Chinese Journal of Polymer Science Vol. 32, No. 3, (2014), 305−314

Chinese Journal of Polymer Science
© Chinese Chemical Society
Institute of Chemistry, CAS
Springer-Verlag Berlin Heidelberg 2014

Flame-retardant Coating by Alternate Assembly of Poly(vinylphosphonic acid) and Polyethylenimine for Ramie Fabrics*

Li-li Wang[a, b], Tao Zhang[a, b], Hong-qiang Yan[b], Mao Peng[a**], Zheng-ping Fang[a, b],
Yan Li[c] and Wang Hao[d]
[a] *MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Institute of Polymer Composites, Zhejiang University, Hangzhou 310027, China*
[b] *Laboratory of Polymer Materials and Engineering, Ningbo Institute of Technology, Zhejiang University, Ningbo 315100, China*
[c] *School of Aerospace Engineering and Applied Mechanics, Tongji University, Shanghai 200092, China*
[d] *Centre of Excellence in Engineered Fibre Composites, University of Southern Queensland, Toowoomba Qld 4350, Australia*

Abstract A novel intumescent flame retardant coating, consisting of poly(vinylphosphonic acid) (PVPA) as the acid source and branched polyethylenimine (BPEI) as the blowing agent, was constructed on the surface of ramie fabrics by alternate assembly to remarkably improve the flame retardancy of ramie. The PVPA/BPEI coating on the surface of individual fibers of ramie fabric pyrolyzes to form protective char layer upon heating/burning and improves the flame retardancy of ramie. Thermogravimetric analysis reveals that the PVPA/BPEI-coated ramie fabrics left as much as 25.8 wt% residue at 600 °C, while the control (uncoated) fabric left less than 1.4 wt% residue. Vertical flame test shows that all PVPA/BPEI-coated fabrics have shorter after-flame time, and the residues well preserved the original weave structure and fiber morphology, whereas, the uncoated fabric left only ashes. Microscale combustion calorimetry shows that the PVPA/BPEI coatings greatly reduce the total heat release by as much as 66% and the heat release capacity by 76%, relative to those of the uncoated fabric.

Keyword: Alternative assembly; Poly(vinylphosphonic acid); Flame retardant; Ramie fabric.

INTRODUCTION

Ramie has been one of the major natural cellulosic textile materials since ancient times[1], whose textile products have better hygroscopicity, gas permeability, abrasion resistance and bacteriostasis in comparison with those of cotton. Due to its high degree of polymerization, orientation and crystallinity, ramie fiber has excellent mechanical properties[2]. Apart from the application in textile industry, ramie fibers have also been widely used in pulp and paper industry, building and furniture industry, automotive and chemical industry *etc*. However, a major drawback of cellulosic fibers is the flammability that reduces its use security and limits its application, therefore, proper treatment of the fibers/fabrics by flame retardant is necessary to diminish the potential fire hazards. To date, plenty of methods have been developed to impart a certain level of flame resistance to the cellulosic fibers/fabrics, including ramie. Among them, flame retardant additives have been considered to be an effective way and can be added into the substrates through various means such as back-coating on the surface of fabric[3], sol-gel technique[4], grafting technique[5], crosslinking technique[6] and nanotechnology[7] and so on.

---

* This work was financially supported by the National Basic Research Program of China (Nos. 2010CB631105 and 2011CB612307).

** Corresponding author: Mao Peng (彭懋), E-mail: pengmao@zju.edu.cn

Received May 7, 2013; Revised August 1, 2013; Accepted August 14, 2013
doi: 10.1007/s10118-014-1408-y

And the phosphorus-based flame retardants have been frequently used nowadays and have gradually replaced those halogen-based flame retardants, as the toxins formed from the decomposition of halogen-based flame retardants are bad for the environment and for human beings.

For the phosphorus-based flame retardants, flammability reduction is attributed to the promotion of charring by acidic phosphorus species in the condensed phase while phosphorus is not consumed in the chemical reactions that form char[8]. However, traditional polyphosphates as flame retardant tend to hydrolyze in water or humid conditions. On the other hand, poly(vinylphosphonic acid) (PVPA) is a phosphorus-containing polymer with each repeat unit linking with one phosphonic acid group[9, 10]. Because flame retardant polymers with covalently bonded phosphates or phosphonates have been widely reported in previous literature[11–14] and PVPA contains approximately 33% phosphorus, it is expected that PVPA can also be an effective flame retardant. Since PVPA contains only carbon-carbon bonds in its main chain, it shows great hydrolysis resistance, in contrast to traditional polyphosphates used as the acid source of intumescent flame retardant. At the same time, the dehydration between the neighboring hydroxyl groups in PVPA upon heating results in the release of water[11], which is also beneficial to improve the flame resistance. However, to the best of our knowledge, there is no report on this in the literature.

