

Synergistic Effects of Hydroxides and Dimethyl Methylphosphonate on Rigid Halogen-Free and Flame-Retarding Polyurethane Foams

Anzhen Zhang,¹ Yihe Zhang,^{1,2} Fengzhu Lv,¹ Paul K. Chu²

¹National Laboratory of Mineral Materials, School of Materials Science and Technology, China University of Geosciences, Beijing 100083, China

²Department of Physics and Materials Science, City University of Hong Kong, Kowloon, Hong Kong, China

Correspondence to: Y. Zhang (E-mail: zyh@cugb.edu.cn)

ABSTRACT: Rigid halogen-free and flame-retarding polyurethane foams are prepared with aluminum hydroxide, brucite, and DMMP. The effects of the hydroxides and DMMP on the foaming process and flame retarding properties of the foams are investigated by thermo gravimetric analysis, limiting oxygen index, and X-ray powder diffraction. The thermal stability of the rigid polyurethane foams is close to that of the hydroxide fillers, with aluminum hydroxide providing better flammability performance than brucite. The hydroxide fillers and DMMP play a synergistic role in the rigid polyurethane foams and the limiting oxygen indices are up to 28.4% and 32.4%, respectively. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: flame retardance; polyurethane; foams

Received 27 April 2012; accepted 12 June 2012; published online

DOI: 10.1002/app.38200

INTRODUCTION

Rigid polyurethane foams are excellent thermal insulators and widely used industrially. However, because of the large surface area, rigid polyurethane foams are highly flammable¹ and several fire disasters involving thermal insulation made of rigid polyurethane foams occurred recently in China, such as Shanghai high-rise flats fire, which leaves 58 people dead and more than 70 people injured on November 15, 2010. Hence, flame-retarding polyurethane foams are needed for safer applications. There are two ways to improve the fire behavior of polyurethane foams, namely additive and reactive flame-retardants, while additive flame-retardants are more easily and widely used. Owing to emission of toxic and dense smoke, the use of halogen flame retardants is limited. As a result, halogen-free flame retardants such as ammonium polyphosphate,^{2–4} expandable graphite,^{5–10} and melamine^{11–15} are used in the flexible polyurethane foams. In fact, inorganic hydroxide fillers have replaced halogen flame retardants in many plastic applications due to benefits such as low cost as well as minimal corrosiveness relative to the antimony-halogen systems and phosphorus-containing fire retardants. Alumina trihydrate and magnesium hydroxide account for >50% by weight of the world-wide sales of fire retardants.¹⁶

Aluminum hydroxide, known as alumina trihydrate or ATH, produced by the Bayer process from the mineral bauxite, makes

up about 90% of the inorganic market by weight.¹⁷ Decomposition of aluminum hydroxide commences at about 200°C, which is suitable for most polymers, especially polyesters, acrylics, ethylene vinyl acetate, epoxies, poly(vinyl chloride), and rubber. There is also growing interest in magnesium hydroxide for its relatively high decomposition temperature (300°C) and better match with many polymer systems than aluminum trihydrate fillers.^{18,19} Magnesium hydroxide has been adopted as a flame retardant in many polymers^{19,20} such as polypropylene,^{21–23} ethylene vinyl acetate,^{24–26} polyethylene,^{27,28} polyamide,²⁹ and poly(vinyl chloride).³⁰ Brucite, the mineral form of magnesium hydroxide with the chemical formula Mg(OH)₂, can be used as a flame retardant. It is more environmentally friendly and economical than other commercial flame retardants, and has high industrial demand.^{31–33}

Dimethyl methylphosphonate (DMMP), a water soluble liquid (boiling point: 185°C), is one of the most effective phosphorus-containing flame retardants and contains a large amount of phosphorus for a phosphorus ester (25 wt %). It is highly effective as a flame retardant on a weight basis. DMMP can be used not only as a flame retardant but also viscosity depressant to accomplish higher flame retarded fillers loading. It could be used in flame-retardant rigid polyurethane foams that it has a higher boiling point and is believed to be less susceptible to undesirable interactions with halogenated aliphatic components, such as blowing agents, or with amine catalysts.³⁴

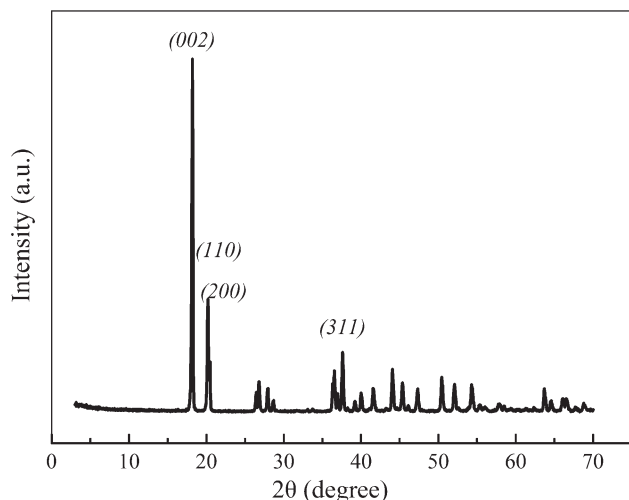


Figure 1. Powder X-ray diffraction spectra of aluminum hydroxide.

