

A Phosphorus-Nitrogen Flame-retardant: Synthesis and Application in Cotton Fabrics

Qiang-Lin LI^{1,2*}, Fang-Qian HUANG², Yu-Jun WEI², Ju-Zhen WU¹, Zheng ZHOU¹, Guo LIU^{1,3}

¹ Chengdu Technological University, Institute for Environmental Governance and Intelligent Monitoring, Chengdu Sichuan 611730, China

² Chengdu Textile College, Chengdu Sichuan 611731, China

³ Chengdu University of Technological, Chengdu Sichuan 610059, China

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Cotton textiles with high air permeability, good hygroscopicity and good soft-feeling due to be natural cellulose fabrics, but their high flammability greatly limit its applications; fire-retardant finishing of cotton fabrics can impart good flame retardant properties. In this research, a novel phosphorous-nitrogen flame retardant (FR), poly-(imino-4-amino-1,3,5-triazin-2,6-imino-(3-oxopropyl)-N-phenylphosphinamido) (PCEPAM) was synthesized with 2-carboxyethyl(phenyl)phosphinic acid (CEPPA) and melamine (MA). Its structure was characterized by FTIR, ¹H-NMR, and the thermal performance was analyzed by TGA-DSC. Cotton fabrics were treated via pad-dry-cure process with PCEPAM. The surfaces of treated fabrics and the combustion residue were characterized by SEM. The fire behavior was performed by limited oxygen index (LOI) and vertical burning test. The LOI of FR fabric is more than 28.5% after washing once. The thermal stability and surfaces of the combustion residue of the fabrics were investigated by TG and SEM, respectively. The results show that PCEPAM is not only an effective FR but also a good char-forming agent for the cotton fabric.

Keywords: flame retardant, cotton fabrics, synthesis, finishing, fire behavior.

1. INTRODUCTION

Textile is widely applied to clothing, knitwear and home textiles because of outstanding softness and breathability. However, due to its highly flammability, it was essential and crucial to impart the flame retardancy to fabrics [1]. Flame retardant (FR) textile can slow down fire spread rate, reduce fire hazards, extend escape time, and thereby protect people's lives and property [2]. Thus, a study on flame retardant fabrics is not only of great significance to the development of the apparel industry and decorative materials, but also of an urgent challenge [3]. In our previous research, we developed a crosslinkable containing-phosphorus FR with active group [4, 5], a series of phosphorus-nitrogen synergist FRs [6, 7], and an excellent insolubility phosphorus-nitrogen-silicone synergist FR [8]. Usually, flame retardant (FR) finishing of fabric is an economic and practical choice, especially, natural fiber textile. Despite many FR finishing methods have been reported [9–11], no good practical finishing method for many fabrics has been developed up to now. It is well known that phosphorus and nitrogen elements, which are of good synergistic effect, are effective FR element for cellulose and polyethylene terephthalate (PET) materials [12]. In this research, a novel phosphorus-nitrogen flame retardant (PCEPAM) is synthesized with 2-carboxyethyl(phenyl)phosphinic acid (CEPPA) and melamine (MA) (Scheme 1). And it is characterized by FT-IR and ¹H-NMR. Its thermal property, flame retardancy

are performed by Simultaneous Thermal Analyzer (Thermal Gravimetric Analysis/Differential Scanning Calorimeter, TGA-DSC), vertical burning and limited oxygen index (LOI). And other properties such as durability of treated fabrics with the FR coating agent are investigated, too.

2. MATERIALS AND METHODS

2.1. Materials

A cotton plain woven fabric weighing 80 g/m² was supplied by Sichuan Cotton Mill Ltd. The 2-carboxyethyl(phenyl)phosphinic acid (CEPPA), melamine (MA) were supplied by Chengdu Changzheng Chemistry industry Company. The acrylic emulsion and the thickener were commercial products supplied by Chengdu Guixi Construction Chemical Company.

2.2. Synthesis and characterization of PCEPAM

CEPPA (21.42 g, 0.10 mol) was added to a glass flask containing 100 mL water and equipped with a stirrer, thermometer, and condenser. The mixture was heated to boiling and stirred until completely dissolved. Then melamine (12.61 g, 0.10 mol) was added into the mixture. The mixture was reacted for 20 min to produce white precipitate. Then the product was cooled to room temperature, filtered and dried to obtain an intermediate CEPAM⁺, white solid. The intermediate was added into an evaporating dish, heated to completely melted and stirred until turning into light yellow viscous melt, about 15 min, no H₂O vapor was released, and the reaction was complete,

* Corresponding author. Tel.: +086-87996647; fax: +086-87996647.
E-mail address: lqlxp1010@163.com (Q.L. Li)

the yellow product was obtained. The solid product was dispersed in 100 mL 70 °C hot water, stirred about 15 min. Finally, through filtration, washing 3 times with hot water and drying, a Novel phosphorus-nitrogen FR, PCEPAM, a pale yellow solid was obtained (yield 86.3 %).

