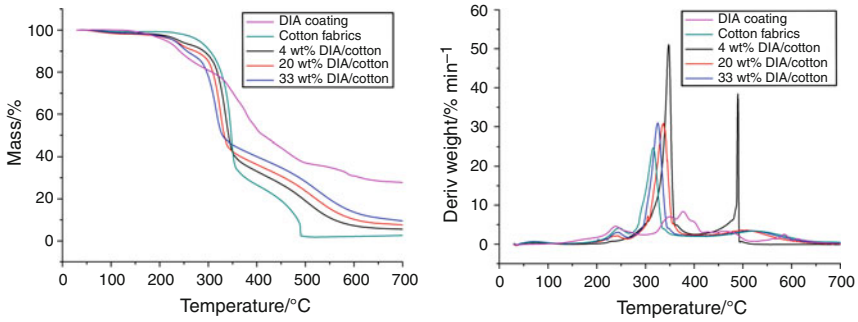


Fig. 2 TG/DTG curves of samples

Table 1 Thermal properties of samples

Samples	$T_{10\%}$/°C	T_{max}/°C	Char residues at 700 °C/wt%
Cotton fabrics	294.5	347.6	1.82
DIA coating	241.4	370.4	27.7
4 wt% DIA/cotton	270.8	336.2	5.43
20 wt% DIA/cotton	253.3	324.8	7.54
33 wt% DIA/cotton	245.6	315.9	9.38

was well known that phosphorus has an effect to promote the char forming, while Si–O inorganic structure had a good thermal stability. Therefore, the organic and inorganic parts both contributed to the yielding of char layers. The char can block the transfer of oxygen and heat, which retarded thermal decomposition of underlying materials. That is, DIA improved the thermal stability of materials.

Released degradation products analysis

TG-FTIR was used to analyze the gas products during the thermal degradation. Figure 3 showed the main absorbance of pyrolysis products for cotton fabrics and 20 wt% DIA/cotton. The data obtained from different samples can be compared quantitatively. It was because that the intensity was replaced by relative intensity to deduct the influence of mass.

The plot of the absorption intensity of H_2O in different time was shown in Fig. 3. DIA coating lowered the temperature of the appearance of peak, which indicated the accelerated dehydrating action from flame retardant. In general, cotton fabrics treated with phosphorus compounds enhanced the intensity of H_2O absorption due to phosphorus compounds superior dehydrating action [8]. However, in this study, the presence of DIA made the intensity of H_2O lower. It can be explained that H_2O may be attracted by surplus unreacted Si–O–H bonds, which prevented H_2O from releasing.

Release of carbonyl compounds, hydrocarbons, and CH_3OH during the thermal decomposition of treated and untreated samples shared a similar trend. DIA coating promoted the formation of the above products at a lower temperature compared with those of cotton fabrics. The results implied that the hybrid coating catalyzed thermal decomposition of cotton fabrics. Moreover, the intensity of

