Smoke-suppressant and flame-retardant rigid polyurethane foam obtained via processing based on saccharomycetes fungus and ammonium molybdate

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Abstract
The present work proposes an environmentally friendly, simple, and efficient way to impart smoke suppression and flame retardancy to rigid polyurethane foam (RPUF) by soaking the pristine RPUF for short periods in the saccharomycetes fungus (SF) solution and then in the ammonium molybdate (AM) solution. The co-addition of SF and AM exhibit good performance on smoke suppression and flame retardant. The level of flammability, thermal degradation behavior, and combustion properties of the samples are evaluated mainly via vertical burning tests, thermogravimetric analysis, and calorimetry, respectively. The proportions of 16SF/3AM/RPUF are varied to maximize the performance of the processed RPUF samples in terms of both smoke suppression and flame retardancy, which are substantially increased by the optimal sample compared to those of pristine RPUF.

1. Introduction

Rigid polyurethane foam (RPUF) has been widely used in the construction, aviation, and food industries, due to its many excellent properties, such as high thermal insulation performance, high strength, cold resistance and good thermal insulation [1]. However, RPUF has poor flame-retardant properties because it burns quickly, and releases a large amount of smoke, which greatly restricts its potential application [2]. At present, the commonly used flame retardants are additive flame retardants, such as polyols and polyvinyl alcohol, phosphorus, borides, etc; reactive flame retardants such as bromine containing polyols, phosphorus containing polyols, and halogenated polyether polyols, etc; the most commonly used synergistic flame retardants are antiflammable vinyl ester resin nanocomposites, intumescent flame retardant and halogen donors, etc [3, 4]. Halogen flame retardants release environmental damaged substances during combustion process, while many efforts have been made to address this important issue through material modification. The saccharomycetes fungus(SF) and ammonium molybdate (AM) have many advantages, such as: a wide range of sources, no pollution and convenient production, which provides the basis for industrial development.

The research on saccharomycetes fungus(SF) and ammonium molybdate(AM) involves many fields: the saccharomycetes’ evolved defense mechanisms naturally protect cells from death in the field of food [5]; In the industry, spent yeast cells are gained as by-products of beer and bioethanol production [6, 7]; Ammonium molybdate improved suppression activity of biocontrol saccharomycetes [8]; Ammonium molybdate improves crystallization and thermal behavior of the materials [9]. The present work represents the first use of SF and AM as the flame retardant in RPUF.

The present work addresses these issues by proposing an environmentally friendly, simple, and efficient process for imparting smoke suppression and flame retardancy of RPUF by soaking the preformed RPUF for
short periods in the SF solution and then in the AM solution. The proportions of 16SF/3AM/RPUF are varied to maximize the performance of the modified RPUF samples in terms of both smoke suppression and flame retardancy.

2. Materials and methods

2.1. Raw materials
Polyether polyol (DEP-560HD) was obtained from Zibo Dexin Lianbang Chemical Industry Co., Ltd (Shandong, China). Diphenylmethane diisocyanate (MDI; technical pure grade) was obtained from Wanhua Chemical Group Co., Ltd (Shandong, China). The foaming stabilizer (lauric diethanolamide; technical pure grade) was supplied by Jiangsu Maysta Chemical Co., Ltd (Beijing, China). SF powder (water content: 8 wt%) was obtained from Angel Yeast Co., Ltd (Hubei, China). Pure glucose (2,3,4,5,6-pentahydroxyhexanal; density: 1.544 g cm$^{-1}$) was obtained from Fan De (Beijing) Biotechnology Co., Ltd (Beijing, China). Ammonium molybdate (AM; technical pure grade) was obtained from Tianjin Damao Chemical Reagent Factory (Tianjin, China).

2.2. Preparation and treatment of RPUF samples
The processing employed for fabricating and treating RPUF samples is illustrated schematically in figure 1. Firstly, polyether polyol was mixed with MDI and stirred for 30 s at 25°C. The mixture was poured into a foaming box with dimensions of 150 mm × 150 mm × 50 mm, and then dried in a drying oven at 80°C for 30 min. The resulting RPUF block was held at 25°C for 24 h prior to subsequent treatment. The saccharomycetes solution was prepared by adding glucose to 200 ml of deionized water at 28°C under continuous stirring, followed by the addition of SF powder under continuous stirring. The mixture was then allowed to ferment under continuous stirring for 30 min at 25°C. The RPUF block was then inserted into the fermented saccharomycetes solution, and turned every 5 min for a total of 30 min. Then, the saccharomycetes-treated RPUF block was removed and allowed to dry for 24 h at 25°C. Lastly, the saccharomycetes-treated RPUF block was submerged in the AM solution (1 g, 2 g, 3 g) for 5 min, removed, and allowed to dry at 50°C for 4 h. The samples subjected to testing included pristine RPUF (PU-1), RPUF/16SF/32glucose (PU-2), RPUF/16SF/1AM (PU-3), RPUF/16SF/2AM (PU-4), and RPUF/16SF/3AM (PU-5) samples.