Meanwhile, layer-by-layer (LbL) assembly technique has brought great convenience to fabricating multifunctional thin films on the surfaces of various substrates since 1991[15]. This technique involves constructing multiple positive/negative pairs by the simple alternate deposition of a positively charged polyelectrolyte (polycation) and a negatively charged polyelectrolyte (polyanion) in a cyclic fashion. The electrostatic attraction between oppositely charged polyelectrolytes or particles results in the irreversible adsorption and the formation of insoluble complexes[16–18]. Besides electrostatic interactions, hydrogen bonding[19, 20], donor/acceptor interactions[21] and covalent bonding[22, 23] can also be used to assemble the multilayers. It is reported that the thickness of bilayers are affected by various factors, such as the molecular weight[24] and charge density[25, 26] of the polyelectrolytes, the concentration[16] and pH[27, 28] of the deposition solutions, deposition time[16] and temperature[29]. Due to the diverse properties of the functional LbL-assembled films, LbL-assembly technique has been used in various fields, such as preparing materials for drug delivery[30], chemical sensors[31, 32] and electrochromic devices[33] *etc*. And it has been demonstrated that LbL assembly technique can be used to construct flame retardant nanofilms on cotton fabric[34, 35]. Recently, Li *et al.*[36] reported intumescent nanocoating capable of extinguishing flame on cotton fabrics by LbL assembly of poly(sodium phosphate) acting as the acid source and poly(allylamine) as the blowing agent.

This study aims to prepare flame retardant ramie fabric that can be used to fabricate polymer composites for aircraft cabinet materials. In this study, we present the first study of the flame retardant behavior of ramie fabrics coated by the alternately assembled coatings of PVPA and branched polyethylenimine (BPEI) from their aqueous solutions. The negatively charged PVPA and positively charged BPEI are water soluble, but when their solutions are mixed, precipitations are observed rapidly. When the alternate deposition of BPEI and PVPA was conducted on pristine ramie fabric, the BPEI/PVPA coatings formed, but different from the uniform LbL assembled PVPA/BPEI coatings on flat silicon wafer, the coatings on ramie fabric are non-uniform and the thickness could not be determined accurately. PVPA in the coating acts as the acid source, the released phosphate groups catalyze the charring of decomposed fabric. BPEI acts as blowing agents, the released low molecular weight compound such as NH_3 that make this carbonaceous residue become porous[37]. The surface morphology and element content of coated fabrics were characterized by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). The flame retardant properties of fabrics were studied by thermogravimetric analysis (TGA), vertical flame test and microscale combustion calorimetry (MCC).

EXPERIMENTAL

Materials

Vinylphosphonic acid (VPA; TCI, 95% purity) was used for the synthesis of PVPA[9] (1.36×10^5 g·mol^{-1}, see supporting information), to prepare 5 wt% deposition solution using 18.2 MΩ deionized water was used. The original pH was adjusted from 0.9 to 6.0 by adding 1 mol·L^{-1} sodium hydroxide (NaOH; Sinopharm Chemical Ltd, Shanghai, China) solution. Branched polyethylenimine (BPEI; Aldrich, Milwaukee, WI, 25000 g·mol^{-1}) was used to prepare the 5 wt% polycation solution, whose pH was adjusted from 11.5 to 10.0 by adding 1 mol·L^{-1} hydrochloric acid (36.5%–38% HCl; Hangzhou Reagent Co., Ltd, Hangzhou, China) solution. Sodium chloride (NaCl; Sinopharm Chemical Co. Ltd., Shanghai, China) was used to adjust the ionic strength of the deposition solutions to a concentraton of 1 mol·L^{-1} NaCl. All reagents were used as received without further purification. The ramie fabric (Jingzhu Fabric Industry Co., Ltd. Jiangxi, China) used as deposition substrates was an orthogonal plain weave with approximately 50 threads per centimeter in both the warp and fill direction. Before experiment, all ramie fabrics were washed with common detergent in water and then dried for about 2 h at 60 °C.

Alternate Assembly

The BPEI/PVPA coatings were prepared manually. As shown in Fig. 1, the fabrics were sequentially dipped into the BPEI and PVPA solutions for 5 min, followed by immersing in deionized water for 5 min and drying. Each BPEI/PVPA pair is referred to as a bilayer (BL). Two groups of samples were prepared in this study. The first group is referred to as the unpresoaked samples, in which the pristine fabrics were directly coated by the BPEI/PVPA coating; whereas, for the second group referred to as the PVPA-presoaked group, the fabrics were presoaked in a 10 wt% PVPA aqueous solution prior to the alternate deposition for 0.5 h followed by washing and drying. And 5, 10 and 15 BL were built for each group. It was expected that, during the presoaking procedure, the hydrogen bonding between the phosphoric acid groups of PVPA and the hydroxyl groups on the surface of ramie fabric can promote the absorption of PVPA and thus facilitate the subsequent alternate assembly procedure. After the desired BL numbers were achieved, the coated fabrics were dried at 60 °C for 2 h.