In this work, the effects of aluminum hydroxide, brucite, and DMMP on the flame retarding properties of rigid polyurethane foams are studied by thermogravimetric analysis, limiting oxygen index, and X-ray powder diffraction. The main objective is to develop new rigid halogen-free and flame-retarding polyurethane foams.

EXPERIMENTAL DETAILS

Commercial polyether polyol (AD-120, N^oOH: 320 ± 20 mg KOH g⁻¹, viscosity 25°C: 1000 ± 300 mPa s⁻¹) was supplied by Tianjin Aide Chemical. Polymeric methylene diphenyl diisocyanate (M20S, NCO%: 30.2–32.0, average functionality: 2.8, acid value HCl%: ≤ 0.05 , viscosity 25°C: $150\text{--}250$ mPa s⁻¹) was supplied by BASF Chemical. Aluminum hydroxide, a commercial flame retardant, was purchased from Aluminum Corporation of China with (Al₂O₃ wt % ≥ 64.5). Brucite was transported from Kuandian Liaoning province and DMMP was supplied by Beijing Chemical.

Rigid halogen-free and flame-retarding polyurethane foams were produced using different content of aluminum hydroxide, brucite, and DMMP. The hydroxides were dried in a cabinet by forced convection prior to use. The polyether polyol was first mixed with different content of flame retardants. Afterward, the mixture was blended with polymeric methylene diphenyl diisocyanate at a mass ratio of 1 : 1 quickly for 10 s. The mixture was poured into a 300 mm × 300 mm × 300 mm aluminum mold for foaming. The foams without surface skin were cut into 10 mm × 10 mm × 100 mm for LOI testing and 100 mm × 100 mm × 100 mm for compressive strength testing by hand using a razor blade and the test samples the surfaces of which was clean and free from flaws were kept at a relative humidity of 50% at 23°C until use.

The phase composition of the flame retarding fillers and the residue from the flame retarding polyurethane foams were measured by X-ray powder diffraction on a D/max-rA 12 kW X-ray powder diffractometer using fine powdered samples. Cu K α radiation (40 kV and 100 mA) and graphite filter with a

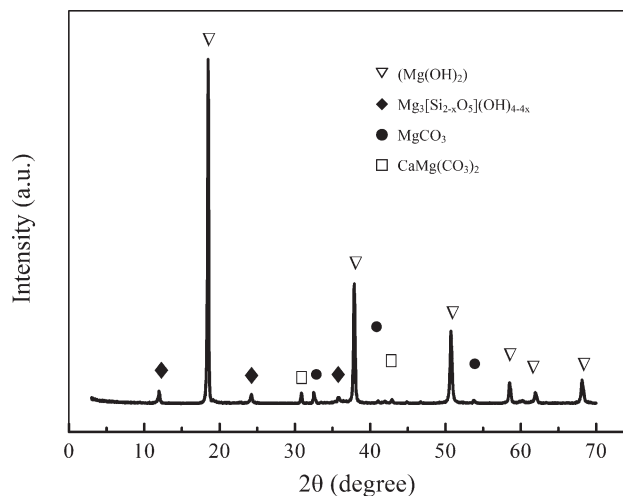


Figure 2. Powder X-ray diffraction spectra of brucite.

scanning speed of 8° min⁻¹ were used. The thermal stability of the polyurethane foams and flame retarding fillers were assessed on a thermogravimetric analyzer (made by Shimadzu, Japan) at a constant scanning rate of 20°C min⁻¹. The samples were examined under flowing N₂ (120 mL min⁻¹) up to 600°C. The flame reaction of the polyurethane foams was determined by means of the limiting oxygen index on the JF-3 type instrument (China) according to the standard oxygen index test ASTM D2863. And the compressive strength was measured by an electronic tensile machine (CMT4304, made by Sans, China) according to the standard GB/T 8813-2008.

RESULTS AND DISCUSSION

It is known that the application of flame retardants is limited by their purity and thermal stability, and many properties of hydroxide fillers including thermal stability, are also influenced by their crystal structure. Hence, powder X-ray diffraction (XRD) is an effective way to investigate the expected flame performance of aluminum hydroxide and brucite, and the powder XRD results are presented in Figures 1 and 2, respectively. Aluminum hydroxide is mainly in the form of α -Al₂O₃·3H₂O with very high purity and the brucite is made up of brucite (Mg(OH)₂), clinochrysotile (Mg₃[Si_{2-x}O₅](OH)_{4-4x}), magnesite (MgCO₃), and dolomite (CaMg(CO₃)₂), and a summary is presented in Table I. Mg(OH)₂ is the effective component in brucite and there is 79 wt % Mg(OH)₂ in the mineral. Figures 3–5 depict the thermogravimetric and derivative thermogravimetric curves of pure rigid polyurethane foams, aluminum hydroxide and natural brucite under a flow of N₂, respectively. Dehydration of aluminum hydroxide shows three