2.3. Test methods
The internal structures of the samples were observed by scanning electron microscopy (SEM) using a Bruker XFlash 6130 microscope under high vacuum at an acceleration voltage of 5 kV. Thermogravimetric analysis (TGA) was conducted using a PerkinElmer simultaneous thermal analyzer (STA) 8000. The sample was placed in an alumina crucible and heated under a nitrogen atmosphere from 50°C to 600°C at a rate of 10°C min$^{-1}$. The level of flammability was evaluated by vertical burning tests (UL-94). The limiting oxygen index (LOI) values were obtained for samples with sizes 100 mm × 10 mm × 10 mm using a Fire Testing Technology (Germany Eager Technology Inc.), according to the ASTM D2863-2013 standard. The combustion behaviors of

![Figure 1. SEM images of PU-1 (a), PU-2 (b), pu-3 (c).](image-url)
the full-sized samples were characterized using Fire Testing Technology (FTT, UK) cone calorimeter at an external heat flux of 50 kW m\(^{-2}\) according to the ISO5660 standard [10].

3. Results and discussion

3.1. Sample morphology

The internal structures of samples PU-1, PU-2, and PU-5 are shown by the SEM images presented in figures 1(a)–(c), respectively. The cell structure of PU-1 (figure 1(a)) contributes greatly to the flammability of polyurethane by providing high air permeability during combustion, resulting in a greatly accelerated combustion rate. The SEM image of PU-2 (figure 1(b)) indicates that the internal structure of PU-1 is substantially altered by the introduction of SF. Here, the cells of the pristine material have been nearly completely filled by much smaller spherical particles. Finally, the SEM image of PU-5 (figure 1(c)) indicates that the inclusion of AM with the SF replaced the structure of PU-1 with folded morphology that can be expected to impede the permeability of air during the combustion process, and thereby greatly enhance the flame retardant performance of the material.

3.2. Fireproofing test

The five samples were subjected to vertical burning tests, and images of the burning samples were captured 0 s, 5 s, 10 s, 15 s, and 20 s after an ignition source for 10 s twice had been applied to the bottoms of the samples. The images obtained for samples are presented in figure 2. As expected, PU-1 combusted completely within 20 s immediately after the ignition source was applied to the bottom of the sample. We also note that PU-2 combusted completely within 20 s, although the ignition source had to be applied for much greater period of time (i.e., ∼10 s) than in the case of PU-1. These results demonstrate that the flame retardancy of saccharomycetes-treated RPUF and SF/AM-treated RPUF are better than that of pristine RPUF. The level of flammability of PU-4 and PU-5 were assessed as V-0 based on the UL-94 standard. The LOI values obtained for PU-4 and PU-5 were 24.5% and 25.1%, which are much greater than that of unmodified RPUF (17%) (table 1). Apparently, the co-addition of SF and AM, shows excellent flame retardancy.
3.3. TGA testing

The temperature at 5 wt% loss ($T_{5\%}$), 50 wt% loss ($T_{50\%}$) and residual weight obtained from TGA for the various samples are listed in Table 1, the curves as shown in Figure 3. We note the introduction of SF substantially decreased the value of $T_{5\%}$ owing to the susceptibility of SF to water loss, while it increased the value of $T_{50\%}$ with an increase that becomes progressively substantial with increasing AM content from 0 to 3-AM. The residue weight of PU-5 was 24.94%, much better than PU-2 and PU-4. The co-addition of SF and AM decreased the rate of thermal decomposition, resulting in greater $T_{50\%}$ and residual weight values than those obtained for samples PU-1 and PU-2. From Figure 3(b), the derived weight speak of RPUF/SF was 0.42%/°C at about 315 °C and the speak of RPUF/SF/3AM was 0.47%/°C at about 310 °C. This phenomenon indicates the addition of AM increased the thermally stable and improved the charring ability [8].