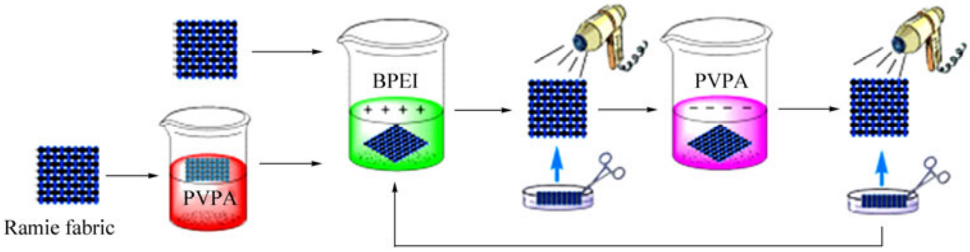

Fig. 1 Schematic representation of layer-by-layer assembly

Characterization

The pH of the deposition solutions were measured with a portable pH meter (pHB-1, Hangzhou Dongxing Equipment Factory, Hangzhou, China). The thermal stability of PVPA, BPEI and ramie fabrics was measured by a SDT Q600 thermal analyzer (TA, USA). The weight of PVPA and BPEI samples were about 3 mg and the weight of ramie samples were about 10 mg. All samples were kept at 100 °C for 5 min first to remove absorbed moisture, and then heated up to 600 °C at a heating rate of 20 K·min^{-1} in air. Vertical flame tests were conducted with a horizontal and vertical flammability cabinet (Model CZF-3, Nanjing Jiangning Analytical Instrument Factory, Nanjing, China) according to ASTM D6413. Microscale combustibility tests were carried out on a Govmak MCC-2 microscale combustion colorimeter (USA). A 4–6 mg of sample was first kept at 100 °C for 5 min to remove the adsorbed moisture and then heated to 650 °C at a heating rate of 1 K·sec^{-1} in a stream of nitrogen at a speed of 80 cm^3·min^{-1}. SEM images of the uncoated and coated fabrics, the residual chars after the vertical flame test, and the element weight content of the surface of coated fabrics were obtained by using a

Hitachi S-4800 field emission scanning electron microscope equipped with an energy dispersive X-ray (EDX) spectrometer.

RESULTS AND DISCUSSION

Characterization of the Assembled Coating

The alternate assembly of BPEI/PVPA on the surface of the ramie fabrics was characterized by SEM observation. As shown in Fig. 2, the surface of the fibers in the control (uncoated) fabric is relatively smooth and the fibers are obviously apart from each other. After the alternate assembly, the fibers appear to be covered by a layer of thin coating. The conformal coating is relatively uniform and all individual ramie fibers are covered by the film. For the 20 BL coatings, the interstices of neighboring fibers are also filled by the PVPA/BPEI film. This is especially obvious for the PVPA-presoaked fabrics. Although the samples in Figs. 2(b) and 2(c) are all coated with a 10 BL PVPA/BPEI coating, it is obvious that for the sample with PVPA-presoaking treatment, the coating is more intact and appears to be thicker, which is more obvious for the PVPA-presoaked one with 20 BL coating.

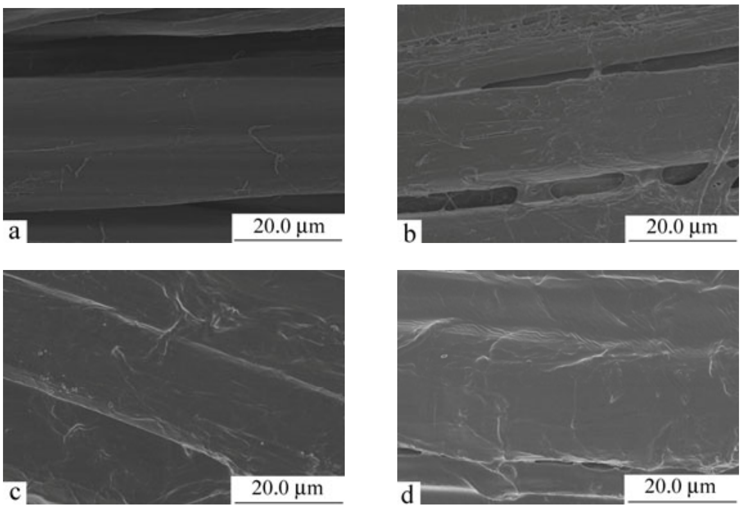

Fig. 2 SEM images of the control (uncoated) fabric (a) and coated fabric with 10 BL coating (un-presoaked) (b), 10 BL coating (PVPA-presoaked) (c) and 20 BL coating (PVPA-presoaked) (d)

The BPEI/PVPA coatings on the surface of ramie fabric are then analyzed by EDX to qualitatively determine the content of phosphorus on the surface of the coated ramie fabrics. The control (uncoated) ramie fabric contains only 0.64 wt% of phosphorus, while the unpresoaked fabrics with 10 BL and 20 BL of BPEI/PVPA coatings contain 3.09 wt% and 5.49 wt% of phosphorus, respectively, suggesting that PVPA is indeed incorporated into the surface coatings of the fabrics. The PVPA-presoaked fabrics with 10 BL and 20 BL of BPEI/PVPA coatings contain 5.47 wt% and 8.76 wt% of phosphorus, respectively, which are much higher than those of pristine and unpresoaked ramie fabrics. Furthermore, the phosphorus content of 20 BL coatings is much higher than that of 10 BL coatings, indicating that the larger the bilayer number, the more PVPA is absorbed. Additionally, at the same bilayer number, the PVPA-presoaked fabrics contain much more phosphorus than the unpresoaked ones, which suggests that the presoaking treatment is able to increase the amount of PVPA in ramie, and the weak cationic charge on the surface of ramie may favor the adsorption of PVPA.

Thermal Stability

In order to understand the influence of BPEI/PVPA coating on the thermal degradation behavior of the coated fabrics, the thermal stability of PVPA and BPEI were first measured by TGA as shown in Fig. 3. The decomposition of PVPA in air begins early at 150 °C and the residue at 600 °C is as much as 41.7 wt%. Water and ethylene are the two major products during the decomposition of PVPA[12]. The decomposition at 150 °C is due to the release of physically bound water. The evolution of ethylene occurs early around 200 °C, which indicating the cleavage of the carbon-phosphorus bond and then the formation of phosphorus acid. As to BPEI, decomposition begins at 270 °C and there is almost no residual weight at 600 °C.