The FTIR spectrum of PCEPAM was obtained with an FTIR spectrophotometer (Nicolet 6700, Thermo Nicolet, Waltham, MA) with a potassium bromide pellet technique, and the ¹H-NMR spectra were obtained on an NMR spectrophotometer (Varian INOVA-400, Varian, Palo Alto, CA) with hexadeuterated dimethyl sulfoxide (DMSO) as a solvent. The data of FTIR (KBr, cm⁻¹): 3360, 3161, 3052, 2952, 2843, 1669, 1506, 1435, 1440, 1256, 1129, 1037, 959, 785, 751, 732, 697, 521. The data of ¹H-NMR (400 MHz, DMSO, TMS, ppm): 7.8-7.6(5H), 6.6(8H), 4.6(2H), 1.4-1.3(4H).

2.3. Treatment process

FR bath was prepared with 30 % PCEPAM (w/w) and 70 % acrylic emulsion (w/w), then controlled viscosity (about 1500 mPa·s) with thickener and water, and the content of PCEPAM was 45 % in the dry coatings. The treatment process of cotton fabrics with FR bath was showed in Fig. 1. The cotton fabrics were immersed in FR bath (the bath ratio was 1:20) to give an approximately 100 % wet pickup regulated by padding. After double-dip-double-nip, the fabrics samples were pre-baked at 105 °C for 5 min and then were cured at 160 °C for 3 min. Part of the fabric samples tested directly without washing, and the others were washed at 40 °C in distilled water for 10 min and finally dried at 90 °C, and then tested. The add-on (%) of coating was calculated from the Eq. 1.

$$\text{add-on\%} = \frac{w_t - w_0}{w_t} \times 100\%, \quad (1)$$

where w_0 and w_t are the weights of the T/C fabrics before and after blade coating with FR coating agent, and w_n denotes the weights of the T/C fabrics after washing n times, respectively.

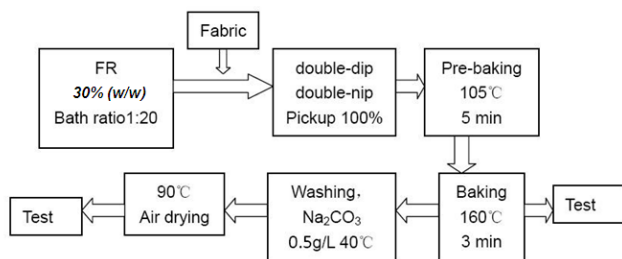


Fig. 1. Schematic diagram of flame-retardant finishing process with PCEPAM

2.4. Combustion performance

The LOI values of the samples were measured on an oxygen index flammability gauge (HC-2C, Nanjing Shangyuan Analytical Instruments, Nanjing, China) according to ASTM D 2863-97. The vertical burning test was conducted on a CZF-2 type instrument (Jiangning, China) according to ASTM D 6413-99. This testing method measures the vertical flame resistance of textiles in general, including after-flame time (t_{flame}), that is, the

length of time the material continues to burn after removal of the burner after a 12 s ignition time; afterglow time (t_{glow}), that is, the length of time the material glows after the flame extinguishes; and char length (L_{char}), that is, the distance from the edge of the fabric that is exposed to the flame to the end of the area affected by the flame.

2.5. Thermal properties

TGA-DSC of FR, treated and untreated fabrics were conducted on a Synchronization Thermal Analysis STA 449C (Netzsch, German) at a heating rate of 10 °C/min. Aluminum sample pans were used. The samples (5–7 mg) were heated in the analyzer at temperatures ranging from 40 to 580 °C under N₂ at a flow rate of 45 mL/min.

