

Fire-resistant nonwovens of EVOH and PET treated with amorphous sodium polyborate

Isao Tsuyumoto · Yuichiro Miura · Yukari Hori

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Abstract Nonwovens made of poly(ethylene terephthalate) (PET) and ethylene–vinyl alcohol copolymer (EVOH) are found to become highly fire resistant by treating with amorphous sodium polyborate (SPB). The fire-resistant nonwovens with 10-mm thickness show a gradual temperature increase up to 127 °C and no hole, when their back sides are fired with a gas burner for 12 min. The analysis using the EPMA and the DTA/TG indicates that the SPB foam promotes the formation of char (carbon) layer, and that the char layer together with the SPB foam insulates inside from the oxygen and the heat.

Introduction

Fire retarding treatment of polymer materials has attracted much attention from the viewpoint of disaster prevention, because polymer materials are widely used in our daily life and their heat release occurs rapidly when they are ignited. Various compounds such as aluminum hydroxide, magnesium hydroxide, antimony oxides, zinc borate, bromides, and chlorides have been used for fire retardants of polymer materials, whereas sodium borate has hardly been applied to synthetic polymer materials [1]. Sodium borate has been mainly used for wood materials, because it has pronounced fire retarding effect on cellulose [2]. Polymers containing hydroxyl group (–OH) are considered to show pronounced fire retarding effect by sodium borate due to the interaction between hydroxyl group and borate, and we found for the

first time that an amorphous sodium polyborate (SPB) has also pronounced fire retarding effect on ethylene–vinyl alcohol copolymer (EVOH). Although a number of reports have appeared on fire retardancy of ethylene–vinyl acetate copolymer (EVA) containing such as ammonium polyphosphate, aluminum trihydrate, melamine, and silicate [3–5], there have been few reports on the fire retardancy of EVOH [6].

The amorphous SPB is prepared by adjusting Na/B ratio to 0.22 ($0.22\text{Na}_2\text{O}\cdot\text{B}_2\text{O}_3\cdot n\text{H}_2\text{O}$), and its high solubility to water (up to 5.4 mol/kg of boron at 20 °C) is very appropriate for impregnation treatment of wood, fibers, clothes, and woven because the dissolved polyborate is efficiently introduced into the materials inside [7]. The amorphous SPB has a film-forming property, and it yields a solid foam ($0.1\text{--}0.3\text{ g/cm}^3$) like polystyrene by evaporating the solution to dryness [8, 9]. This property of the amorphous SPB greatly contributes to the fire retarding effect because the foam layer insulates the materials from the heat conduction and the oxygen diffusion and enhances a char layer formation. The char layer generally consists of an amorphous carbon and also insulates the underlying layer from the flame [10]. The thermal stability of the char layer is enhanced by the existence of the polyborate. The synergy effect of the polyborate foam layer and the resultant char layer is the main reason why the amorphous SPB has greater fire retarding effect than the other borates. In our previous study, we have developed fire-resistant solid wood and laminated wood satisfying the criterion that the total amount of heat release at a heat flux of 50 kW/m^2 for 20 min is below 8 MJ/m^2 through a process of pressure-impregnation of the amorphous SPB solution [11]. The amorphous SPB was found to have pronounced fire retarding effect also on some kinds of adhesives containing hydroxyl groups such as resorcinol formaldehyde (RF),

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

polyvinyl alcohol (PVOH), and ethylene–vinyl alcohol copolymer (EVOH), and to have various potential applications in fields of synthetic polymer materials. In the present study, we focus on fire retarding treatment of EVOH and its fire retarding mechanism. We present here new fire-resistant nonwovens consisting of the core/clad fiber whose core and clad are polyethylene terephthalate (PET) and EVOH, respectively, treated with SPB.

Experimental

Materials

The nonwovens consisting of core/clad fibers, in which the core of PET 10 μm in diameter is concentrically surrounded by the clad of EVOH, were used for investigation. The fibers were fusion bonded at a cross-point of EVOH, and the total diameter of the fibers was 20 μm . The ethylene content in the EVOH was 44 mol%. The size of the specimen was 100 mm \times 100 mm \times 10 mm, and the density was 0.15 g/cm³.