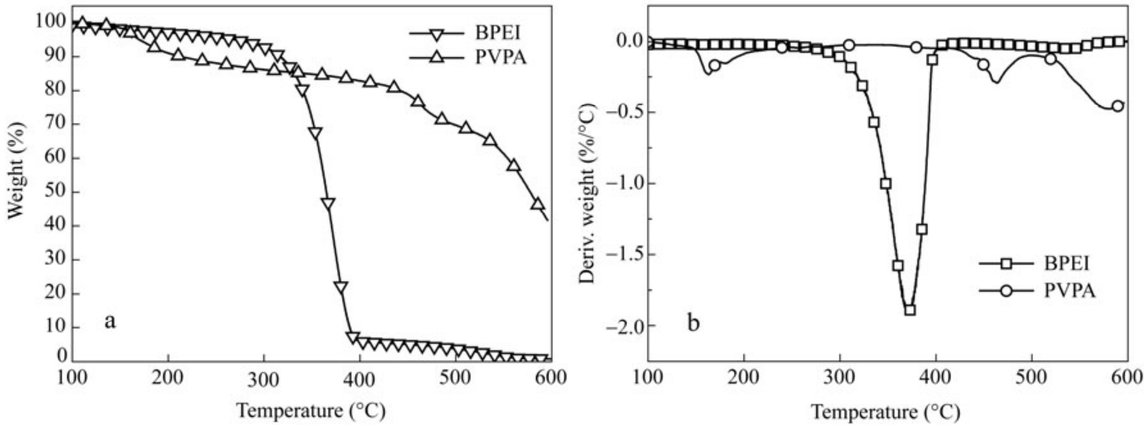

Fig. 3 TGA (a) and DTG (b) curves of PVPA and BPEI in air

As shown by the TGA and DTG curves in Fig. 4, the first decomposition step of the pristine ramie fabric starts from 330 °C to 380 °C with a weight loss of 76.1 wt% in air. At about 550 °C, the pristine ramie fabric almost totally decomposes and the amount of residue is below 1.4 wt%. As to the BPEI/PVPA-coated fabrics, all samples start decomposition at a lower temperature (280 °C to 360 °C), but the weight loss for the first decomposition step is only about 50 wt%. The final residue at 600 °C ranges from 14.5 wt% to 25.8 wt%, which is much higher than that of pristine ramie fabric. Since PVPA and BPEI start decomposing at relatively low temperatures, the decomposed BPEI/PVPA coating forms a protective char layer on the surface of ramie and retards the decomposition of ramie.

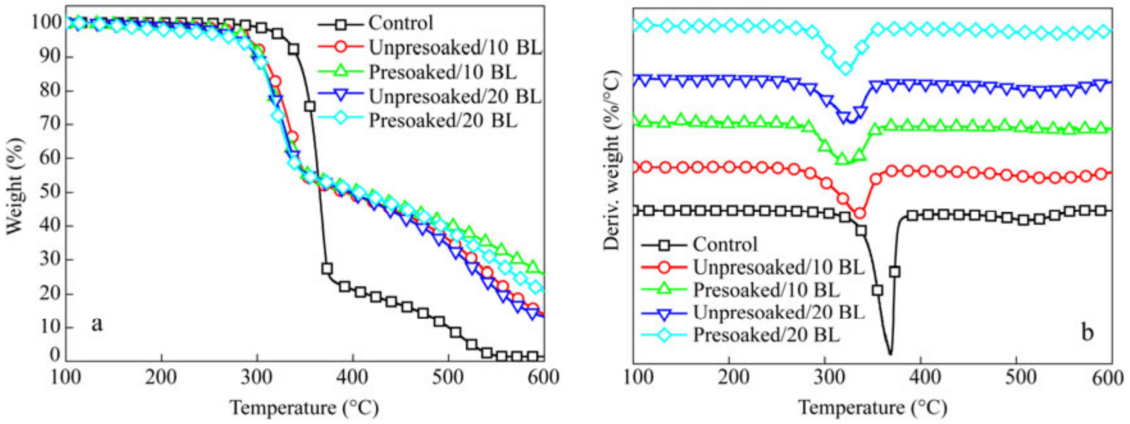

Fig. 4 TGA (a) and DTG (b) curves in air for the control (uncoated) ramie fabric and coated ramie fabrics with 10 BL and 20 BL coatings (on both un-presoaked and PVPA-presoaked fabrics)

The weights of PVPA/BPEI coatings obtained after alternate assembly, the initial degradation temperatures ($T_{-5\%}$), the maximum degradation temperatures ($T_{\max}$) and the amount of residues obtained from TGA testing are summarized in Table 1. It should be noted that the PVPA-presoaking treatment contributes to an additional increase of the weight of the assembled coatings by nearly 10 wt%. The lower initial degradation temperatures of PVPA and BPEI lead to a much lower $T_{-5\%}$ of all coated fabrics than those of the control. All coated fabrics showed a lower $T_{\max}$ but an apparent increase of the residual weights, confirming the typical character of intumescent flame retardant system. It is noted that the residue weights of the coated fabrics are larger than the theoretical summary of the residual weight of the pure PVPA, BPEI and the uncoated fabric at 550 °C. This is because the decomposition of PVPA and BPEI start at temperatures lower than that of ramie, and the decomposed PVPA/BPEI coatings form char protective shield, which not only prevents the decomposition of the underlying ramie but also promotes its char formation. Furthermore, the PVPA-presoaked fabrics show more residues at the same temperature than the unpresoaked ones, further confirming that PVPA facilitates the char formation of ramie fabrics. It is somewhat unexpected that all 10 BL coated fabrics left more residues than the 20 BL coated fabrics, which may be caused by the increased amount of BPEI in the 20 BL coated fabrics.