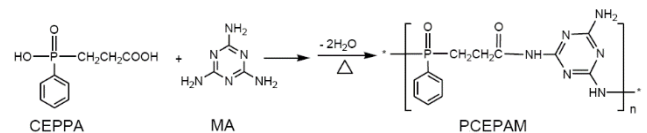
2.6. Measurements of the surface morphology of the treated fabrics

The surface morphology of the untreated and treated cotton fabrics before and after washing were investigated by SEM (XL30 ESEM-TMP, Philips-FEI, Eindhoven, Netherlands) at 10 kV. The residues of the untreated and treated cotton fabrics obtained from the fabric after combustion in air were also investigated by SEM. All samples were coated with gold before examination.

3. RESULTS AND DISCUSSION

3.1. Synthesis and characterization of PCEPAM

PCEPAM was prepared via the reactions of forming salt and dehydration. First, the -NH₂ of melamine were formed ammonium salts with the COOH and P-OH of CEPPA molecular in aqueous solution. Then, the ammonium salts were dehydrated to produce oligomer of phosphoramidite and amide.



Scheme 1. Synthetic route of PCEPAM

The FTIR spectrum of PCEPAM is shown in Fig. 2. The N-H and NH⁺ stretching vibration were around 3360 cm⁻¹ and 3161 cm⁻¹, respectively; and CH₂ stretching vibration were showed at the 2952 and 2843 cm⁻¹; C=O and P=O stretching vibration were found at 1669 cm⁻¹ and 1256 cm⁻¹, respectively; stretching vibrations of N-C(=O) and N-P(=O) appeared at 1129 cm⁻¹ and 697 cm⁻¹, respectively. Also, the bands at 3052, 1508, 785 and 732 cm⁻¹ were the characteristic absorbing peaks of the benzene ring.

The ¹H-NMR spectrum of PCEPAM shows (Fig. 3 a) the aromatic protons resonated at 7.8 (d, J = 7.2 Hz, 2H, arC-H_o), 7.7 (s, 1H, arC-H_p), and 7.6 ppm (d, J = 7.1 Hz, 2H, arC-H_m). The chemical shifts of CH₂ were found at 1.4 (d, J = 8.2 Hz, 2H, P-CH₂) and 1.3 ppm (d, J = 7.4 Hz, 2H, CH₂-C=O). 4.39–4.29 ppm (m, 2H, CH₂-C=O), and 4.1 ppm (s, 4H, OH). The chemical shifts of the active hydrogen, -NH₂ and -NH-, resonate at 6.6 and 4.6 ppm. The ¹³C-NMR spectrum of PCEPAM shows (Fig. 3 b) the carbon resonance of triazine is 183 (arC-NH-C=O), 178

(arC-NH-P=O) and 154 ppm (arC-NH₂), carbon resonance of C=O is 174 ppm, phenyl carbons resonated at 134 (arC-P), 132 (arC_m), 130 (arC_o), and 127 ppm (arC_p). The chemical shifts of CH₂ were found at 25 (P-CH₂) and 26 ppm (CH₂-C=O).

