

Flame-Retardant Rigid Polyurethane Foams Prepared with Amorphous Sodium Polyborate

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ABSTRACT: Highly flame-retardant rigid polyurethane (RPU) foams were prepared by vacuum impregnation or pressure impregnation of sodium polyborate (SPB) solution. The RPU foams (10 mm thickness, 134–690% SPB) endured the flame of a butane gas burner for 167–1144 s, and the backside temperatures remained below 45°C until penetration occurred. The heat releases from the RPU foams with 150 and 400% SPB in air in the cone calorimeter tests were 8.8 and 4.1 MJ/m², respectively. The

analyses with thermogravimetry, differential scanning calorimetry, and scanning electron microscopy indicated the flame-retardant mechanism, in which the SPB foam and the formed char layer together insulated the inside from oxygen gas and heat. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 1707–1711, 2011

Key words: flame retardance; polyurethanes; thermal properties

INTRODUCTION

Rigid polyurethane (RPU) foams are widely used as insulating materials in buildings, household appliances, and automobiles because their thermal conductivities (0.022–0.029 W m⁻¹ K⁻¹) are much smaller than those of the other insulating materials, such as polystyrene foam, glass wool, and rock wool. Their high flammability, however, is undesirable for such applications from the viewpoint of disaster prevention, and their fire-retardant treatments are essential in actual use. A wide variety of fire retardants have been investigated by many researchers, and the most widely used fire retardants in RPU foams are based on halogen or phosphorus or a combination of both.^{1–7} There are, however, environmental concerns with their use because the fire retardants themselves are toxic in most cases and toxic products may be released not only in normal use but also in fires and in disposal.⁸ Therefore, fire retardants with low environmental pollution risk are particularly needed. Halogen-free and phosphorus-free fire retardants, such as expandable graphites,^{9,10} silicones,^{11–13} aluminum trihydroxide,¹⁴ and magnesium hydroxide,¹⁵ have been developed, and all of them have been adapted for polyurethane foams. On the other hand, sodium borate has been conventionally used for

wood materials because it has pronounced fire-retardant effects on cellulose.¹⁶ Despite its potential applications, there has been no report on the fire retarding of polyurethane foam with sodium borate. An amorphous sodium polyborate (SPB) prepared by the adjustment of the Na/B ratio to 0.22 has been found to be soluble in water up to 5.4 mol/kg of boron at 20°C.^{17–19} The dissolved polyborate can be efficiently introduced into the materials' inside with a high-concentration solution, and thus, it is very appropriate for the impregnation treatment of wood, fibers, clothes, and wovens. Furthermore, the amorphous SPB has a film-forming property and generates a solid foam by evaporating the solution to dryness.^{18,19} The foam layer insulates the materials from heat conduction and oxygen diffusion and enhances char-layer formation. The char layer and the foam layer insulates the underlying layer from the flame.¹⁷ Amorphous SPB has a greater fire-retardant effect than other borates because of the synergy effect of the polyborate foam layer and the resultant char layer. In our previous study, we found a pronounced fire-retardant effect of amorphous SPB on ethylene–vinyl alcohol copolymer and developed new fire-resistant nonwovens consisting of the core/clad fiber, whose core and clad were poly(ethylene terephthalate) and ethylene–vinyl alcohol copolymer, respectively.²⁰ In this study, we aimed to develop fire-resistant insulating materials from organic polymer foams. We found a pronounced fire-retardant effect of amorphous SPB also on RPU foams and first developed fire-resistant RPU foams.

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EXPERIMENTAL

Materials

RPU foam made from polymeric methylene di-phenyl diisocyanate (PMDI) and poly(ether polyol) was used. The thickness and the density were 10 mm and 0.056 g/cm³, respectively. SPB solutions containing 5.4 and 9.9 mol/kg boron were prepared by the dissolution of boric acid (H₃BO₃) and sodium tetraborate decahydrate [borax, Na₂B₄O₅(OH)₄·8H₂O] into water to adjust the Na/B ratio to 0.22, according to our previous reports.¹⁹ The solutions were prepared around 60°C to accelerate the dissolutions. In the fire-retardant treatment, a solution of 5.4 mol/kg was used at room temperature after cooling, whereas one of 9.9 mol/kg was used at 40°C to prevent precipitation.