Table 1. TGA data of BPEI, PVPA and all ramie fabrics

Sample	Add on (wt%)	$T_{-5\%}$ (°C)	$T_{\max}$ (°C)	550 °C residues (wt%)	600 °C residues (wt%)
PVPA	–	171	580	61.10	41.70
BPEI	–	271	372	1.50	0.84
Control	–	330	369	1.68	1.39
Unpresoaked					
10 BL	9.58	292	337	23.95	14.11
20 BL	20.84	283	326	21.43	13.39
PVPA-presoaked					
10 BL	17.12	291	324	33.54	25.83
20 BL	25.74	280	321	29.54	20.86

Flammability

Microscale combustion calorimetry

As an ideal method for studying the flammability of materials at conditions close to the real combustion environment, cone calorimeter requires 25–100 g of samples for accurate measurements. In this study, microscale combustion calorimeter (MCC) was used as a small scale alternate to cone calorimeter to estimate the combustibility of ramie fabrics using only milligram samples[38] and obtained the key fire parameters including temperature at maximum heat release rate (T_p), peak heat release rate (PHRR in $W \cdot g^{-1}$), the total heat release (THR in $kJ \cdot g^{-1}$) as well as the maximum heat release capacity (HRC) obtained by dividing the maximum value of HRR by the heating rate, which is a good predictor of flammability[39].

The MCC curves are shown in Fig. 5, and the HRC, THR, T_p and PHRR values are summarized in Table 2. It is shown that the HRC, HRR and THR values of the coated fabrics decrease remarkably compared with those of the control sample. The maximum reduction for HRC and THR is 76% and 66%, respectively. However, the T_p values become lower than that of the control sample, due to the lower initial decomposition temperature of PVPA and BPEI and also the dehydration of the cellulosic material at lower temperatures under the catalization of PVPA. Figure 5 shows that the HRR curve for the control sample has a single sharp peak, indicating that there is only one step of decomposition. On the contrary, the HRR curves for all the PVPA/BPEI coated ramie fabrics show two peaks, indicating that there are two steps of decomposition. Similar to the TG results, the main HRR peaks of the coated fabrics shift to lower temperatures than that of the uncoated one, because of the pyrolysis of PVPA and BPEI at lower temperatures; whereas, the size of the main HRR peaks is greatly decreased because of the formation of an expanded protective char barrier on the surface of ramie fabrics that protects the underlying ramie from burning and reduce its heat release. With the increase of temperature, further appearance of a small HRR peak at above 500 °C occurs, because of the decomposition of the char precursor to a thermally stable structure.

The PVPA-presoaked samples show smaller HRC and HRR and higher T_p values than the unpresoaked ones, suggesting that the PVPA-presoaking treatment improves the flame retardancy of ramie, in good agreement with the aforementioned TGA results. On the other hand, the fabrics with 20 BL have relatively lower HRC, THR and the peak HRR values, because with the increase of the BL number, thicker protective char can be formed to prevent burning and reduce the heat release. These results suggest that PVPA imparts excellent flame retardancy to ramie fabric.

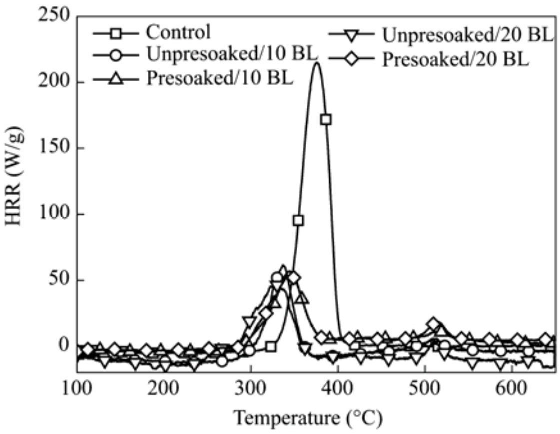

Fig. 5 HRR curves of the control (uncoated) ramie fabric and coated ramie fabrics with 10 BL and 20 BL coatings (on both un-presoaked and PVPA-presoaked fabrics)

Table 2. Flammability data of BPEI, PVPA and all ramie fabrics

Sample	HRC (J/(g·K))	THR (kJ/g)	T_p (°C)	PHRR (W/g)	
Control	216	8.5	375.6	217	–
Unpresoaked					
10 BL	72	3.1	336.5	71	6
20 BL	56	2.9	332.0	56	2
PVPA-presoaked					
10 BL	60	4.3	342.7	59	11
20 BL	52	3.0	344.1	54	18

Vertical flame test

Vertical flame test (ASTM D6413) was further conducted to understand the combustion behavior of the PVPA/BPEI-coated fabrics. The ignition time of the coated fabrics did not increase obviously, but the flame is much less vigorous than that of the uncoated fabrics, as shown by the images of the samples at 5 s after ignition in Fig. 6. The glows were also observed to be much less for the coated fabrics after the burner flame was removed. Furthermore, all the coated fabrics exhibited a reduced after-flame time, *i.e.* the time for the specimens continuing flame after the burner flame being shut off, compared with the uncoated one. Furthermore, presoaking of ramie with PVPA greatly improves the flame retardancy. The PVPA-presoaked and 10 BL coated fabric showed the shortest after-flame time which was 4 s less than the uncoated fabric. The uncoated fabric was burned out rapidly, leaving small amount of ashes, while the coated fabrics had much more residual left and were preserved as complete and continuous carbonized fabrics after burning (Fig. 6).