Table I. Phase Composition of Brucite

Phase	Brucite (Mg(OH) ₂)	Clinochrysotile (Mg ₃ [Si _{2-x} O ₅] (OH) _{4-4x})	Magnesite (MgCO ₃)	Dolomite (CaMg (CO ₃) ₂)
Content (wt %)	79%	9%	7%	5%

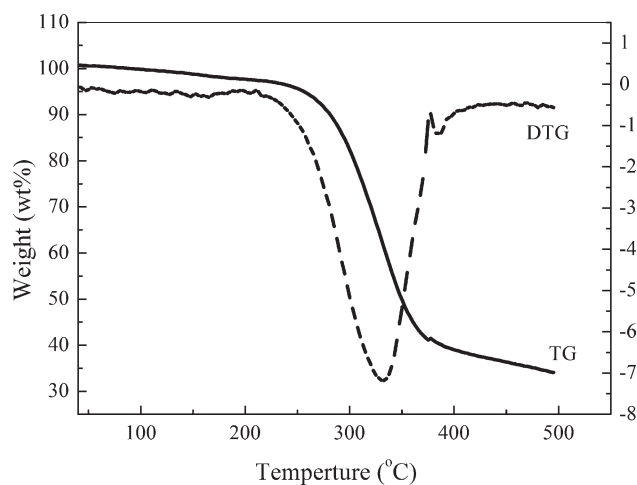


Figure 3. Thermogravimetric analysis of pure rigid polyurethane foams.

endothermic peaks: $\alpha\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O} \rightarrow \alpha\text{-AlOOH}, \alpha\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3$, and $\alpha\text{-AlOOH} \rightarrow \gamma\text{-Al}_2\text{O}_3$ at about 230, 310, and 500°C, respectively,³⁵ whereas the reaction: $\alpha\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3$ is the main endothermic decomposition route. The curves of brucite show a two-step weight loss. The first step is considered to involve the dehydration reaction of $\text{Mg}(\text{OH})_2$ between 300 and 450°C resulting in about 22 wt % weight loss corresponding to the XRD results.³⁶ The second step is due to the decomposition of residual minerals at higher temperature. In addition to the purity and decomposition behavior, the particle size of the fillers plays an important role in the flammability resistance,¹⁷ that the smaller the particle size, and the better the flame retardancy. The particle size distribution of the brucite measured by a laser particle size analyzer is shown in Figure 6(a) and the average size is 4.71 μm , while the aluminum hydroxide is 7.35 μm in Figure 6(b).

To achieve adequate flame reaction, a large concentration of the hydrated fillers is required. However, a large amount of fillers can impair the processing and mechanical properties of the polymer composites, especially the polyurethane foams, because

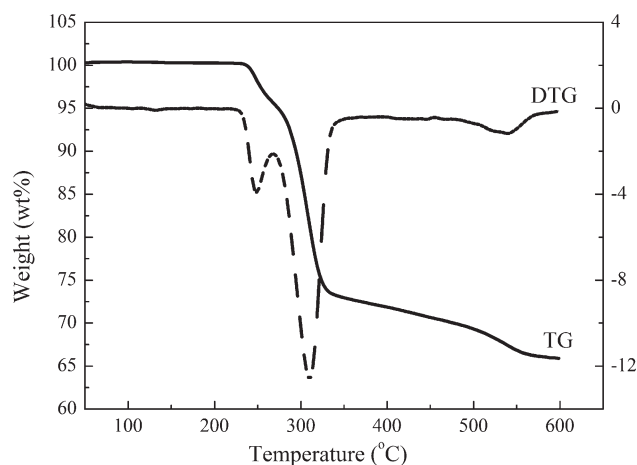


Figure 4. Thermogravimetric analysis of aluminum hydroxide.

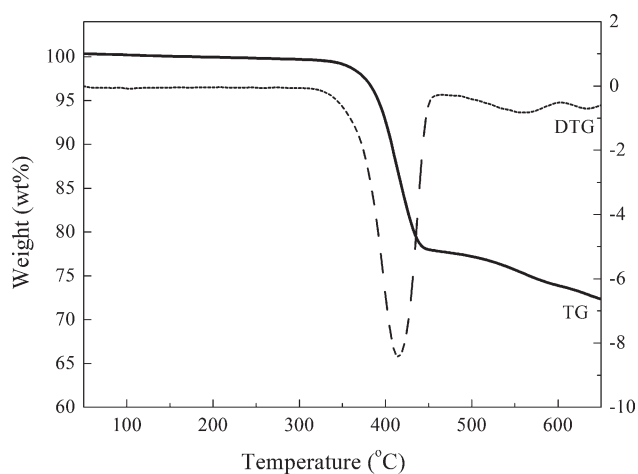


Figure 5. Thermogravimetric analysis of natural brucite.

of the two-component liquid. To achieve a better foaming process, the viscosity of the mixture of polyether polyol and flame retardant is limited to no more than 8000 mPa s^{-1} in this study. Hence, the content of the aluminum hydroxide or brucite is no more than 35 wt % of the rigid polyurethane foams.

