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Highly flame retardant coating consisting of starch and amorphous sodium polyborate

Isao Tsuyumoto · Yuichiro Miura · Masato Nirei · Shota Ikurumi · Takenori Kumagai

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Abstract Mixture of starch and amorphous sodium polyborate (SPB) is found to show high flame retardancy, when its aqueous solution is deposited and dried on organic polymer materials such as polyethylene terephthalate (PET) nonwoven, rigid polyurethane (RPU) foam, and polypropylene (PP) nonwoven. The PET nonwoven (10 mm thickness) and the RPU foam (10 mm thickness) coated with the mixture endure the premixed flame of butane gas burner with length of 100 mm for more than 12 min. The PP nonwoven (0.7 mm thickness) endures the nonpremixed flame with length of 65 mm in the 45 degrees Meckel burner test for more than 2 min. The backside temperatures in the both tests remain below 130 °C. The thermal analyses and the SEM observation indicate the mechanism that the SPB foam promotes the carbonization of starch and that the carbonized layer together with the SPB foam insulate inside from oxygen and heat.

Introduction

Flame-retardant treatment of organic polymer materials is essential from the viewpoint of disaster prevention, because their heat release occurs rapidly after ignition. A wide variety of flame retardants have been developed and widely used in the organic polymer materials for buildings, household appliances, and automobiles. There are, however, environmental concerns in the use of halogen or phosphorus based flame retardants, because the flame retardants themselves are toxic in most cases and toxic products may be released in fire, disposal, and normal use [1]. Therefore, halogen-free and phosphorus-free flame retardants with low environmental pollution risk are particularly needed. New flame retardants such as expandable graphites [2, 3], silicones [4] have been developed and applied to organic polymer materials. Intumescent polymers and their flame retardance have been also intensively investigated [5].

Sodium borate has high flame retardant effect on cellulose-based materials such as wood, paper, and cotton [6]. Its solubility to water has been found to rise up to 5.24 mol/kg (as to boron) at 20 °C by adjusting Na/B ratio to 0.22, while that of the conventional borax (sodium tetraborate octahydrate, $Na_2B_4O_5(OH)_4\ 8H_2O$) is one order of magnitude lower at room temperature [7–9]. The dry residue of the solution is amorphous sodium polyborate (SPB), and its film-forming property as well as the high concentration contributes the flame retardant effect to base materials. We have found that SPB has high flame retardant effect also on EVOH (ethylene–vinyl alcohol copolymer) and polyurethane, and we have successfully prepared a flame retardant polyethylene terephthalate (PET) nonwoven with EVOH adhesive and a flame retardant rigid polyurethane (RPU) foam by impregnation of the SPB solution [10, 11].

In flame retardant treatment, coating process would be advantageous over the impregnation process in that the equipment is simple and post-treatment is possible on ready-made building materials and commodities. The pure SPB solution is not suitable for the coating process, because the SPB powder precipitates nonuniformly on the base material and its adhesiveness to the base material is low. A binder or primer is essential to provide flame retardance by coating with the SPB. As mentioned above, sodium borate has high flame retardant effect on cellulose-based materials, and we considered that starch is appropriate for the binder

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I. Tsuyumoto (✉) · Y. Miura · M. Nirei · S. Ikurumi · T. Kumagai
Department of Applied Chemistry, College of Bioscience and Chemistry, Kanazawa Institute of Technology, Ishikawa, Japan
e-mail: tsuyu@neptune.kanazawa-it.ac.jp

of the SPB. The SPB is supposed to have high flame retardant effect on starch, because the carbonized layer formation due to the dehydration of cellulose contributes the flame retardancy and this should apply to the other general carbohydrates such as starch. The synergy effect of flame retardancy due to the carbonized layer formation is expected together with the binding effect of starch.

In the present study, we found a significant flame retardant effect of the mixture of starch and the SPB, and successfully developed highly flame retardant RPU foam, PET/EVOH nonwoven, and polypropylene (PP) nonwoven by simply coating with the mixture. We present their flame retardant performance and discuss the mechanism of the synergy effect.