As aforementioned, there is a layer of thin film of PVPA/BPEI complex covering the surfaces of the ramie fibers, and the original morphology of the fabric is basically not changed (Fig. 2). Figure 7 presents the SEM images of the samples after the vertical flame test to examine the surface morphology and fabric structure. For the uncoated fabric, the residual ashes on the specimen holding clamp were collected for SEM observation, while for the PVPA/BPEI-coated fabrics, the samples were taken from the center of the residual char. As shown in Figs. 7(a1) and 7(a2), the uncoated fabric is damaged seriously after burning, and the yarns become highly porous and are broken into thin strips. In contrast, the fabric structure is retained for the PVPA/BPEI-coated fabrics (Figs. 7(b1) and 7(c1)), whose surface was obviously covered by a layer of intumescent char after burning, and there are large amount of bubbles on the char layer. Especially for the PVPA-presoaked fabric, the ramie fibers are almost totally covered with a layer of thick and compact char on the surface (Fig. 7(c2)). This char layer prevents the release of volatile gases from the inner surface and promotes the char formation of the ramie fabrics, therefore, the fabric structure remains after burning. These results provide the evidences for the intumescent behavior of the PVPA/BPEI-coatings.

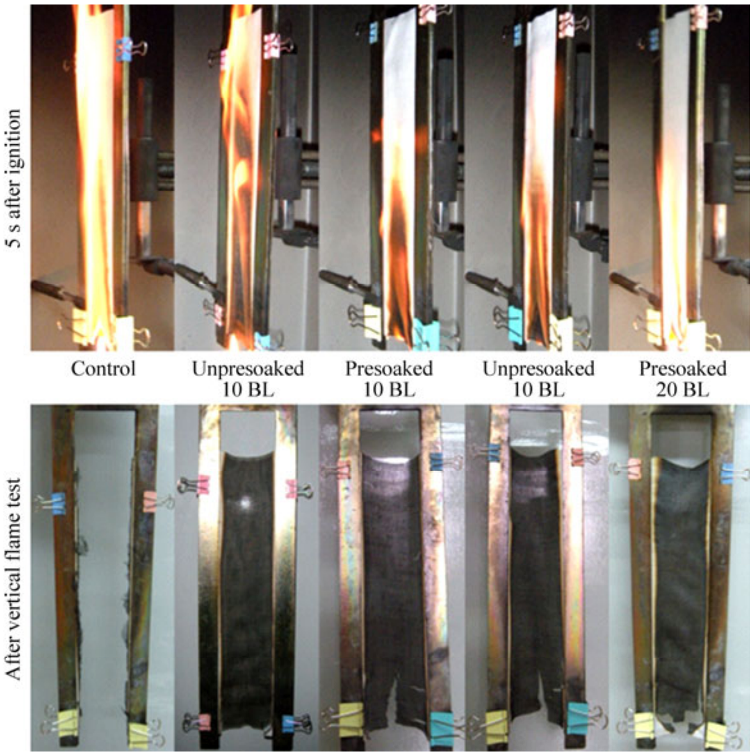

Fig. 6 Images of the control (uncoated) and coated ramie fabrics at 5 s after ignition and their corresponding images after the vertical flame test

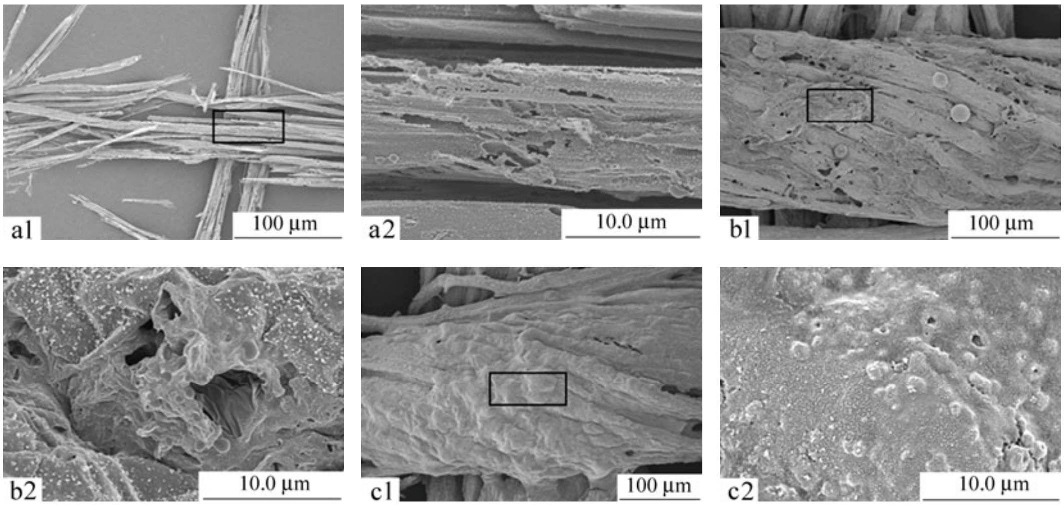

Fig. 7 SEM images of fabrics after vertical flame test: uncoated fabric (a1) and (a2), 10 BL coated fabric (b1) and (b2), PVPA-presoaked and 10 BL coated fabric (c1) and (c2)