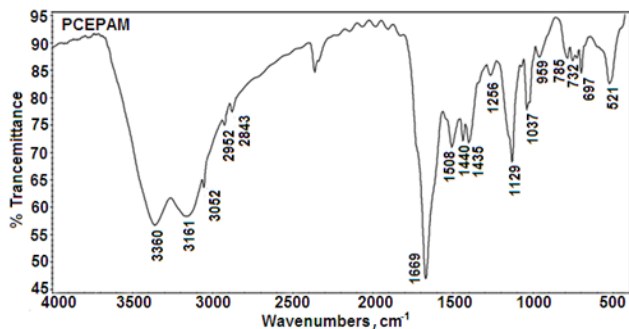


Fig. 2. FTIR spectra of PCEPAM

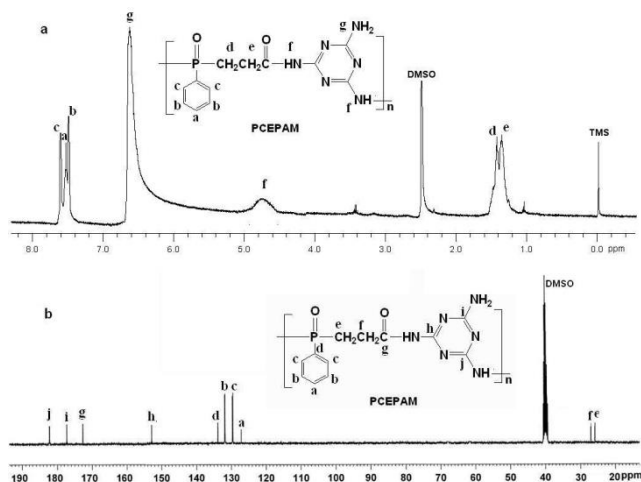


Fig. 3. ¹H-NMR a – ¹³C-NMR; b – spectra of PCEPAM

3.2. Micrographs of treated fabrics

The cotton fabrics were treated via pad-dry-thermosol finishing using coating agent containing PCEPAM. As shown in the SEM photographs in Fig. 4, the surface of the untreated cotton fabrics (Fig. 4 a) was smooth and relatively neat. As far as the treated cotton fabrics (Fig. 4 b) were concerned, the surface became rough, many granular species packed on the fiber, and FRs filled in between fibers. After it was washed once (Fig. 4 c), the fiber was still somewhat shaggy, and the surface of fiber is covered by an uniform and compact layered coatings, and a small amount of flame-retardant particles are fixed onto the surface of fabric by physical absorption. These results indicate that FRs have been fixed onto fiber.

3.3. Thermal stability of CEPAM+ and PCEPAM

TGA-DSC thermograms of CEPAM⁺ and PCEPAM are shown in Fig. 5 and the relevant thermal decomposition data are listed in Table 1. It is interesting that the curve 1 (CEPAM⁺) shows two stages but the curve 3 (PCEPAM) only one continuous decomposition stage, and the second stage of curve 1 is markedly similar with curve 3. So in the curves 1, the first stage, which is the dehydration to PCEPAM stage, appeared in 127~151 °C. *T*_{1max} is found at 146 °C, and weight loss is 7.4 %; the second

decomposition stage is in 229–542 °C, which is a continuous decomposition stage of PCEPAM, *T*_{2max} is found at 318 °C, and weight-loss is 42.4 %. The degradation of PCEPAM is shown in curve 3, which is a continuous and long decomposition stage in 230–540 °C. *T*_{max} is found at 317 °C, and the weight loss is 39.5 %. Finally, the residue of CEPAM⁺ and PCEPAM at 580 °C is 50.0 % and 54.5 %, respectively. It can be seen that there are appeared many endothermic peaks in DSC curve 2 and curve 4. In the second decomposition stage of CEPAM⁺, its DSC curve 2 is also very much similar with curve 4, which showed this stage is just the decomposition of PCEPAM. This result indicates that the decomposition of PCEPAM occurred via multi-stage, which can play a good endothermic role during fire-retarding. And it may greatly inhibit the decomposition of substrate polymer and decrease the concentration of incombustible gas [13].

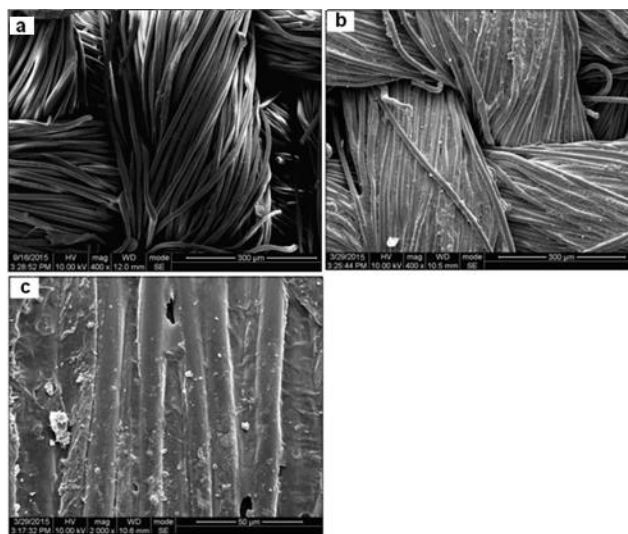


Fig. 4. SEM micrographs a–400X of surface of blank fabric, b–400X and c–2 000X of surface of treated fabrics by PCEPAM after washing once

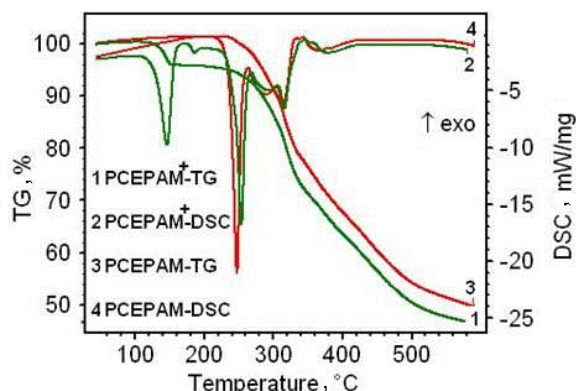


Fig. 5. TGA-DSC curves of CEPAM⁺ and PCEPAM in N₂ at heating rate of 10 °C/min

Degradation of FR cotton fabrics are shown in Table 1 and Fig. 6, too. It is well known that *T*_{on} of effective FR must be close to or slightly lower than that of substrate polymer, namely, FR begins to decompose to play a flame-retarding role before substrate material pyrolysis. Moreover, the ideal FR acts on flame retardancy during the whole pyrolysis process of the matrix material [14].