The SPB solution containing 5.4 mol/kg of boron was prepared by dissolving 200 g of boric acid (H_3BO_3) and 250 g of sodium tetraborate decahydrate (borax, $\text{Na}_2\text{B}_4\text{O}_5(\text{OH})_4 \cdot 8\text{H}_2\text{O}$) into 1000 g of water, according to our previous reports [8]. The Na/B molar ratio and the density of the solution were 0.22 and 1.14 g/cm³ 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. In this study, the solution was used to penetrate the SPB component into the nonwovens. The solid amorphous SPB obtained by evaporating the solutions to dryness was also used for comparison in a different treatment process.

Fire retarding treatment

Both wet and dry processes were investigated for fire retarding treatment. In the wet process, the nonwovens were immersed in the SPB solution containing 5.4 mol/kg of boron at ordinary temperatures and pressures for 30 s to 5 min, sandwiched between dry clothes to drain off the solution, and dried at 115 °C for 24 h. The amount of incorporation was evaluated by weight percent gain (WPG) of the nonwovens weighed after drying. For comparison, the conventional borax solution containing 4.8 mol/kg of boron was prepared by dissolving 558 g of borax into 1000 g of water and used for the immersion at 95 °C, because the solubility of borax is extremely low at low temperature. In the dry process, the fire retarding powders were placed evenly on upside surface of nonwovens and sucked from underside with a suction device. The powders

remaining over the specimens were brushed off after the suction. The amorphous SPB (Na/B = 0.22), borax, and boric acid were individually used in this process for comparison. The mixture of borax and boric acid was also examined by sucking borax after boric acid. The amorphous SPB was used after closely grinding in a mortar with a pestle, because the SPB solution yields a solid foam by evaporation.

Measurement

Fire retarding effect was evaluated by two kinds of tests: a muffle furnace test and a burner combustion test. In the muffle furnace test, the specimens were heated at 750 °C for 20 min in air, and the effect was evaluated from the weight loss (WL). In the burner combustion test, the specimens were placed perpendicularly and heated by a butane gas burner whose flame was directed horizontally. The distance between the specimen and the top of the burner, the whole length of the flame, and the length of the reducing flame were adjusted to 12, 10, and 3 cm, respectively. The holing time of the specimen and the temperature change at its back side were monitored to evaluate the effect. In the burner combustion test, the specimens through the dry processes were heated from the upside surface, where the fire retarding powders were placed.

The thermal conductivities of the SPB-treated and untreated nonwovens were measured by the heat flow method according to ASTM-C518, ISO-8301, and JIS A 1412 (Eko Instruments HC-071H). The thermogravimetry and differential thermal analysis (TG/DTA, Shimadzu DTG-60) were performed for the SPB-treated and untreated nonwovens in air at a heating rate of 20 °C/min. The surface morphology and elemental distribution in the SPB-treated nonwovens before and after heating in air were investigated by using the scanning electron microscope (SEM) and the electron probe micro analyzer (EPMA, JEOL JXA-8200).

Results and discussion

The WL in the muffle furnace test and the holing time in the burner combustion test along with the WPG and the treatment procedures are summarized in Table 1. The temperature changes at the back side are shown in Fig. 1. The specimen treated with the SPB through the wet process showed no hole even by heating for over 720 s, and the temperature at its back side was increased very gradually from room temperature to 120 °C for 11 min. The back side remained touchable by hand for several minutes even though the opposite side was heavily heated by the gas

Table 1 The WL in the muffle furnace test and the holing time in the burner combustion test along with the WPG for the specimens through different treatment processes

	Muffle furnace test		Burner combustion test	
	WPG (%)	WL (%)	WPG (%)	Holing time (s)
Wet SPB	94	60	95	>720
Wet borax	204	51	188	150
Dry SPB	47	74	20	50
Dry borax	37	94	20	70
Dry borax + boric acid	45	91	20	160
Untreated	0	100	0	20