The curves in Figure 7 indicate the changes in the limiting oxygen index of the polyurethane foams with aluminum hydroxide and with brucite. The pure rigid polyurethane foams are highly flammable with a limiting oxygen index of about 19.8%. The limiting oxygen index of polyurethane foams increases slightly with the increase of hydroxide or brucite content due to the endothermic nature. The limiting oxygen index of the rigid polyurethane foams with 35 wt % fillers increases from 19.8 to 22.6% for aluminum hydroxide and from 19.8 to 21.8% for brucite. They are only 2.8 and 2% higher than that of pure rigid polyurethane foams, respectively. Compared to brucite, aluminum hydroxide shows a better flame performance; however, the enhancement is not substantial. As shown in Figure 8, the compressive strength of the composites decrease both with the increase of aluminum hydroxide and brucite content, while the composite filled with brucite show better compressive strength than that with aluminum hydroxide.

To improve the flame retardance of the composites, a larger amount of hydrated fillers or some synergistic effects are required. The limiting oxygen index of the polyurethane foams with DMMP is shown in Figure 9. With 10 wt % DMMP, the limiting oxygen index of the polyurethane foams can be improved to 25.4%, which is much higher than those achieved by aluminum hydroxide and brucite. However, introduction of DMMP increases smoke emission and ductility,³⁷ and so after careful consideration, 10 wt % DMMP is incorporated into the polyether polyol as a flame retardant and viscosity depressant in this study.

The amount of aluminum hydroxide and brucite can be up to 60 wt % in the polyurethane foams by incorporating DMMP. As shown in Figure 10, DMMP improves the flame retardance of polyurethane foams filled by the hydrated fillers. With 10 wt % DMMP, the limiting oxygen index of the foams filled 35 wt

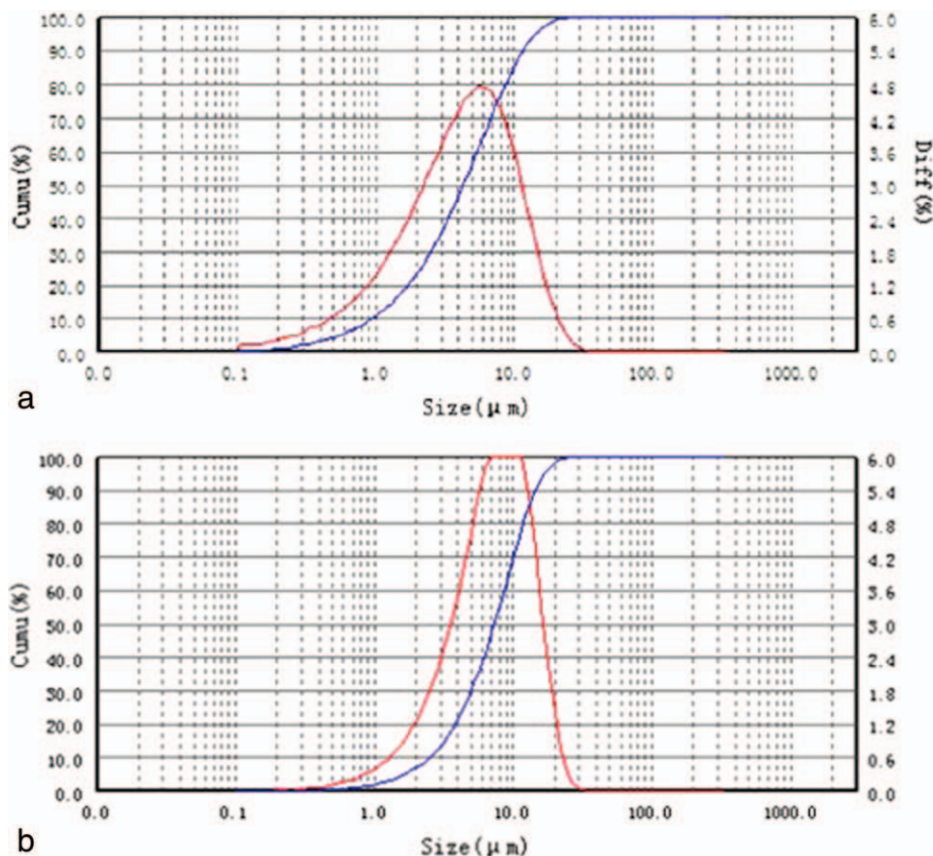


Figure 6. Particle size distribution of natural brucite (a) and aluminum hydroxide (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

% brucite and aluminum hydroxide increases from 21.8 and 22.6% to 27 and 29%, which are about 5.2 and 6.4% higher than those of the foams without DMMP, respectively. The limiting oxygen index of the foams can be increased to 28.4 and 32.4% with 60 wt % brucite and aluminum hydroxide, respectively. Using DMMP, the limiting oxygen index of rigid polyurethane foams filled with brucite and aluminum hydroxide

increases by about 9.4 and 12.6%, respectively. As shown in Figure 11, the compressive strength of the composites decreases from 0.4 to 0.39 MPa with the addition of 10 wt % DMMP and the compressive strength of the composites decrease with the increase of aluminum hydroxide and brucite content. The better compressive strength of brucite may be due to the much smaller particle size.