Table 1. TGA data of CEPAM⁺, PCEPAM, cotton and FR-cotton

Sample	T_{on} , °C	580 °C residue, %	First weight-loss stage				Second weight-loss stage			
			$T_{on}^a - T_{end}^b$, °C	T_{max}^c , °C	v_{max}^d , %/min	W_{loss} , %	$T_{on} - T_{end}$, °C	T_{max} , °C	v_{max} , %/min	W_{loss} , %
CEPAM ⁺	127	50.0	127–151	146	2.45	7.4	229–542	318	4.55	42.4
PCEPAM	230	54.5	–	–	–	–	230–540	317	4.54	39.5
Cotton	303	21.4	–	–	–	–	303–380	362	26.52	71.3
FR-cotton	252	44.0	252–355	326	9.41	32.9	355–447	410	1.74	12.3

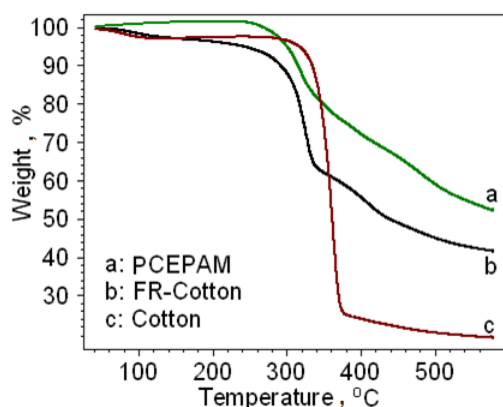
^a T_{on} denotes onset temperature; T_{end} denotes end temperature;
^b T_{max} denotes maximum weight-loss temperature;
^c v_{max} denotes maximum weight-loss rate;
^d W_{loss} denotes weight-loss rate during certain stage.

Table 2. Flame retardancy of treated fabrics with PCEPAM undergoing different times washing

Washing times	FR add-on, %	Burning rank	LOI, %	Vertical burning test		
				Char length, mm	After-flame time, s	After-glow time, s
blank	0	Failed	19.2 ± 0.2	N.R. ^a	N.R.	N.R.
0	28.5	B1	35.2 ± 0.1	38	N.O. ^b	N.O.
1	23.9	B2	28.6 ± 0.2	52	2.0	0
5	18.4	Failed	26.2 ± 0.1	162	5.3	0
10	15.2	Failed	25.4 ± 0.2	T.D. ^c	N.R.	N.R.

^a N.R. denotes no record due to the complete destruction of the fabric;
^b N.O. denotes no record due to the self extinguishments of fabric during the 12-s ignition time;
^c T.D. denotes the case that fabrics were completely destroyed during the test.

So PCEPAM may be an efficient FR for cotton fabric, because its T_{on} is lower than that of cotton ($T_{on} = 303$ °C), and its temperature range of decomposition ($T_{on} - T_{end} = 230$ °C–540 °C) contains that of cotton fabric ($T_{on} - T_{end} = 303$ °C–380 °C). As can be seen that the degradation of cotton fabrics becomes from one weight-loss stage to two weight-loss stage after treated with PCEPAM coating, and T_{max} of FR fabric is decreased from 362 °C to 326 °C, its maximum weight-loss rate is highly reduced from 26.52 %/min to 9.41 %/min. The residue at 580 °C is greatly increased 22.6 % than blank cotton. So the result again indicates that PCEPAM is an excellent charring agent for cotton.