Experimental

Base materials

Three types of base materials were tested: PET/EVOH nonwoven, RPU foam, and PP nonwoven. The PET/EVOH nonwovens consisted of core/clad fibers of PET/EVOH. The core of the fiber was made of PET with diameter of 10 μm, and it was concentrically surrounded by the clad of EVOH. The fibers were fusion bonded at a cross point of EVOH, and the total diameter of the fibers was 20 μm. The thickness of the specimen was 10 mm, and the density was 0.15 g/cm^3. The RPU foams were made from polymeric methylene diphenyl diisocyanate (PMDI) and polyether polyol. The thickness was 10 mm, and the density was 0.056 g/cm^3. The PP nonwoven (0.7 mm thickness, 83.5 g/m^2) was made of the PP fiber by the melt blown method. All the samples were 20 cm × 20 cm in size.

Flame retardant

The SPB solution 22.9 wt%, containing 5.4 mol/kg of boron, was prepared by dissolving 20 g of boric acid (H_3BO_3) and 25 g of sodium tetraborate decahydrate (borax, $Na_2B_4O_5(OH)_4 \cdot 8H_2O$) into 100 g of water, according to our previous reports [7]. The Na/B molar ratio and the density of the solution were 0.22 and 1.14 g/cm^3 at 20 °C, respectively. The dissolution was carried out above 60 °C to accelerate the preparation, and the solution was used after cooling down to room temperature. More concentrated solutions than 22.9 wt% can be prepared at elevated temperatures by dissolving more boric acid and borax, e.g., 34.9 wt% at 40 °C, 42.4 wt% at 50 °C, and 57.7 wt% at 80 °C.

A given amount of starch powder (potato starch for food) was mixed with the SPB solution around over 90 °C to dissolve and to increase viscosity. The mixed solution was deposited on the base materials and dried at 115 °C to evaluate the flame retardant performance. The mixture placed on the base material was manually spread using a spatula to form a homogeneous layer. The adhesive amount of the mixture was mostly determined by its viscosity because the mixture was spread as widely as possible. Transparent smooth films were formed on the base materials, and the appearance was the same as that of starch glue. The adhesive amount of the flame retardant was evaluated by weight percent gain (WPG) weighed after the drying. As for the mixture composition, the concentration of starch was changed in the range 1–5 wt% by fixing the concentration of SPB at 22.9 wt%, because the saturated concentration of SPB at room temperature is 22.9 wt%. More dilute solutions were also used to investigate the effect of WPG.

Measurement

Flame retardant effect was evaluated by two types of burner combustion tests: a perpendicular burner test and the 45 degrees Meckel burner method. In the perpendicular burner test, the samples were placed perpendicularly and heated by a premixed butane gas burner whose flame was directed horizontally. The distance between the sample and the top of the burner, the whole length of the flame, and the length of the reducing flame were adjusted to 120, 100, and 30 mm, respectively. In the 45 degrees Meckel burner method, the samples were arranged at 45° angles to the horizontal plane and heated by the Meckel burner whose nonpremixed flame was 65 mm in length and directed perpendicularly. In both tests, the holing time of the sample and the temperature change at its backside were monitored. The PET nonwoven and the RPU foam were tested by the perpendicular burner test, whereas the PP nonwoven was tested by the 45 degrees Meckel burner method. The heating capability of the premixed flame with length of 100 mm in the perpendicular burner test was greater than that of the nonpremixed flame with length of 65 mm in the 45 degrees Meckel burner method, and thus the former test was appropriate for flame retardant materials with large thickness.

The thermal properties in air were investigated by the differential thermal analysis and thermogravimetry (DTA-TG, Shimadzu DTG-60) at a heating rate of 20 °C/min. The surface morphology was investigated by using the scanning electron microscopes (SEM, JEOL JSM-5610).

Results and discussion

The concentrations of starch and SPB in the deposited mixture, starch to SPB weight ratio, the WPG, holing time and backside temperature for the PET/EVOH nonwoven in the burner combustion test are shown in Table 1. Compared among the mixture compositions with 22.9 wt% of SPB, the flame retardant effect was significantly increased by mixing starch with SPB. The surfaces of the specimens were only carbonized, and did neither ignite nor burn. This is the first observation of a significant synergy effect from the combined use of starch and SPB. In particular, the PET/EVOH nonwoven treated with the mixed solution with 3.0 wt% of starch and 22.9 wt% of SPB endured the premixed flame of butane gas burner with length of 100 mm for more than 12 min. The mixture composition with 3.0 wt% of starch and 22.9 wt% of SPB was found to show higher flame retardant effect than those with 1.0 or 5.0 wt% of starch. The flame retardancy was closely dependent on the WPG, and thus changing the WPG is the most effective measure to control the flame retardant performance. The level of flame retardancy is controllable by adjusting the concentration, the viscosity and the WPG.