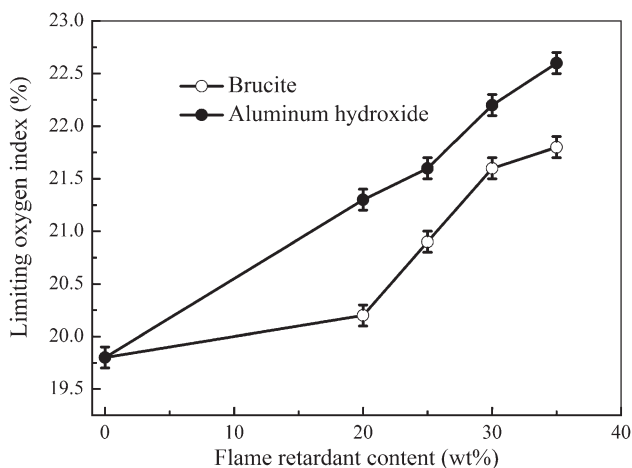


Figure 7. Effects of aluminum hydroxide and brucite content on the limiting oxygen index of polyurethane foams.

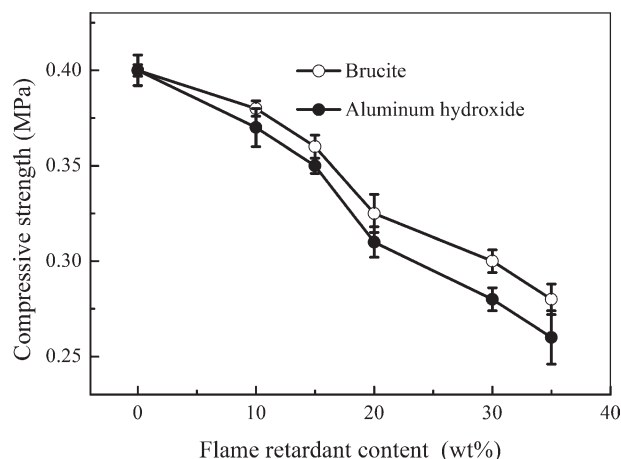


Figure 8. Effects of aluminum hydroxide and brucite content on the compressive strength of polyurethane foams.

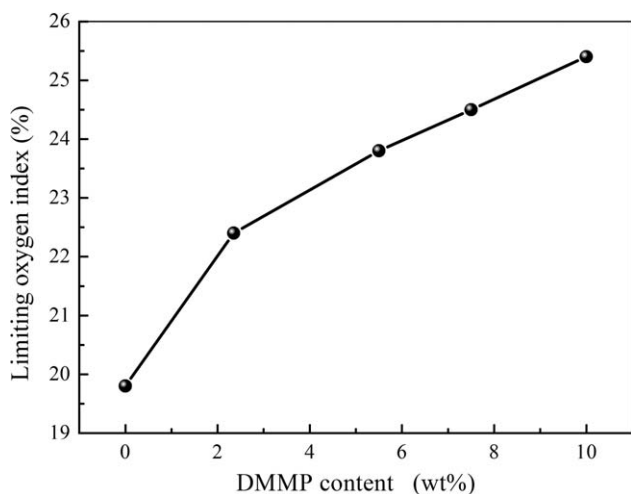


Figure 9. Effects of DMMP content on the LOI of rigid polyurethane foams.

The limiting oxygen indices show that although introduction of aluminum hydroxide and natural brucite improves the flame retardance of rigid polyurethane foams, the enhancement is not good enough. The flame retarding effect of the fillers is close to the difference of the thermal stability between pure rigid polyurethane and flame retardant fillers. As shown in Figure 3, the degradation of pure rigid polyurethane foams starts at below 150°C with an endothermic peak at about 300°C and the decomposition occurs mainly between 200 and 400°C. To reduce degradation and combustion, the effective temperature range of the flame retardant must match. The main weight loss of aluminum hydroxide occurs between 230 and 500°C, and the weight loss of natural brucite is 350 and 600°C. The decomposition temperatures of the flame retardants are somewhat higher than those of the foams, with brucite being significantly higher.