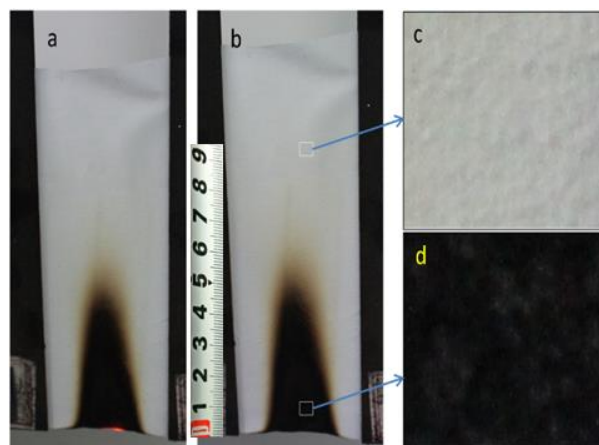
**Fig. 6.** TGA curves: a–PCEPAM; b–FR-cotton; c–cotton in N₂ at heating rate of 10 °C/min

3.4. Burning performance

To evaluate flame retardancy of the treated fabrics, LOI and vertical burning test are used, and the data are given in Table 2. The add-on of FR coating is 28.5 % without washing. Its LOI is more than 35.2 % (LOI of blank is 19.2 %). LOI decreases to 28.6 % after washing once. The vertical burning test shows that FR-fabrics are promptly self-extinguished after igniting. And the

maximum damaged length (L_{damage}) is only 52 mm, and the burning rank reaches B2. LOI after washing 5 and 10 times are 26.2 and 25.4, respectively.

As can be seen from Fig. 7 a and b, during the vertical burning test, a little smoke produces while igniting, and the fire is self-extinguishes after igniting 12 s, carbon length is only 52 mm. The coated fabric is charred significantly (Fig. 7 d), but the side of the without igniting was remaining gray, and the original appearance of fabric is maintained completely (Fig. 7 c). The surfaces of char layer of coated side are uneven but smooth (Fig. 7 d), which may contribute to inhibit the exchange of combustible gas and oxygen to prevent continuous burning.

**Fig. 7.** Digital photos of vertical burning test: a–igniting 12s; b–after self-extinguishment; c–original FR-fabrics without burning; d–the char layer after burning

3.5. Morphology of residue after fabric burning

The residue of treated fabrics retains the origin morphology of fabric (Fig. 8 a) after vertical burning test. Fig. 8 b shows that the fibers are adhered together except for some gas holes on the surface. The residue of a yarn is

showed in Fig. 8c, which is a uniformly distributed sandy-like char structure. Fig. 8d shows that the char is discontinuous and snowflake-like as a result of enhancing char-forming effect of FR. By forming a barrier between flame and the underlying fiber, the surface char layer blocks the fiber with contacting fiber and inhibits the transmission of heat. The results also show that PCEPAM is not only a durable flame retardant but also a good char-forming agent for cellulose [15].

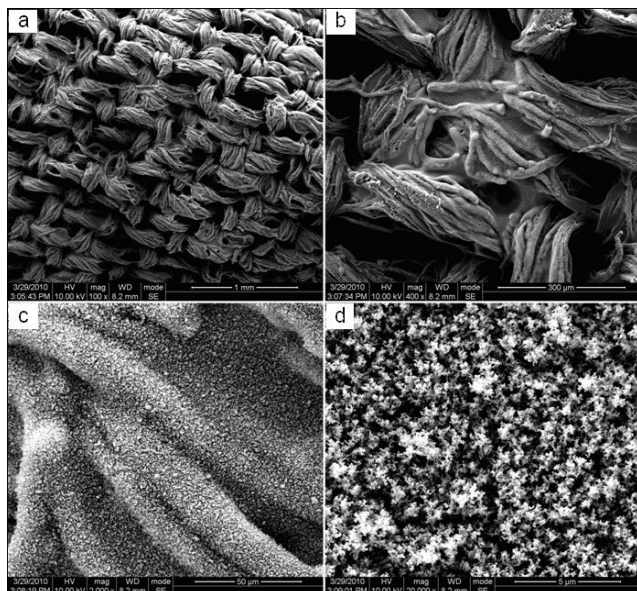


Fig. 8. SEM micrographs of the residual char of cotton fabrics treated with PCEPAM: a–100X; b–400X; c–2000X; d–20000X

4. CONCLUSIONS

A Novel phosphorus-nitrogen flame retardant (PCEPAM) was synthesized via the reactions of a forming salt and dehydration. And a flame retardant agent with PCEPAM was prepared by acrylic emulsion. The cotton fabric was treated via pad-dry-thermo sol finishing using the coating. SEM micrographs show that the surface of fiber is covered by uniform and compact layered coatings. The LOI of FR fabric is more than 35 % before washing when add-on 28.5 %. LOI still reaches to 28.6 % after washing once, and LOI was 26.2 % after washing 5 times. The results of SEM of residue after fabric burning and TGA all indicate that PCEPAM is an excellent charring agent for cotton.

Acknowledgments

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