Fire-retardant treatment

The fire-retardant SPB was introduced into the RPU foam in wet processes with the SPB aqueous solution. Because the RPU foam shed water and was not permeable to the SPB solution at ordinary pressure, we used two types of procedures for the treatments: pressure impregnation and vacuum impregnation. In the pressure impregnation process, the SPB solutions were impregnated in an autoclave at gauge pressures of 0.2–1.0 MPa for 20 min. In the vacuum impregnation process, the pressure of a vacuum desiccator with the samples was diminished to gauge pressures of –0.8 to –0.4 MPa (absolute pressure = 0.2–0.6 MPa) with a rotary pump, and then, the SPB solution was introduced into the desiccator. The samples were immersed in the solution for 10 min. All of the samples were dried at 115°C in an oven after the impregnations. The introduced amount of SPB was evaluated by weight percentage gain (WPG) in SPB grams per gram of RPU, which was weighed after the drying.

Measurement

The fire-retardant effect was evaluated by a burner combustion test and a cone calorimeter (CCM) test. In the burner combustion test, the samples were placed perpendicularly and heated by a 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 12, 10, and 3 cm, respectively. The penetration time of the sample and the temperature change at its backside were monitored. In the CCM test, heat release from a sample with a surface area of 99 × 99 mm² was monitored when it was irradiated with infrared in air at a heat flux of 50 kW/m². The amount of heat

TABLE I
Treatment Conditions, WPGs in SPB (g/g of RPU), and Penetration Times of the Samples in the Burner Combustion Tests

| Sample | Gauge pressure (MPa) | Concentration (mol/L as to B) | WPG (%) | Penetration time (s) |
|--------|----------------------|-------------------------------|---------|----------------------|
| A | 1.0 | 5.4 | 255 | 796 |
| B | 0.8 | 5.4 | 248 | 609 |
| C | 0.6 | 5.4 | 255 | 461 |
| D | 0.4 | 5.4 | 232 | 256 |
| E | 0.2 | 5.4 | 260 | 227 |
| F | –0.8 | 9.9 | 690 | 1144 |
| G | –0.6 | 9.9 | 526 | 671 |
| H | –0.8 | 5.4 | 362 | 548 |
| I | –0.6 | 5.4 | 221 | 187 |
| J | –0.4 | 5.4 | 134 | 167 |

Gauge pressures were positive for the pressure impregnation and negative for the vacuum impregnation.

release from the sample was calculated from O₂ consumption in the exhaust gas and recorded for 20 min. A total amount of heat release below 8 MJ/m² at a heat flux of 50 kW/m² for 20 min was the necessary criterion for noncombustible materials by Japanese Building Standards.

Thermogravimetry (TG; Shimadzu DTG-60, Kyoto, Japan) was performed for the SPB-treated and the untreated RPU foams in air at a heating rate of 20°C/min. Differential scanning calorimetry (DSC; Shimadzu DSC-60) was also performed for the SPB-treated and the untreated RPU foams in air at a heating rate of 10°C/min. The surface morphology was investigated with scanning electron microscopy (SEM; Keyence VE-9800, Hitachi S-3000).

RESULTS AND DISCUSSION

The treatment conditions, WPG, and penetration time in the burner combustion test are summarized in Table I. In the pressure impregnation, the fire resistance indicated by the penetration time increased with increasing gauge pressure, although the WPG was almost constant irrelevant to the gauge pressure. This was because the SPB solution was impregnated into the foam more homogeneously at higher pressures. In general, flame retardants must be permeated homogeneously into the base materials on the microscopic scale to achieve high fire resistance because the materials ignite from their easily burnable parts and thermally damage the other parts. As for vacuum impregnation, the WPG and penetration time increased with increasing gauge pressure. Unlike the pressure impregnation, WPG reached 363 and 690% at –0.8 MPa with 5.4 and 9.9 mol/kg solutions, respectively. The temperature change at the backside of the heated sample is shown in Figure 1. The temperatures increased