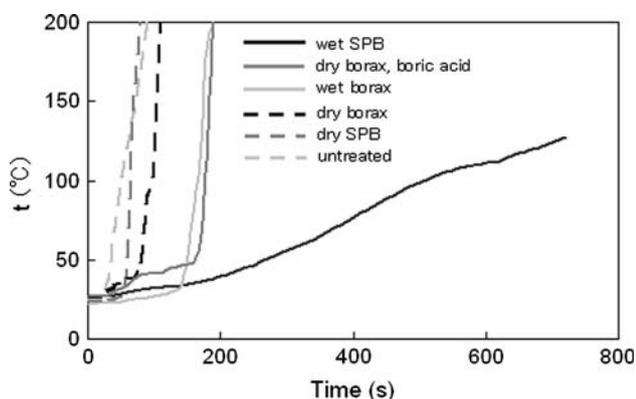


Fig. 1 Temperature changes at the back sides of the samples from the different treatment processes when their adverse sides were heated by a gas burner

burner. The specimen treated with borax through the wet process showed a hole in 150 s, though the WPG was 188%. Figure 1 shows a sudden change of the slope of the temperature change around 150 s, indicating the holing of the specimen. Taking into account the holing time, the back side temperature change and WPG, it can be said that the SPB solution containing 5.4 mol/kg of boron at 20 °C is advantageous over the conventional borax solution containing 4.8 mol/kg of boron at 95 °C. The WPG of the dry process specimens were 19–20%, much smaller than those of the wet processes. The dry process has a disadvantage in introducing large amount of fire retarding agent probably because of the clogging in the nonwovens. The specimen treated with both of boric acid and borax through the dry process showed a holing time of 160 s, though the WPG was as small as 20%. The specimens through the dry processes showed rather high fire resistance despite their small WPG, because the fire retarding powders were partially aggregated near the surface and the fire spreads from the surface. The mixture of boric acid and borax showed

high fire resistance probably because its Na/B molar ratio was close to that of the SPB. However, the fire resistance of the SPB powders through the dry process was not so great compared to the mixture of boric acid and borax, because they were not sufficiently introduced inside the specimens due to adsorption of moisture and agglomeration in ambient atmosphere. Our results indicate that it is essential to introduce the amorphous SPB homogeneously inside in order to make the nonwovens highly fire resistant, and that the immersion into the SPB solution was the most appropriate treatment process for this. Thus, we analyzed and characterized the nonwovens through the wet process.

The thermal conductivities of the SPB-treated and untreated nonwovens were 0.049 and 0.041 W m⁻¹ K⁻¹, respectively. The thermal conductivity was slightly increased because the SPB phase partly contributes the thermal conduction. The thermal conductivities of the conventional plastic foam insulator are in the range of 0.020–0.052 W m⁻¹ K⁻¹. The low rate of temperature increase in Fig. 1 is due to the low thermal conductivity as well as the high fire resistance. The low thermal conductivity is a favorable factor for fire-resistant materials because it takes long time for the whole part of the material to reach the degradation temperature.

The TG and DTA curves for the SPB-treated and untreated nonwovens are shown in Fig. 2. The untreated nonwoven showed the weight loss of 100% around 600 °C, whereas the SPB-treated nonwoven showed the weight loss of 45% around 1000 °C. The weight loss of the SPB-treated nonwoven started around 250 °C, which was lower than the untreated one, and it was not completed at 600 °C, at which the untreated nonwoven vanished. The degradation mechanism was drastically changed by the SPB treatment. The endothermic peak of the untreated nonwoven around 390 °C indicates a gasification due to the degradation of the polymer, and various kinds of flammable gas are formed