The flame retardant performance of the RPU foam coated with SPB and starch mixture are shown in Table 2. The flame retardant effect coated with SPB alone was small, and such specimens showed holes within 48 s. In contrast, the specimens coated with the mixture of starch and SPB endured the 100 mm flame of premixed gas burner for more than 12 min. The surface of the specimens was only carbonized, and did neither ignite nor burn, similarly to the treated PET/EVOH nonwoven. The flame retardant effect by coating with the mixture of SPB and starch stood comparison with that by the vacuum or pressure impregnation of SPB solution, which we have reported previously on the RPU foam [10]. The coating process was advantageous over the impregnation process in that the equipment was simple and the treatment and drying processes were speedy. The backside temperatures were generally lower than those of the treated PET/EVOH nonwoven, because the thermal conductivity of the RPU foam, 0.022 W m^{-1} K^{-1}, is lower than that of the PET/EVOH nonwoven, 0.041 W m^{-1} K^{-1}.

The holing time and backside temperatures of PP nonwovens in the 45 degrees Meckel burner test is shown in Table 3, and their appearance after the test are shown in Fig. 1. The untreated PP nonwoven was easily ignited and the whole area was consumed. The PP nonwoven coated with SPB alone was ignited in 10 s, and some part of the sample, 128 cm^2 in 400 cm^2, was slowly consumed by combustion in 67 s. The PP nonwoven coated with the mixture of starch and SPB endured the flame of Meckel burner for more than 2 min. The surface was only carbonized and did not show ignition nor melting. It was first found that the SPB and starch mixture was also highly effective for PP. This may suggest that the flame retardant effect of the mixture is irrelevant to the kind of base materials, and thus there are potential applications to all kinds of combustible materials.

Table 1 Holing time and backside temperature of the PET/EVOH nonwoven coated with the SPB and starch mixture in the burner combustion test

	Starch (wt%)	SPB (wt%)	Starch/SPB ratio	WPG (%)	Holing time (s)	Backside temperature (°C)					
						30 s	1 min	3 min	6 min	9 min	12 min
Premixed burner with 100 mm flame	0	0	0	0	10	–	–	–	–	–	–
	0	22.9	0	18.0	30	42.6	–	–	–	–	–
	0	22.9	0	37.5	50	24.1	41.2	–	–	–	–
	0	22.9	0	79.2	90	24.1	27.7	–	–	–	–
	1.0	22.9	0.044	42.5	700	23.5	28.6	98.8	133.9	153.0	–
	3.0	22.9	0.134	48.4	No hole	23.8	30.4	52.5	95.0	115.1	129.6
	5.0	22.9	0.226	52.3	110	24.0	27.7	–	–	–	–
	0.4	21.1	0.019	34.3	410	23.9	26.0	46.3	95.5	–	–
	0.8	19.5	0.041	33.2	170	25.0	31.1	–	–	–	–
	1.1	17.7	0.062	18.8	150	24.9	30.7	–	–	–	–
	1.1	17.7	0.062	21.8	210	25.0	27.5	63.4	–	–	–
	2.3	12.2	0.189	22.2	150	24.9	41.3		–	–	–
	3.2	8.3	0.386	8.6	20	–	–	–	–	–	–
	4.5	2.3	1.96	9.9	20	–	–	–	–	–	–
Meckel burner with 65 mm flame	1.1	17.7	0.062	4.0	No hole	29.2	37.9	100.2	127.2	131.5	131.9
	2.1	12.2	0.172	10.6	No hole	25.5	33.3	53.6	68.3	111.0	111.0

The concentrations of starch and SPB in the mixed solution are shown. The samples were coated manually using a spatula and thus the WPG was dependent on the viscosity of the mixed solution

Table 2 Holing time and backside temperature of the rigid polyurethane foam coated with the SPB and starch mixture in the burner combustion test