The XRD results are used to investigate the decomposition behavior of the fillers and the synergistic mechanism of the fill-

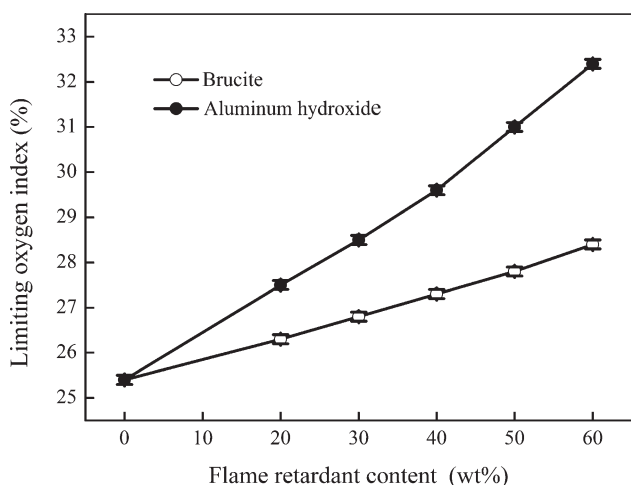


Figure 10. Effects of aluminum hydroxide and brucite content on the limiting oxygen index of polyurethane foams filled with DMMP.

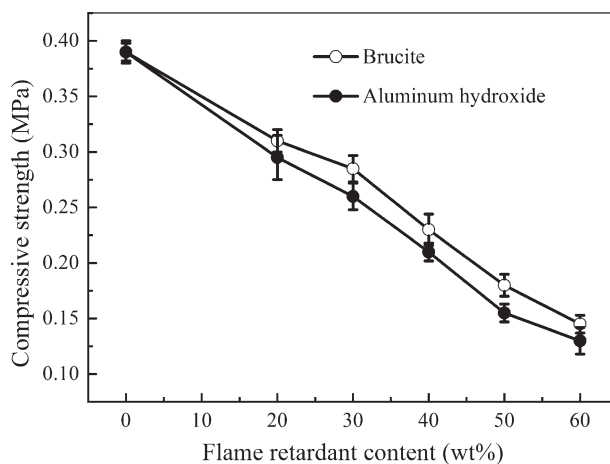


Figure 11. Effects of aluminum hydroxide and brucite content on the compressive strength of polyurethane foams filled with DMMP.

ers and DMMP. The powder XRD results of the residues of hydroxides filled polyurethane foams from LOI testing are shown in Figure 12. Aluminum hydroxide is almost completely decomposed with $\text{AlO}(\text{OH})$ and Al_2O_3 left in the residue whereas only little brucite decomposes because only a small amount of MgO exist in the residue. Degradation of rigid polyurethane occurs much earlier than aluminum hydroxide and natural brucite, implying that there is not enough time and temperature for the hydroxides to fulfill their function when the composite foams burning. This is because of the flame retarding properties of the hydroxide result from the endothermic decomposition of the hydroxide, cooling of the solid or condensed phase, release of water, and diluting and cooling the flammable combustion products in the vapor phase.¹⁷ The flame retardant effects are weakened by the delay in endothermic decomposition, and consequently, aluminum hydroxide and brucite only improves the flame reaction slightly, although aluminum hydroxide is the better one.

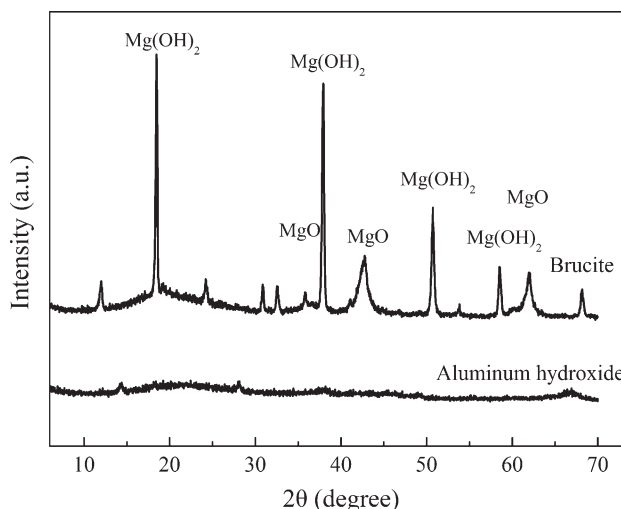


Figure 12. Powder X-ray diffraction spectra of the residue of polyurethane foams filled with aluminum hydroxide and brucite.