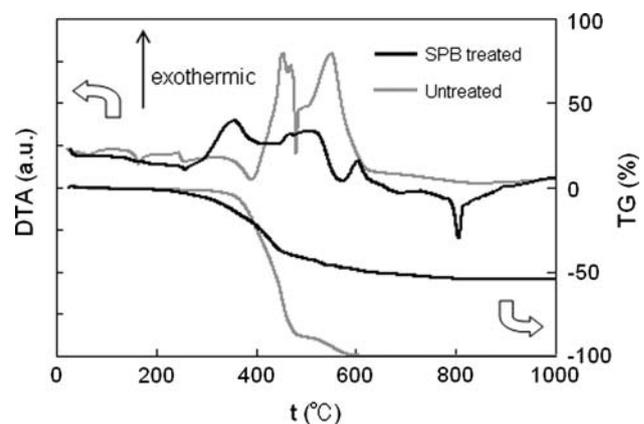
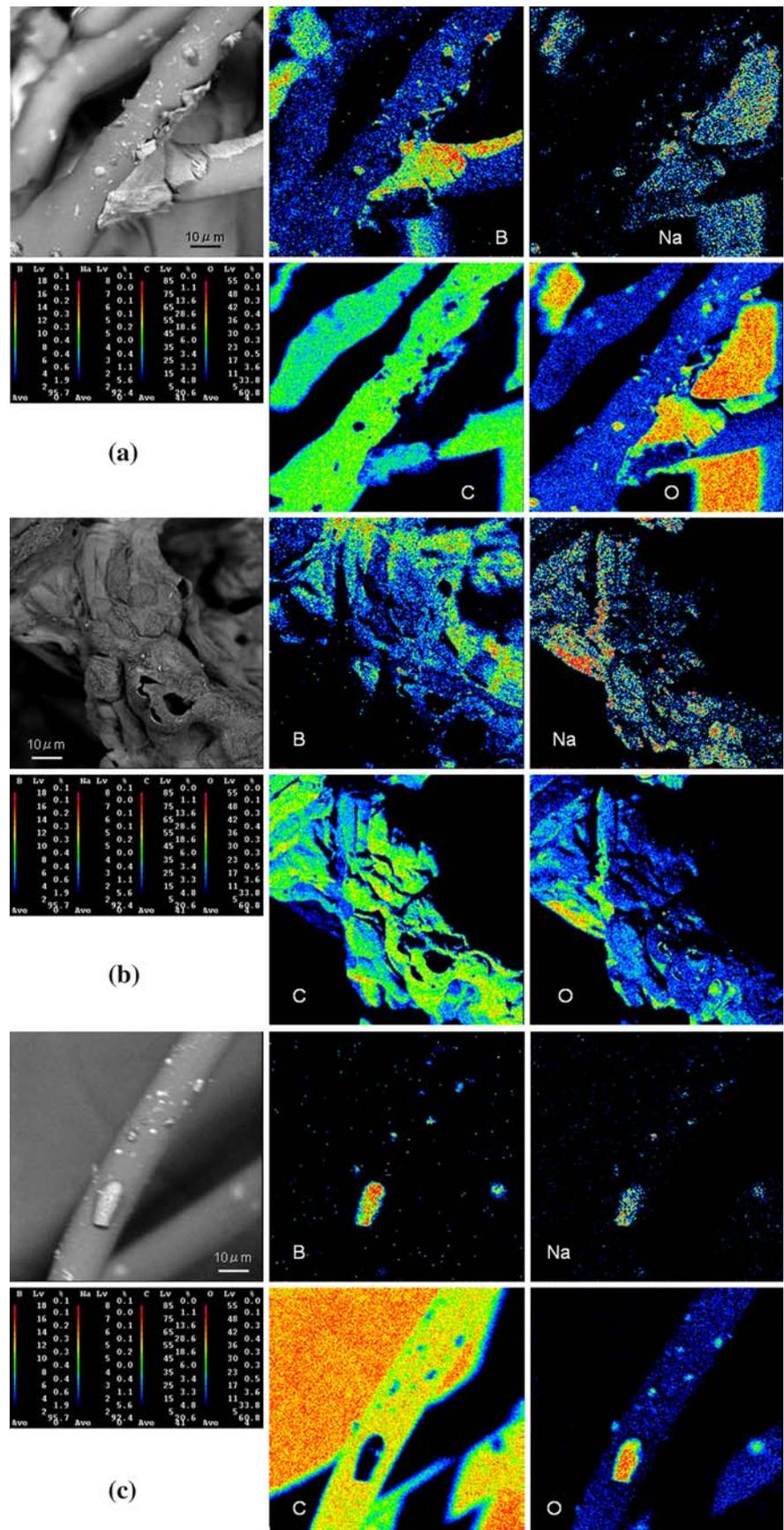


Fig. 2 TG and DTA curves of the SPB-treated nonwoven through the wet process (black line) in comparison with the untreated nonwoven (gray line)

Fig. 3 SEM images and element distribution maps (B, Na, C, and O) for the SPB-treated nonwoven of EVOH/PET (a), the char formed by heating the SPB-treated nonwoven of EVOH/PET in air (b), and the SPB-treated nonwoven of only PET (c)



above this temperature. The endothermic peak simultaneously indicates that 390 °C was lower than their ignition temperatures. Two large exothermic peaks appeared around 450 and 550 °C, indicating that the flammable gases ignited above their ignition temperatures, and the degradation of the polymer was further enhanced as a chain reaction. This is one of the ordinary thermal degradation processes of organic polymer materials. In contrast, the SPB-treated nonwoven showed an exothermic peak around 350 °C due to the carbonization involving the char formation. The small exothermic peak around 600 °C is probably due to the combustion of a portion of carbon in the char. In the SPB-treated nonwoven, the carbonization occurs instead of the gasification because the SPB foam insulates inside from the oxygen and the heat, and the formed char layer also insulate inside from the oxygen and the heat. As a result, the total heat release up to 1000 °C in air was drastically reduced by the SPB treatment. The endothermic peaks at 170, 250, and 810 °C depict the melting points of EVOH, PET, and SPB, respectively.