		Starch (wt%)	SPB (wt%)	Starch/ SPB ratio	WPG (%)	Holing time (s)	Backside temperature (°C)					
							30 s	1 min	3 min	6 min	9 min	12 min
Premixed burner with 100 mm flame	Potato starch	0	0	0	0	13	–	–	–	–	–	–
		0	22.9	0	8.9	21	–	–	–	–	–	–
		0	34.9	0	23.8	48	22.8	–	–	–	–	–
		3.0	22.9	0.131	51.1	No hole	24.8	27.8	61.5	75.2	88.2	89.0
		3.0	34.9	0.086	105.5	No hole	21.3	22.1	43.4	65.6	80.1	93.3
		3.0	47.4	0.063	184.1	No hole	23.5	25.3	38.9	46.0	51.6	60.3

The concentrations of starch and SPB in the mixed solution are shown. The samples were coated manually using a spatula and thus the WPG was dependent on the viscosity of the mixed solution

The DTA/TG curves of the starch powder alone and of the dry residue of the mixed solution containing 1.0% starch and 22.9% SPB are shown in Fig. 2. The pure starch showed thermal decomposition and the combustion of the decomposition product in the range 300–400 °C. The endothermic and exothermic peaks in the DTA curve are due to the decomposition and the combustion, respectively, and they are superimposed in the temperature range 300–400 °C. The broad exothermic peak around 540 °C is due to the combustion of carbonized residue. In contrast, the dry residue of the mixed solution showed an endothermic peak around 250 °C and exothermic peaks at 596 and 662 °C. The endothermic peak is due to the dehydration of starch involving carbonized layer formation, which is enhanced by SPB, and the exothermic peaks are due to the combustion of the carbonized layer. The endothermic peak at 815 °C is the melting point of SPB. SPB suppresses the combustion involving thermal decomposition and promotes the carbonization. Such behavior is closely related to the flame retardant mechanism of the SPB and starch mixture.

Figure 3 shows the DTA/TG curves of the untreated PET/EVOH nonwoven and that coated with the mixture of starch and SPB. The untreated PET/EVOH nonwoven showed an endothermic peak in the range 330–400 °C due to thermal decomposition, and two broad exothermic peaks in the range 400–600 °C due to the combustion of the thermal decomposition product. As for the PET/EVOH nonwoven coated with the mixture of starch and SPB, the exothermic peaks in the range 400–600 °C were suppressed and a small exothermic peak appeared around 615 °C. This indicates that the thermal decomposition and its combustion were suppressed and carbonization proceeded instead. The exothermic peak around 615 °C is due to the combustion of carbonized layer. Figure 4 shows the DTA/TG curves of the untreated RPU foam and that coated with the mixture of starch and SPB. The untreated RPU foam showed four broad exothermic peaks in the range 200–600 °C due to the combustion of thermal decomposition product. As for the RPU foam coated with the mixture of starch and SPB, such exothermic peaks in the range 200–600 °C were suppressed, and broad exothermic peaks in the range 650–800 °C appeared instead. It is considered that carbonization was enhanced in the range 200–600 °C due to the suppression of the thermal decomposition, and the combustion of carbonized layer gradually occurred in the range 650–800 °C. Figure 5 shows the DTA/TG curves of the untreated PP nonwoven and that coated with the mixture of starch and SPB. The untreated PP nonwoven showed monotonous weight decrease and heat emission in the range 220–400 °C due to thermal decomposition and the combustion of the decomposition product. By the treatment with the mixture, heat emission in the range 220–400 °C was suppressed, and exothermic peaks appeared at 600 and 670 °C. Similarly to the case with the treated RPU foam, the carbonization was

Table 3 Holing time and backside temperature of the PP nonwoven coated with the SPB and starch mixture in the burner combustion test

		Starch (wt%)	SPB (wt%)	Starch/ SPB ratio	WPG (%)	Holing time (s)	Backside temperature (°C)					
							10 s	20 s	30 s	60 s	90 s	120 s
Meckel burner with 65 mm flame	Potato starch	0	0	0	0	10	184.7	–	–	–	–	–
		0	42.4	0	287	10	119.2	–	–	–	–	–
		3.0	42.4	0.07	311	>120	49.0	55.6	58.1	62.6	77.9	84.9

The concentrations of starch and SPB in the mixed solution are shown. The samples were coated manually using a spatula and thus the WPG was dependent on the viscosity of the mixed solution