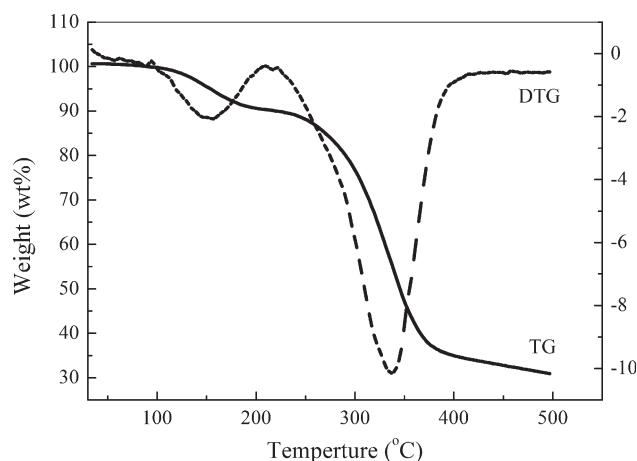


Figure 13. Thermogravimetric analysis of DMMP/polyurethane foams

DMMP significantly improves the flammability performance of the polyurethane foams. This can be seen as the increase in the limiting oxygen index and the thermogravimetric curves in Figure 13. DMMP and hydroxide are effective in different stages. DMMP plays an important role in the earlier stage, which involves the gas phase, as confirmed by the powder XRD results in Figures 12 and 14 that the absence of phosphorus compounds in the residue. There is no reaction between DMMP and the fillers. Decomposition of DMMP at a lower temperature than the polyurethane foams delays burning, while hydroxides play an important role at a higher temperature. The synergistic effects offered by the hydroxide and DMMP increase the limiting oxygen index. The difference in the decomposition temperature gives rise to the difference observed from aluminum hydroxide and brucite. A combination of DMMP and aluminum hydroxide is effective between 100 and 350°C. The higher decomposition temperature of brucite leads to worse flammability performance than aluminum hydroxide.

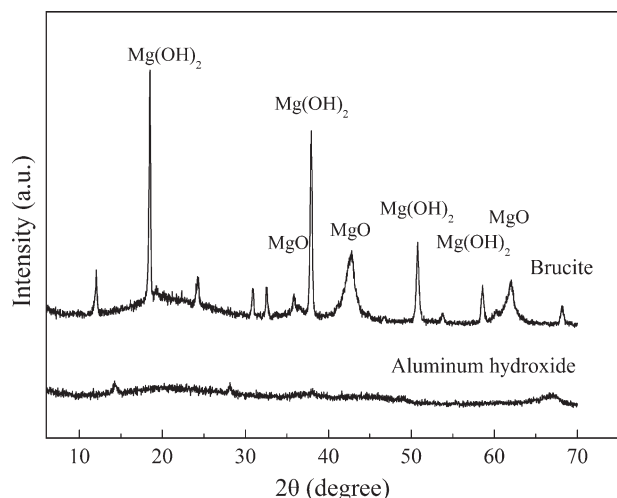


Figure 14. Powder X-ray diffraction spectra of the residue of polyurethane foams filled with hydroxides and DMMP.

CONCLUSION

Series of rigid halogen-free and flame-retarding polyurethane foams are prepared with aluminum hydroxide, brucite, and DMMP. The effects of the fillers on the flame retarding properties of the composites and the synergistic effects when combined with DMMP are investigated. The aluminum hydroxide gives rise to better flammability performance of the rigid polyurethane foam because the dehydration temperature is closer to that of the foam than is brucite. The hydroxide fillers play a limited role in the rigid polyurethane foams when they are introduced individually, but incorporation of 60 wt % hydroxide fillers with 10 wt % DMMP, the limiting oxygen indices increase to 28.4% for brucite and 32.4% for aluminum hydroxide, respectively.

ACKNOWLEDGMENTS

This work is jointly supported by Special fund of coconstruction of Beijing Education Committee, National High Technology Research and Development Program ("863"Program) of China (2012AA06A109), the project of China Geological Survey (No.1212011120309), the open foundation of National Laboratory of Mineral Materials of China University of Geosciences (Grant No. 519002310062 08A004, 08A006, and 08A003), and City University of Hong Kong Strategic Research Grant (SRG) No. 7008009.

REFERENCES

- Michele, M.; Alessandra, L. *FR Design for Foam Materials, Fire Retardancy of Polymeric Materials*, 2nd ed.; CRC Press: US, **2009**, Chapter 25.
- Duquesne, S.; Delobel, R.; Le Bras, M.; Camino, G. *Polym. Degrad. Stabil.* **2002**, *77*, 333.
- Meng, X. Y.; Ye, L.; Zhang, X. G.; Tang, J. H.; Ji, X.; Li, Z. M. *J. Appl. Polym. Sci.* **2009**, *114*, 853.
- Tarakcilar, A. R. *J. Appl. Polym. Sci.* **2011**, *120*, 2095.
- Camino, G.; Duquesne, S.; Delobel, R.; Eling, B.; Lindsay, C.; Roels, T. *Abstr. Pap. Am. Chem. Soc.* **2000**, *220*, 333.
- Duquesne, S.; Brasa, M. L.; Bourbigota, S.; Delobel, R.; Caminoc, G.; Eling, B.; Lindsay, C.; Roels, T. *Polym. Degrad. Stabil.* **2001**, *74*, 493.
- Duquesne, S.; Brasa, M. L.; Bourbigota, S.; Delobel, R.; Vezin, H.; Camino, G.; Eling, B.; Lindsay, C.; Roels, T. *Fire Mater.* **2003**, *3*, 103.
- Modesti, M.; Lorenzetti, A.; Simioni, F.; Camino, G. *Polym. Degrad. Stabil.* **2002**, *77*, 195.
- Bian, X. C.; Tang, J. H.; Li, Z. M.; Lu, Z. Y.; Lu, A. *J. Appl. Polym. Sci.* **2007**, *5*, 3347.
- Ye, L.; Meng, X. Y.; Ji, X.; Li, Z. M.; Tang, J. H. *Polym. Degrad. Stabil.* **2009**, *6*, 971.
- Konig, A.; Fehrenbacher, U.; Kroke, E.; Hirth, T. *J. Fire Sci.* **2009**, *27*, 187.
- Konig, A.; Fehrenbacher, U.; Hirth, T.; Kroke, E. *J. Cell. Plast.* **2008**, *44*, 469.
- Price, D.; Liu, Y.; Milnes, G. J.; Hull, R.; Kandola, B. K.; Richard Horrocks, A. *Fire Mater.* **2002**, *26*, 201.