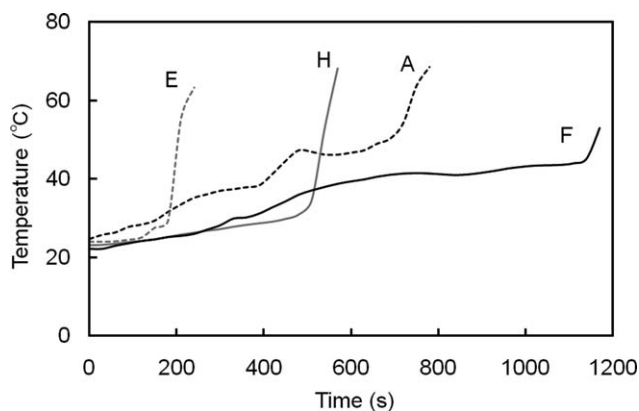


Figure 1 Temperature changes at the backsides of samples A, E, F, and H (see Table I) when their adverse sides were heated by a gas burner.

gradually with heating until steep increases took place just before the penetration. The backside temperatures before penetration were all below 60°C, and this indicated that the SPB-treated RPU foam acted as a highly effective insulator against flame. In contrast, the untreated RPU foam showed a steep temperature increase immediately after heating, and its penetration time was 15 s. It is noteworthy that the SPB-treated RPU foams of 1 cm thickness with densities of 0.19 g/cm³ (WPG = 255%) and 0.44 g/cm³ (WPG = 690%) endured the flame of the butane gas burner for 796 and 1144 s, respectively. The fire-resistant and heat-insulating performance of this RPU foam reached the level of practical use.

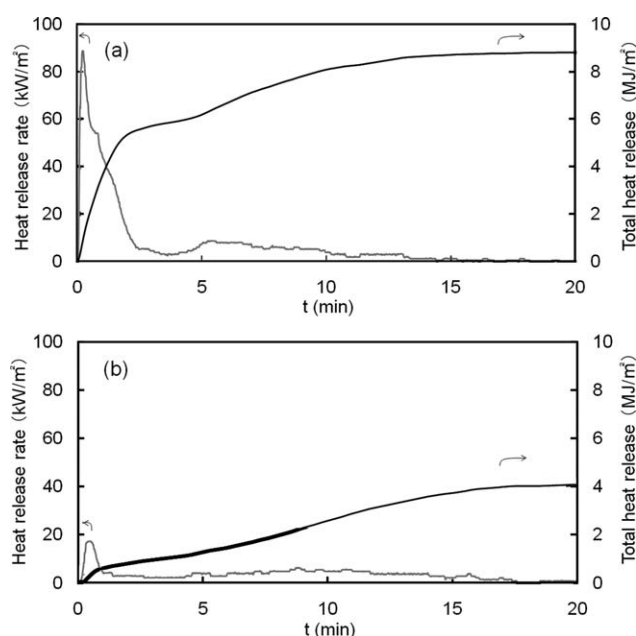


Figure 2 Heat release rate and total heat release from the vacuum impregnated RPU foams with (a) 150% SPB and (b) 400% SPB in the CCM test ($t = \text{time}$).

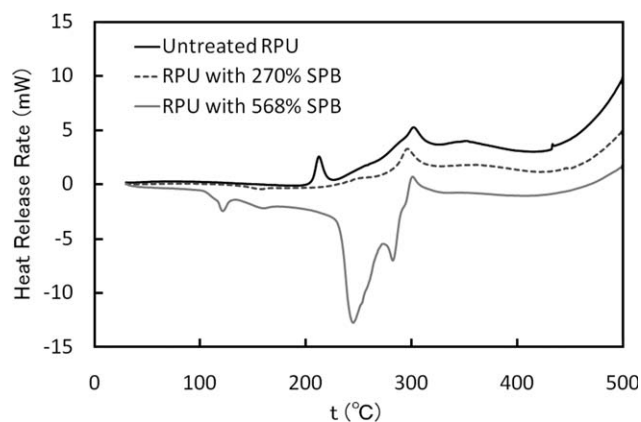


Figure 3 DSC curves of the vacuum impregnated RPU foams with 270 and 568% SPB in comparison with the untreated RPU foam in air ($t = \text{temperature}$).