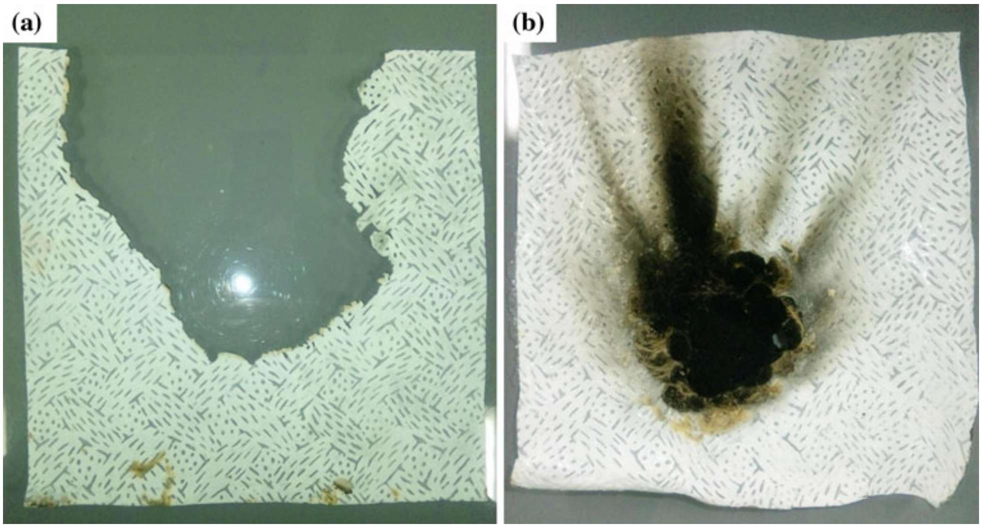

Fig. 1 The appearance of the PP nonwovens coated with the SPB only (**a**) and coated with the mixture of the SPB and starch (**b**), after the 45 degrees Meckel burner test

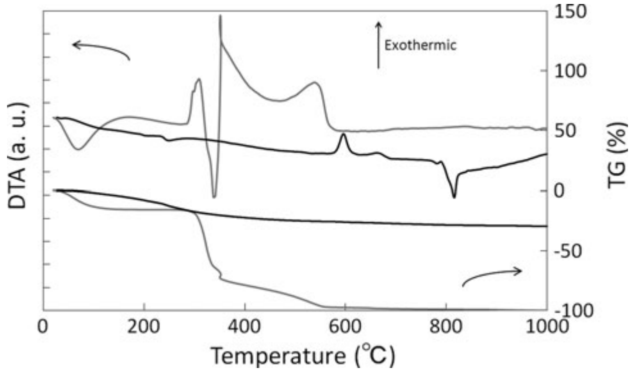

Fig. 2 The DTA/TG curves of the starch powder alone (*gray line*) and of the dry residue of the mixed solution containing 1.0% starch and 22.9% SPB (*black line*)

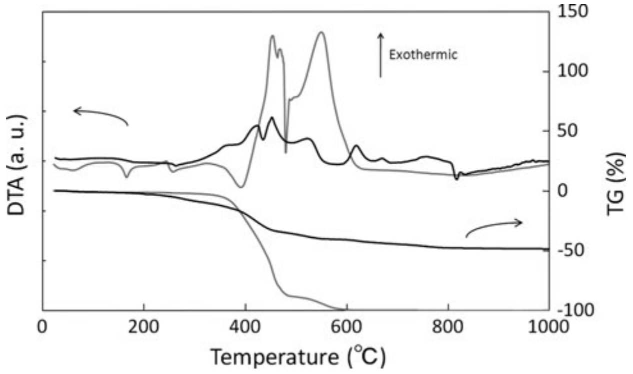

Fig. 3 The DTA/TG curves of the untreated PET/EVOH nonwoven (*gray line*) and that coated with the mixture of starch and SPB (*black line*)

enhanced in the range 220–400 °C and the combustion of the carbonized layer occurred at 600 and 670 °C.