14. Dick, C. M.; Denecker, C.; Liggat, J. J.; Mohammed, M. H.; Snape, C. E.; Seeley, G.; Lindsay, C.I.; Eling, B. *Polym. Int.* **2000**, *49*, 1177.
15. Kageoka, M.; Tairaka, Y.; Kodama, K. *J. Cell. Plast.* **1997**, *33*, 219.
16. Le Bras, M. *Fire Retardancy of Polymers: New Applications of Mineral Fillers*. Royal Society of Chemistry: UK, **2005**.
17. Hornsby, P. *Fire-Retardant Fillers: Fire Retardancy of Polymeric Materials*, 2nd ed.; CRC Press: US, **2009**, Chapter 7.
18. Li, X.; Ma, G. B.; Liu, Y. Y. *Ind. Eng. Chem. Res.* **2009**, *48*, 763.
19. Rothon, R. N.; Hornsby, P. R. *Polym. Degrad. Stabil.* **1996**, *54*, 383.
20. Kaliskyo, R.; Simons, J. *Chim. Oggi Chem. Today* **1995**, *13*, 39.
21. Sain, M.; Park, S. H.; Suhara, F.; Law, S. *Polym. Degrad. Stabil.* **2004**, *83*, 363.
22. Chen, X. L.; Yu, J.; Guo, S. Y.; Lu, S. J.; Luo, Z.; He, M. *J. Mater. Sci.* **2009**, *44*, 1324.
23. Oyama, H. T.; Sekikawa, M.; Ikezawa, Y. *J. Macromol. Sci. B Phys.* **2011**, *50*, 463.
24. Li, Z. Z.; Qu, B. J. *Polym. Degrad. Stabil.* **2003**, *81*, 401.
25. Lv, J.; Qiu, L. Z.; Qu, B. J. *Nanotechnology* **2004**, *15*, 1576.
26. Zhang, G.; Ding, P.; Zhang, M.; Qu, B. J. *Polym. Degrad. Stabil.* **2007**, *92*, 1715.
27. Sener, A. A.; Demirhan, E. *Mater. Des.* **2008**, *29*, 1376.
28. Cai, Y. B.; Wei, Q. F.; Shao, D. F.; Hu, Y. J. *Energy Inst.* **2009**, *82*, 28.
29. Liu, Y.; Li, J.; Wang, Q. *Mater. Manufact. Process.* **2008**, *23*, 284.
30. Du, G. X.; Ding, H.; Wang, B. K.; Xue, Q. *Mater. Sci. Forum* **2009**, *1*, 610.
31. Dai, S. J.; Hu, Z. G.; Bai, L. M.; Lv, D.; Yang, S. Y. International Conference on Advances in Materials and Manufacturing Processes Shenzhen, *People's Republic of China*, Nov 06–08, **2010**.
32. Ma, Z. L.; Wang, J. H.; Zhang, X. Y. *J. Appl. Polym. Sci.* **2008**, *107*, 1000.
33. Simandl, G. J.; Paradis, S.; Irvine, M. *Geosci. Canada* **2007**, *34*, 57.
34. Lorenzetti, A.; Modesti, M.; Besco, S.; Hrelja, D.; Donadi, S. *Polym. Degrad. Stabil.* **2011**, *96*, 1455.
35. Le Bras, M. *Fire Retardancy of Polymers: New Applications of Mineral Fillers*. Royal Society of Chemistry: British, **2005**; p 20.
36. Yang, N. R.; Yue, W. H. *The Handbook of Inorganic Metalloid Materials Atlas (in Chinese)*; Wuhan University of Technology Press: Wuhan, **2000**.
37. Joseph, P.; Ebdon, J. R. *Phosphorus-Based Flame Retardants: Fire Retardancy of Polymeric Materials*, 2nd ed.; CRC Press: US, **2009**; Chapter 5.