The amount of heat release from the vacuum impregnated samples of 10 mm thickness in the CCM test is shown in Figure 2. The total amounts of heat release for 20 min were 8.8 and 4.1 MJ/m² for the samples with WPGs of 150 and 400%, respectively. At the initial stage of the irradiation up to 2 min, the SPB foam layer and the char layer were formed by the gasification of the RPU. The considerable heat release was observed only in this stage, and the moderate heat release was observed after this because of the two kinds of layers insulated the inside from oxygen gas and heat. The appearance of the samples after the CCM tests was black on the surface and light brown on the reverse because of the carbonization. Because the total amount of heat release below 8 MJ/m² is the necessary criterion for noncombustible materials by the Japanese Building Standards, this was the first development of noncombustible organic polymer-based materials that satisfy the criterion.

Figures 3 and 4 show the DSC and the TG curves of the vacuum impregnated and untreated RPU

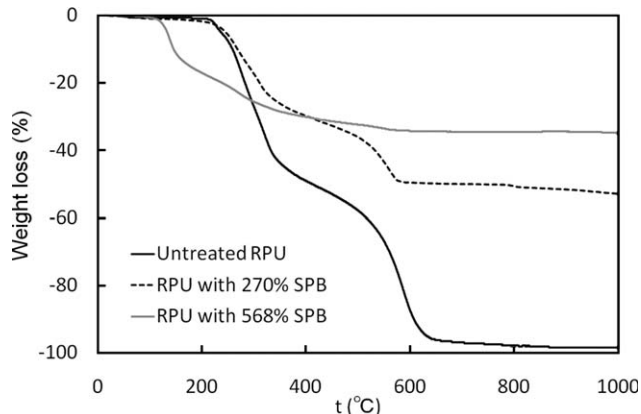


Figure 4 TG curves of the vacuum impregnated RPU foams with 270 and 568% SPB in comparison with the untreated RPU foam in air ($t = \text{temperature}$).

foams, respectively, in air. In the DSC curve, the heat release of the untreated RPU foam started around 210°C because of the combustion of the gasification product, and the heat release rate was increased with increasing temperature.^{21,22} The TG curve indicates that this gasification (degradation) process proceeded up to around 650°C for the untreated RPU foam. In the DSC curves of the SPB-treated RPU foam, the heat releases were suppressed in comparison with the untreated sample, and interestingly, the sample with 568% SPB showed endothermic decomposition instead of heat release. In general, the degradation processes occurring at elevated temperature were thermodynamically endothermic, and thus, the endothermic DSC curve indicated that the gasification (degradation) without the combustion proceeded because of the insulation of oxygen gas by the SPB foam. This result supports the flame-retardant mechanism in which the SPB foam insulated the inside from oxygen gas. As shown in the TG curve of Figure 4, the thermal degradation of the untreated RPU foam occurred in two stages: 200–400 and 400–620°C. By the vacuum impregnation of 270% SPB, the degradation temperature regions moderately decreased to 200–370 and 370–570°C, and the total weight loss ratio was reduced to 53%, although the thermal degradation curve was similar to that of the untreated RPU foam. The lowering of the temperature at which the thermal degradation occurred may have been due to the reduction of the fraction of closed cell space by the vacuum impregnation. The reduction of the total weight loss was due to the existence of SPB, which usually showed only about a 14% weight loss, mainly by the desorption of hydrated water. Unlike these, the RPU with 568% SPB started the weight loss around 100°C. Given that the first steep weight loss of about 15% around 150°C was due to the desorption of hydrated water of the SPB, the thermal degradation of the RPU foam gradually proceeded above 150°C. The gasification (degradation) proceeded without oxygen because the SPB foam insulated the inside from air. The gasification products did not ignite because oxygen gas was diluted around the products, and the ignition temperatures of the products formed without oxygen were higher than their formation temperature. The total weight losses until 1000°C were 53 and 35% for the samples with 270 and 568% SPB, respectively, and these values suggest that the base material, RPU foam, mostly disappeared. However, we found that black glassy residues remained even after the samples were heated at 1000°C in air. There is a possibility of the formation of high-value-added fire-resistant materials, such as carbon fiber and boron fiber, because the pure SPB yielded white sodium borate by heating at 1000°C.