Figure 6 shows the cross-sectional SEM image of the RPU foam coated with the mixed solution containing 22.9 wt% of SPB and 3.0 wt% of starch (WPG 56.7%) after enduring the 12 min-heating by the premixed flame with length of 100 mm. The upper half shows the SPB foam formed by heating and the lower half shows the carbonized cells of the RPU foam. Because the SPB has the film-forming property, the SPB transformed to the SPB foam by incorporating the water vapor emitted by the thermal decomposition of starch. The surface cellular film of the SPB foam insulated both starch and base materials from oxygen, and the carbonization of both starch and base materials was enhanced. The RPU foam transformed to that with the carbonized cells as observed in the lower half of Fig. 6. The carbonized layer originated from starch is considered to exist between the SPB foam and the carbonized RPU foam. Both the SPB foam and the carbonized materials insulate inside from oxygen and heat, and contribute the flame retardant effect. Figure 7a and b shows the cross-sectional SEM images of the PP nonwoven

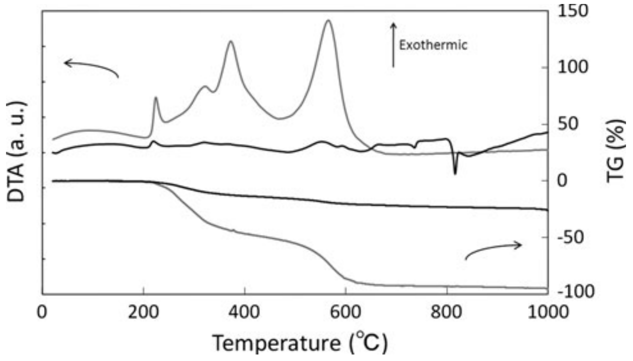

Fig. 4 The DTA/TG curves of the untreated RPU foam (*gray line*) and that coated with the mixture of starch and SPB (*black line*)

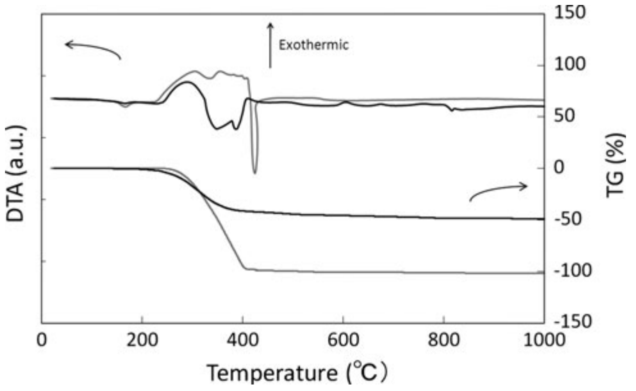

Fig. 5 The DTA/TG curves of the untreated PP nonwoven (*gray line*) and that coated with the mixture of starch and SPB (*black line*)

coated with the mixed solution containing 42.4 wt% of SPB and 3.0 wt% of starch (WPG 311%) after enduring 2 min-heating by the Meckel burner. The images were taken from the backside of the sample. The layer appearing on the extreme left in Fig. 7a is the SPB foam, and the accumulated layers appearing on its right are carbonized PP nonwoven. The carbonization of the PP nonwoven was enhanced by the SPB foam. In Fig. 7b, microspheres of SPB are observed on the left hand and a dense carbonized layer originated from starch is observed on the right hand. Similarly to the case with the RPU foam, the SPB foam layer and the carbonized layers originated from both starch and PP nonwoven are generated and accumulated on the surface, and both contribute the flame retardant effect by insulating inside from oxygen and heat.

In the present study, we first found a significant synergy effect of the combined use of starch and SPB. The combined use of SPB and starch was inspired by the experimental fact that SPB has great flame retardant effect on cellulose [6]. The mechanism of the synergy effect of the combined use is deduced from our present experimental results and the flame retardant mechanism of SPB on cellulose. Starch mixed with SPB decomposes to carbon and water vapor by heating, because SPB insulates starch from oxygen. The emission of water vapor enhances the formation of SPB foam and simultaneously dilutes the decomposition product gas. The SPB foam enhances the carbonization of base materials and starch by insulation of oxygen. Both the SPB foam and the dense carbonized layer insulate inside the base materials from oxygen gas and heat conduction. The mechanism suggests that the mixture of SPB and starch is categorized into a kind of intumescent flame retardant. Furthermore, starch also acts as a binder of SPB to improve adhesiveness to the base materials. The improvement of the adhesiveness also contributes the significant flame retarding effect.