Figure 3 shows the SEM images and the elemental distribution maps of the SPB-treated nonwoven of EVOH/PET used in this study (a), the formed char (b), and the SPB-treated nonwoven of PET (c) for comparison. Figure 4 shows the magnified SEM image of the formed char. The elemental distribution maps shows that B and Na were homogeneously distributed on the fiber surfaces of the SPB-treated nonwoven of EVOH/PET. Such homogeneous distribution of B and Na were not observed for the SPB-treated nonwoven of PET. The SPB was homogeneously adhered to the fiber surfaces of EVOH, whereas the SPB was segregated and not efficiently adhered on the fiber surfaces of PET. This good adherence of SPB to EVOH is related to the pronounced fire retarding effect on EVOH. In Fig. 4, minute foam

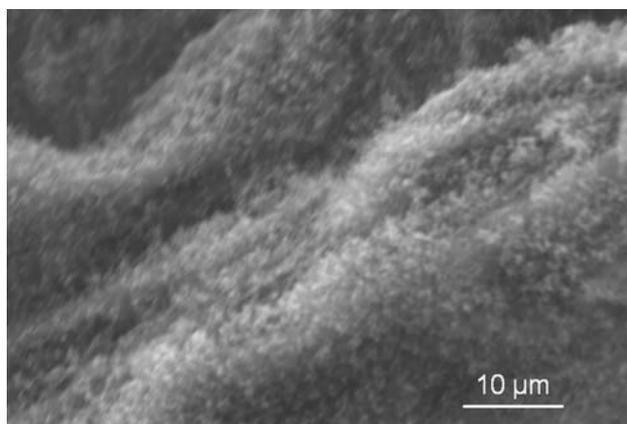


Fig. 4 Magnified SEM image of the char formed by heating the SPB-treated nonwoven of EVOH/PET in air

with the pore sizes of 100 nm scale is observed on the surface of the underlying char. This indicates that the char formation was promoted by the insulation effect of the foam. It is interesting to note that boron and carbon are observed at the same spot in the element distribution map of the char, though the concentrations are not uniformly distributed. This may indicate that boron (borate) and carbon are mixed at nanometer scale in the char or the minute foam and this composition greatly contributes the fire resistance. Thermal stability of the char is enhanced by the coexistence of an inorganic component in addition to carbon. Our results give the idea to prepare new fire-resistant composites from the char obtained by heating the mixture of polymer and SPB. This may lead to new preparation techniques of high-value-added materials such as carbon fibers, boron fibers, silicon carbide fibers.

Conclusions

Fire-resistant nonwovens consisting of core (PET)/clad (EVOH) fibers were successfully prepared by immersing the nonwovens in the SPB solutions. The nonwoven with 10-mm thickness and 94% WPG endured the flame of a butane gas burner for more than 12 min, and its backside temperature was 127 °C at 12 min. Similar fire-resistant nonwovens were also prepared through a dry process by sucking from underside of the nonwoven on which borax and boric acid were placed, though the fire-resistant properties were disadvantageous over the wet process. It was demonstrated in the TG/DTA curves that the SPB-treated nonwoven shows the carbonization instead of the gasification in the range of 300–400 °C because of the SPB foam. The SPB foam and the formed char layer together insulate inside from the oxygen and the heat. This mechanism is also supported by the element distribution maps showing the composition of boron (borate) and carbon mixed at nanometer scale. The good adherence of the SPB to EVOH surface also contributes the pronounced fire retarding effect. The SPB-treated nonwovens are expected to be alternative materials for heat insulators such as asbestos, glass fibers, rock wools, because they are light and firm as well as fire resistant. Furthermore, the precise investigation of the char formed from the mixture of polymer and the SPB may lead to the preparation of new high-value-added materials such as carbon fibers, boron fibers, silicon carbide fibers.

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