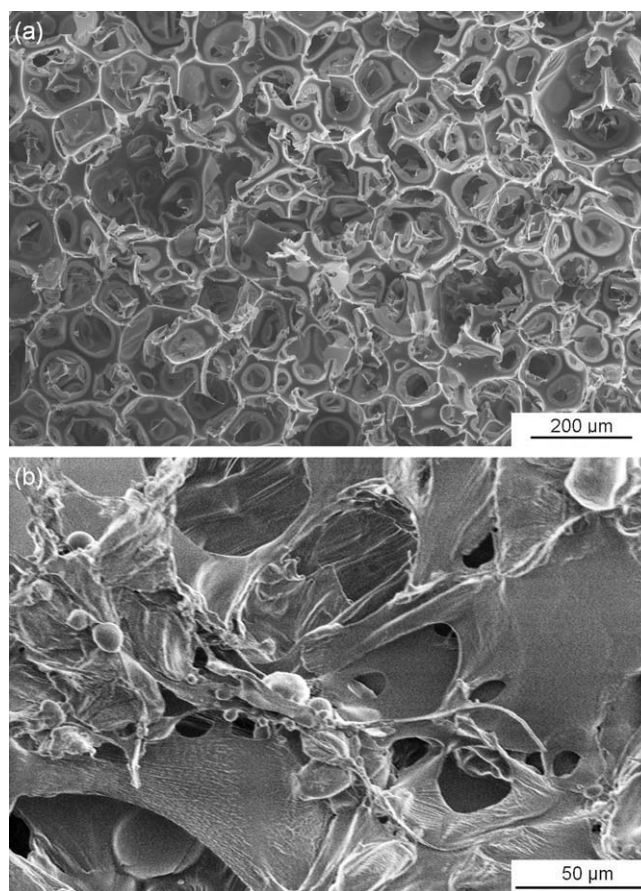


Figure 5 SEM images of (a) the vacuum impregnated RPU foam and (b) that after heating by the gas burner. The sample for part b was carbonized, and its appearance to the naked eye was black char with white fine powder on it. The images in parts a and b were taken at accelerating voltages of 15 and 2 kV with and without carbon coating, respectively.

Figure 5 shows the SEM images of the RPU foam after the vacuum impregnation of SPB [Fig. 5(a)] and that after heating by the gas burner [Fig. 5(b)]. As shown in Figure 5(a), the closed cells in the RPU foam were partly ruptured by the pressure difference, and the SPB solution was considered to be impregnated inside through the ruptured cells and precipitated on the foam wall. The RPU foam structure mostly remained the same after the vacuum impregnation except for the point that the closed cells were partly ruptured. The microstructure also indicated that the stiffness and the thermal insulating properties were not reduced by the vacuum impregnation. The carbonized part of the SPB-treated RPU foam formed by heating endured the flame of the burner for 3–19 min, as already shown in Table I and Figure 1. The SEM image in Figure 5(b) indicates that the enduring carbonized part consisted of overlapped highly viscous dense char. Interestingly, imbricate, scalelike incrustation was observed on the char at the lower left. This was

probably a fine precipitate of the SPB because the carbonized part consisted of black char and fine white powder on it by naked eye observation. This supported the mechanism in which the SPB foam insulated the inside from oxygen and accelerated the carbonization.

CONCLUSIONS

Flame-retardant RPU foams were successfully prepared by the vacuum impregnation or pressure impregnation of SPB solutions. The RPU foam with 10 mm thickness and 690% SPB endured the flame of a butane gas burner for 19 min, and its backside temperature was below 45°C for 19 min. The flame retardance was controllable by changes in the impregnation conditions and WPG. The total heat releases for 20 min in the CCM test were 4.1 and 8.8 MJ/m² for the samples with WPGs of 150 and 400%, respectively. This was the first organic polymer material that satisfied the necessary criterion (<8 MJ/m² for 20 min) for noncombustible materials. DSC and TG analyses indicated that the heat releases were suppressed because of the insulation of oxygen gas by the SPB foam. In the SEM image, overlapped dense char was observed in the carbonized part of the sample, which endured the flame of the gas burner. These results support the flame-retardant mechanism in which the SPB foam and the formed char layer together insulated the inside from oxygen gas and heat. The RPU foam developed in this study was a flame-retardant heat insulator with light weight (<0.44 g/cm³). There are various applications in industries, including heat insulators for buildings, household appliances and automobiles, gaskets for sealing, and fire-resistant clothes. This could be an alternative to materials such as asbestos, glass fibers, and rock wools. Further analysis of the char may lead to new preparation techniques of

high-value-added materials, such as carbon fibers, boron fibers, and silicon carbide fibers.

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