Figure 8 shows the low magnification SEM images of the uncoated ramie fabric before burning and of all samples after burning. Although the residual ashes of the uncoated fabric on the specimen holding clamp retain the weave structure to some extent, the size of the yarns are greatly reduced and the gaps between the yarns are much larger than those before burning. The weave structure of the coated fabrics is much better retained than that of uncoated fabric, although the sample was taken in the center of the char, and the gaps between yarns are only slightly increased. This is especially obvious for the PVPA-presoaked ones, Figs. 8(e) and 8(f). At the same BL number, the PVPA-presoaked fabrics have smaller gaps between the yarns than the unpresoaked fabrics; moreover, the gaps for the 10 BL coated (PVPA-presoaked) fabric are even smaller than those for the 20 BL coated (unpresoaked) fabric. As aforementioned, the TGA result shows that the amount of the residual char of the PVPA-presoaked ramie fabric is higher than that of unpresoaked fabric. This is because that the pre-soaking treatment helps increase the amount of PVPA on the fabric surface, which improves the char forming capability of ramie, so as to better protect the coated fabric presoaked by the PVPA solution.

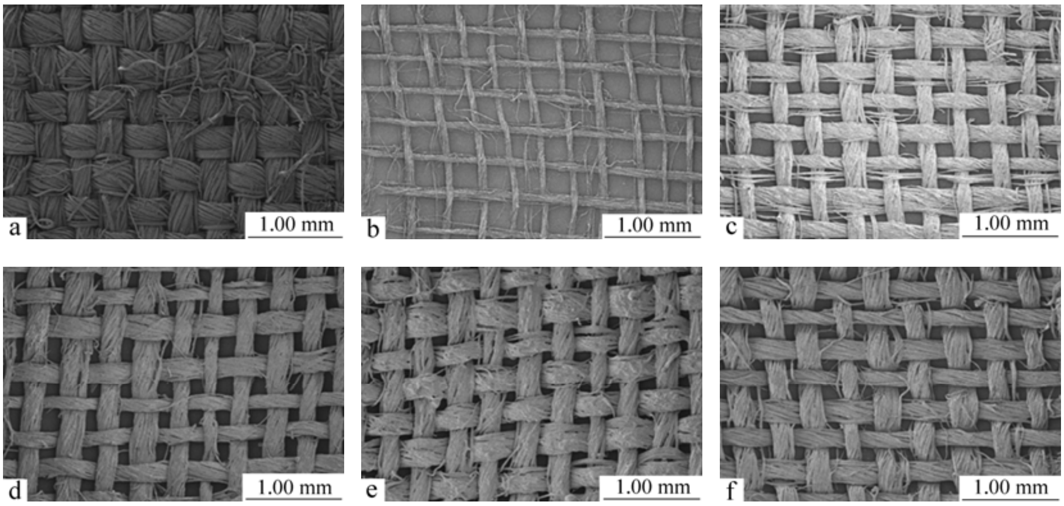

Fig. 8 SEM images of fabrics before and after vertical flame test: uncoated fabric before burning (a), residues of uncoated fabric (b), 10 BL coated fabric (c), 20 BL coated fabric (d), PVPA-presoaked and 10 BL coated fabric (e) and PVPA-presoaked and 20 BL coated fabric (f) after vertical flame test

CONCLUSIONS

Alternately-assembled coatings consisting of PVPA as the polyanion and BPEI as the polycation were successfully prepared on the surface of ramie fabrics, which greatly improved the flame retardancy of the fabric. The weight percentage of phosphorus on the surface of the fabric was proportional to the number of assembled BLs. Presoaking treatment by PVPA further increased the phosphorus content. A significant residue as much as 25.8 wt% was left over from coated fabric at the end of TGA tests, while it was less than 1.4 wt% for the uncoated fabric. Moreover, the residues of all the coated fabrics were more than the theoretical summary of the residual weight of pure PVPA, BPEI and ramie. All coated fabrics left abundant char after the vertical flame test and retained the original weave structures and the after-flame time of all coated fabrics was decreased. In the MCC experiment, the coatings greatly improved the flame resistance of ramie fabrics by reducing THR, HRC and PHRR. Thus, the PVPA/BPEI coating is a new and effective flame retardant system for ramie fabrics. We believe that, in addition to ramie fabrics, PVPA can also be used as the acid source for the intumescent flame retardant for other materials.

ACKNOWLEDGEMENT The authors thank Prof. Y. Hu of the University of Science and Technology of China for his kind help in the MCC measurement.