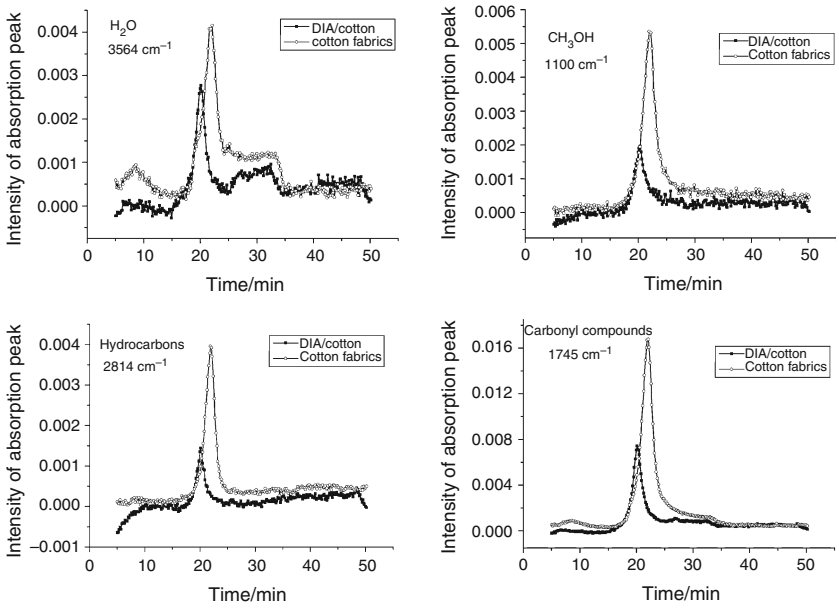


Fig. 3 Absorbance of pyrolysis products for pure cotton fabrics and DIA/cotton versus time: H_2O; CH_3OH; hydrocarbon; carbonyl compounds

carbonyl compounds, hydrocarbons, and CH_3OH decreased greatly when samples were treated. The phenomenon indicated that the hybrid coating can reduce the formation of such flammable small molecule products during thermal degradation process, which benefited for thermal stability of the underlying materials.

MCC test

Figure 4 described the heat release rate (*HRR*) curves of cotton fabrics treated with different DIA content. The corresponding combustion data were presented in Table 2. With the increase of DIA content, *HRR* value of the first peak got higher. It was attributed to the addition of organic group containing phosphorus, which broke at a low temperature. Simultaneously, the more the ratio of DIA coating put on the cotton fabrics, the less the value of the peak heat release rate (*PHRR*). The same thing took place to the heat release capacity (*HRC*) that was used for evaluating polymer flammability. It can be interpreted that hybrid coating led to the increase of residual char, which held back the release of heat. Furthermore, the reduction of *PHRR* can be explained from the information of TG-FTIR. It was owing to the decrease of flammable thermal degradation products such as carbonyl compounds, hydrocarbons, and CH_3OH.

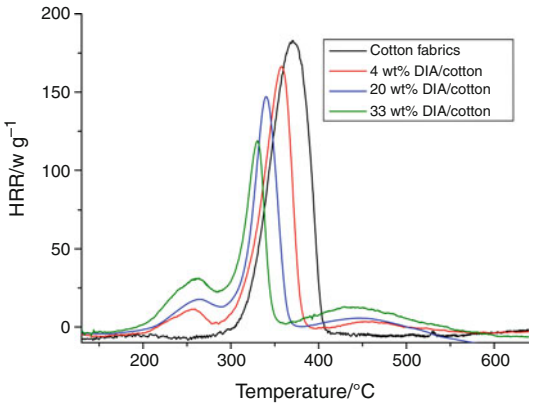


Fig. 4 HRR curves of cotton fabrics and DIA/cotton

Table 2 MCC data of samples

Samples	HRC/J g^{-1} k^{-1}	PHRR/w g^{-1}	Ignition temperature/°C
Cotton fabrics	181.4	182.1	370.6
4 wt% DIA/cotton	164.2	166.0	358.2
20 wt% DIA/cotton	146.0	146.3	339.6
33 wt% DIA/cotton	116.8	117.3	330.2

When it came to the ignition temperature, it decreased with the presence of the hybrid material. The result can be ascribed to the presence of the coating that catalyzed the dehydration of materials. In sum, phosphorus-modified sol–gel product improved the thermal stability of cotton fabrics.

Conclusions

The modified organic–inorganic hybrid coating was synthesized successfully. It had a positive effect on the thermal stability for cotton fabrics. Both of the organic and inorganic parts of the coating contributed to the increase of char layers. Furthermore, it caused an obvious decline of *PHRR*. In addition, the data of TG-FTIR showed that DIA coating can decrease the combustible degradation products, which lessen the flammability of samples. In a word, DIA hybrid coating improved the thermal stability of cotton fabrics.

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