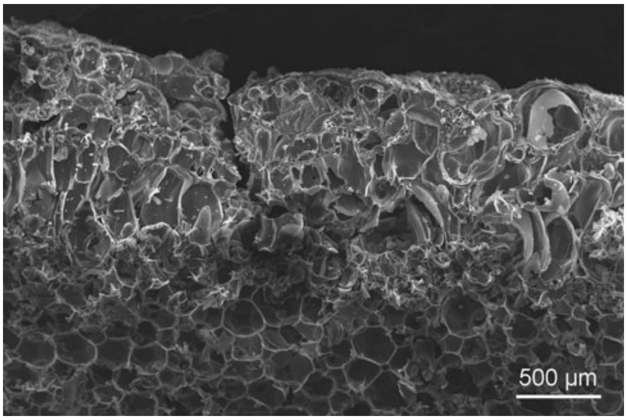

Fig. 6 The cross-sectional SEM image of the RPU foam coated with the mixture of the SPB and starch after enduring the 12 min-heating by the premixed flame

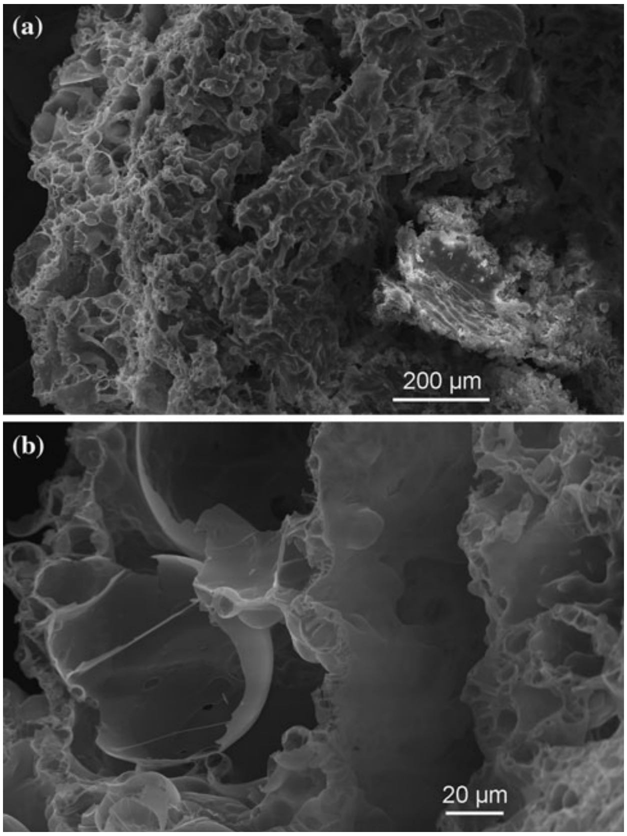

Fig. 7 The cross-sectional SEM images of the PP nonwoven coated with the mixed solution of SPB and starch after enduring 2 min-heating by the Meckel burner

Conclusions

Mixture of SPB and starch was first found to show significant flame retardant effect when deposited on organic polymer materials. Three kinds of base materials were investigated using the mixture: the PET/EVOH nonwoven, the RPU foam, and the PP nonwoven. The treated PET/EVOH nonwoven and the treated RPU foam (both 10 mm thickness) endured intensive heating by premixed gas burner for 12 min, while the treated PP nonwoven (0.7 mm thickness) endured heating by Meckel burner for 2 min. It is noteworthy that the present flame retardant coating was also effective for PP, and this suggests that the mixture can give the flame retardant effect to all kinds of combustible materials. In the SEM images of the heated samples, SPB foam was formed on the surface, and dense carbonized layer was formed beneath the SPB foam. Both the SPB foam and the carbonized layer insulate the samples inside from oxygen gas and heat conduction. The mixture of SPB and starch can be categorized into a kind of intumescent flame retardant, because starch enhances the formation of both the SPB foam and the carbonized layer simultaneously by its dehydration. Only one significant problem at this moment is that the coating of the mixture of starch and SPB is weak in water, though starch contributes the improvement of adhesiveness to the base materials as a binder of SPB. We are trying to improve water resistance using the other polysaccharides. Nevertheless, it is important to note that a high flame retardancy can be given by simply coating with the conventional starch glue containing SPB as a post-processing technique. There are a wide variety of potential applications for this technique such as decorative materials in buildings, interior decoration of automobiles, housing of machines, household appliances, and furniture. We believe the present flame retardant is advantageous over the conventional ones in costs, convenience, and environmental load.

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