REFERENCES

1 Liu, F.H., Li, Z.J., Liu, Q.Y., He, H., Liang, X.N. and Lai, Z.J., Genet. Resour. Crop Evol., 2003, 5: 793
2 Bledzki, A.K. and Gassan, J., Prog. Polym. Sci., 1999, 24: 221
3 Horrocks, A.R., Davies, P.J., Kandola, B.K. and Alderson, A., J. Fire Sci., 2007, 25: 523
4 Hu, S., Hu, Y., Song, L. and Lu, H.D., J. Therm. Anal. Calorim., 2012, 109: 27
5 Yuan, H.X., Xing, W.Y., Zhang, P., Song, L. and Hu, Y., Ind. Eng. Chem. Res., 2012, 51: 5394
6 Siriviriyanun, A., O'Rear, E.A. and Yanumet, N., Cellulose, 2008, 15: 731
7 Monticelli, O., Musina, Z., Frache, A., Bellucci, F., Camino, G. and Russo, S., Polym. Degrad. Stab., 2007, 92: 370
8 Bourbigot, S. and Duquesne, S., J. Mater. Chem., 2007, 17: 2283
9 Bingöl, B., Meyer, W.H., Wagner, M. and Wegner, G., Macromol. Rapid Commun., 2006, 27: 1719
10 Wagner, T., Manhart, A., Deniz, N., Kaltbeitzel, A., Wagner, M., Brunklaus, G. and Meyer, W.H., Macromol. Chem. Phys., 2009, 210: 1903
11 Price, D., Cunliffe, L.K., Bullett, K.J., Hull, T.R., Milnes, G.J., Ebdon, J.R., Hunt, B.J. and Joseph, P. Polym. Degrad. Stab., 2007, 92: 1101
12 Jiang, D.D., Yao, Q., McKinney, M.A. and Wilkie, C.A., Polym. Degrad. Stab., 1999, 63: 423
13 Price, D., Pyrah, K., Hull, T.R., Milnes, G.J., Ebdon, J.R., Hunt, B.J. and Joseph, P., Polym. Degrad. Stab., 2002, 77: 227
14 Price, D., Pyrah, K., Hull, T.R., Milnes, G.J., Ebdon, J.R., Hunt, B.J., Joseph, P., and Konkel, C.S., Polym. Degrad. Stab., 2001, 74: 441
15 Decher, G. and Hong, J.D., Macromol. Symp., 1991, 46: 321
16 Dubas, S.T. and Schlenoff, J.B., Macromolecules, 1999, 32: 8153
17 Kříž, J. and Dautzenberg, H., J. Phys. Chem. A, 2001, 105: 3846
18 Peng, M., Li, D.S., Chen, Y. and Zheng, Q., Macromol. Rapid Commun., 2006, 27: 859
19 Stockton, W.B. and Rubner, M.F., Macromolecules, 1997, 30: 2717
20 Bergbreiter, D.E., Tao, G.L., Franchina, J.G. and Sussman, L., Macromolecules, 2001, 34: 3018
21 Biel, O.C., Dordi, B., Reinhoudt, D.N. and Huskens, J., J. Am. Chem. Soc., 2005, 127: 7594
22 Kohli, P. and Blanchard, G.J., Langmuir, 2000, 16: 8518
23 Major, J.S. and Blanchard, G.J., Langmuir, 2001, 17: 1163
24 Lulevich, V.V., Nordschild, S. and Vinogradova, O.I., Macromolecules, 2004, 37: 7736
25 Steitz, R., Jaeger, W. and Klitzing, R., Langmuir, 2001, 17: 4471
26 Sun, Q.L., Tong, Z., Wang, C.Y., Ren, R.Y., Liu, X.X. and Zeng, F., Polymer, 2005, 46: 4958
27 Kim, B.Y. and Bruening, M.L., Langmuir, 2003, 19: 94
28 Mendelsohn, J.D., Barrett, C.J., Chan, V.V., Pal, A.J., Mayes, A.M. and Rubner, M.F., Langmuir, 2000, 16: 5017
29 Kölhler, K., Shchukin, D.G., Sukhorukov, G.B. and Möhwald, H., Macromolecules, 2004, 37: 9546
30 Qiu, X.P., Leporatti, S., Donath, E. and Möhwald, H., Langmuir, 2001, 17: 5375
31 Yang, X., Johnson, S., Shi, J., Holesinger, T. and Swanson, B., Sens. Actuators, B, 1997, 45: 87
32 Ram, M.K., Carrara, S., Paddeu, S. and Nicolini, C., Thin Solid Films, 1997, 302: 89
33 DeLongchamp, D. and Hammond, P.T., Adv. Mater., 2001, 13: 1455
34 Li, Y.C., Schulz, J. and Grunlan, J.C., ACS Appl. Mater. Interfaces, 2009, 1: 2338
35 Li, Y.C., Schulz, J., Mannen, S., Delhom, C., Condon, B., Chang, S., Zammarano, M. and Grunlan, J.C., Acs Nano, 2010, 4: 3325
36 Li, Y.C., Schulz, J., Morgan, A.B., Chang, S., Yang, Y.H., Condon, B. and Grunlan, J.C., Adv. Mater., 2011, 23: 3926
37 Nedel'ko, V.V., Korsunskii, B.L., Dubovitskii, F.I. and Gromova, G.L., Polym. Sci. U.S.S.R., 1975, 17:1697
38 Morgan, A.B. and Galaska, M., Polym. Adv. Technol., 2008, 19: 530
39 Lyon, R.E. and Walters, R.N., J. Anal. Appl. Pyrolysis, 2004, 71: 27