These results further verify that the thermal stability of RPUF is significantly improved with the co-addition of SF and AM, and the optimal thermal stability is obtained with a SF to AM ratio of 16:3 (i.e., PU-5). This behavior can be analyzed from the perspective that the treated RPUF has a composite structure composed of the

| Samples | $T_{5\%}$ (°C) | $T_{50\%}$ (°C) | Residue (wt%) | LOI |
|---------|---------------|----------------|---------------|-----|
| PU-1 (pure RPUF) | 220 | 335 | 14.14 | 17.0 |
| PU-2 (16 saccharomyces/RPUF) | 141 | 344 | 21.56 | 22.5 |
| PU-3 (16 saccharomyces/1 AM/RPUF) | 187 | 359 | 23.94 | 24.0 |
| PU-4 (16 saccharomyces/2 AM/RPUF) | 160 | 356 | 24.58 | 24.5 |
| PU-5 (16 saccharomyces/3 AM/RPUF) | 159 | 347 | 24.94 | 25.1 |

Figure 3. HRR and THR of pure RPUF, RPUF/SF, RPUF/SF/AM ((a):HRR; (b):THR).

Figure 4. SPR and TSR of pure RPUF, RPUF/SF, RPUF/SF/AM ((a):SPR; (b):TSR).

Table 1. TGA data of the various samples.
hard cell structure of the pristine RPUF and soft regions composed of the saccharomycetes particles. Here, the first differential heat peaks in the DSC curves of the treated samples at relatively low temperature represent the partial decomposition of the soft saccharomycetes particles [11, 12].

3.4. Cone calorimeter testing
As shown in figure 3(a), PU-5 produced very short period of heat release, and therefore burned very quickly after ignition with peak HRR (PHRR) of 225 kW m$^{-2}$, while the PHRR values of all other samples were greater, where the highest PHRR of 320 kW m$^{-2}$ was obtained for PU-1, and their periods of heat released much greater as well. These characteristics resulted in the highest THR value were obtained for PU-1 (figure 3(b)), the THR values of the treated samples decreased in the order of PU-2 > PU-3 > PU-4 > PU-5. The SF and AM attached to the surface of the RPUF first burned and to some extent, it slowed down the burning rate, therefore, the total heat rate of PU-5 was the lowest. The SPR results (figure 4(a)) demonstrate high degree of variability in the various samples, where PU-2 and PU-3 produced smoke over much longer periods than the other samples, but the peak SPR (PSPR) of PU-3 is considerably less than that of PU-2. Here, the limiting TSR values of the samples decreased in the order of PU-1 > PU-2 > PU-3 > PU-4 > PU-5, where PU-5 yielded the lowest limiting TSR value of 220 m$^2$/m$^3$. These results demonstrated that, the co-addition of SF and AM provided a definite fire-retardant effect, the addition of AM decreased the amount of smoke generated from organic combustion. Nonetheless, the quantity of molybdenum trioxide increased with the sufficiently high AM addition in PU-5, which formed a thermal insulation layer that restricted the chain reactions of organic matter, and thereby reduced the amount of smoke produced by the sample.

4. Conclusion
The present work proposed an environmentally friendly, simple, and efficient process to impart smoke suppression and flame retardancy to RPUF by soaking the pristine RPUF for short periods of time in the SF solution and then in the AM solution. The present work represented the first use of SF as flame retardant in RPUF. Sample PU-5 (i.e., RPUF/16SF/3AM) represented the optimal proportions of SF and AM based on the level of flammability, thermal degradation behavior, and combustion properties of the samples. Compared to the pristine RPUF (PU-1), the LOI of PU-2 was increased by 22.5% and the PU-5 was increased by 25.1%. The residual weight of PU-2 was increased by 52.5% and PU-5 was increased by 76.4%. The THR value of PU-5 was 8.5 MJ m$^{-2}$, much lower than PU-1 (18.5 MJ m$^{-2}$) and PU-2 (17.5 MJ m$^{-2}$). The TSR of PU-5 was decreased by 41.3%, much higher than PU-1 and PU-2. The system of SF and AM exhibited better thermal stability than SF. Moreover, PU-5 failed to sustain combustion under vertical burning testing, rated a flammability of V-0 based on the UL-94 standard, and showed excellent smoke suppression and good flame retardant effect in RPUF. The system of SF and AM showed excellent smoke suppression and good flame retardant effect in RPUF, which made the development and application of rigid polyurethane foam in many fields.

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Data availability statement
No new data were created or analysed in this study.

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