

Flame retardancy of polyurethane foam reinforced by hollow glass microspheres and ammonium polyphosphate

Ye Niu

yniu@aku.edu.cn

Ankang University

Yiyang Liu

Haoli Wang

Shuo Wang

Short Report

Keywords: flame retardant, hollow glass microspheres, polyurethane foam, ammonium polyphosphate

Posted Date: October 9th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-11071437/v1>

License:  This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Flame retardancy of polyurethane foam reinforced by hollow glass microspheres and ammonium polyphosphate

Ye Niu*, Yiyang Liu, Haoli Wang, Shuo Wang*

Ankang Research Centre of New Nano-materials Science and Technology, Innovation Research Institute of Advanced Energy Storage Materials and Battery Technology for Future Industrialization, Ankang University, Shaanxi, Ankang 725000, P. R. China. School of Chemistry and Environment, Shaanxi Provincial University Key Laboratory of Interfacial Porous Materials,

*Corresponding author. Ye Niu, E-mail address: yniu@aku.edu.cn (Y. Niu).

*Corresponding author. Shuo Wang, E-mail address: swang@aku.edu.cn (S. Wang).

Abstract

Aiming at the characteristics of traditional polyurethane foam and easy combustion. In this work, a simple “one pot method” was used to prepared flame-retardant polyurethane foam through hollow glass microspheres (HGM) and ammonium polyphosphate (APP). The experimental results indicate that HGM and APP has good compatibility with polyurethane foam. The prepared polyurethane foam has rich macroporous structure and elasticity. In addition, compared with pure foam, flame retardant foam is hydrophobic. Furthermore, compared with pure PU foam, PU-FR foam has excellent flame retardancy, compared with PU foam, the peak heat release rate (pHRR) of PU-FR foam is reduced by about 12.9%. PU-FR foam has the characteristics of simple preparation process and excellent flame retardant performance, providing theoretical support for the industrial preparation of high-performance flame retardant polyurethane sponge.

Keywords: flame retardant; hollow glass microspheres; polyurethane foam; ammonium polyphosphate

1. Introduction

Polyurethane foam is widely used in many fields such as building energy conservation[1], transportation[2], furniture manufacturing[3], aerospace and other fields[4], and has become an indispensable functional material in modern industry and people's livelihood fields due to its low density, low thermal conductivity, outstanding thermal insulation and sound insulation effects[5-7]. Polyurethane foam is widely used in building exterior wall insulation, cold chain transportation insulation and other aspects, which greatly promotes the development of energy-saving materials[8, 9]. However, the molecular chains of polyurethane foam are composed of elements such as carbon, hydrogen and oxygen, and its porous structure formed after foaming tends to retain oxygen, resulting in high flammability[10]. With a limiting oxygen index (LOI) of only about 19%, it is classified as a flammable polymer material[11]. When exposed to heat or open flame, polyurethane foam burns rapidly, releasing a large amount of heat, dense black smoke, as well as toxic gases including carbon monoxide and hydrogen cyanide[12]. This not only accelerates the spread of fire but also poses a severe threat to human life, severely restricting the application of polyurethane foam[13]. Therefore, the efficient and environmentally friendly flame-retardant modification of polyurethane foam to improve its flame retardancy and thermal stability is crucial for eliminating potential safety hazards and expanding its application scope, which possesses important application value and research significance[14]. However, polyurethane foam is composed of carbon, hydrogen, oxygen and other elements. The porous structure formed after foaming is easy to store oxygen, leading to its

flammability[10]. The limiting oxygen index is only about 19%, which belongs to flammable polymer materials[15]. When heated or exposed to open fire, polyurethane foam will burn rapidly and release a lot of heat, dense black smoke, carbon monoxide, hydrogen cyanide and other harmful gases, which will not only accelerate the spread of fire, but also pose a great threat to human life safety, and also severely limit the application of polyurethane foam[16, 17]. Therefore, efficient and environmentally friendly flame-retardant modification of polyurethane foam to improve its flame-retardant performance and thermal stability is the key to solve its application safety and expand its application range, which has important application value and research significance.

Halogenated flame retardants release corrosive hydrogen halide gases and toxic carcinogenic substances during combustion, which violates the requirements of green environmental protection and safe application. Consequently, they have been rarely used at present, and environmentally friendly flame retardants featuring halogen-free, low-smoke and non-toxic properties have become the main research direction for flame retardancy of polyurethane foams. As a typical halogen-free phosphorus-nitrogen flame retardant, ammonium polyphosphate exhibits many advantages including high flame retardant efficiency, excellent smoke suppression performance, strong thermal stability and good compatibility with polymer matrices. During combustion, flame retardancy can be achieved by dehydration and charring, diluting combustible gas, blocking heat transfer and other multiple actions, and it is one of the preferred flame retardants for halogen-free flame retardant modification of polyurethane foam[18, 19]. However, the

single modification with ammonium polyphosphate suffers from problems such as uneven dispersion and deteriorated mechanical properties of polyurethane foams at high loading levels, making it difficult to simultaneously meet the dual requirements of flame retardancy and mechanical performance[20]. In contrast, the combined use of inorganic flame-retardant fillers with ammonium polyphosphate can achieve enhanced flame retardant effects. Hollow glass microspheres are lightweight[21-23], hollow and heat-resistant inorganic glassy particles, characterized by high thermal stability, low thermal conductivity and low cost[24-26]. Their unique hollow structure can not only form a physical barrier during material combustion, but also promote the rapid formation of a compact char layer on the polymer matrix to inhibit the combustion reaction[27]. Meanwhile, as inorganic fillers, they improve the stability of composite materials. The flame retardancy of polyurethane foam can be significantly improved when hollow glass microspheres and ammonium polyphosphate are mixed in polyurethane foam[28-30].

Based on this, composite flame-retardant polyurethane foams were prepared by a one-step method in this study. The hollow glass microsphere and ammonium polyphosphate were introduced as the composite flame retardant to study the effect of the composite flame retardant on the flame retardancy, thermal stability and microstructure of polyurethane foam, and analyze its synergistic flame retardant mechanism. A kind of polyurethane foam with high efficiency, environmental protection and excellent flame retardancy was developed to provide theoretical basis and experimental support for the development and application of flame retardant

polyurethane foam.

2. Materials and methods

2.1 Materials

polyether polyol was purchased from Jiangsu Haian Petrochemical Co., Ltd. Hollow glass microsphere (K46) were purchased from 3M Co., Ltd. Stannous octoate、dimethyl silicone oil、isocyanate and Triethanolamine (TEOA) were purchased from Macklin Co., Ltd. Pure water was purchased from laboratory.

2.2 Methods

2.2.1 Preparation of PU foam.

Add 50 g of polyether polyol, 0.5 g of stannous octoate, 1.5 g of triethanolamine, 2 g of dimethyl silicone oil and 2 g of water into the beaker, mix evenly, then add 60 g of isocyanate, stir to foam, pour into the mold, mature at room temperature for 24 h and demold to obtain polyurethane foam (PU foam).

2.2.2 Preparation of PU-FR foam.

Add 50 g polyether polyol, 0.5 g stannous octoate, 1.5 g triethanolamine, 2 g dimethyl silicone oil, 2 g water, 0.8 g HGM, 0.8 g ammonium polyphosphate into the beaker, mix evenly, then add 60 g isocyanate, stir to foam, pour into the mold, mature at room temperature for 24 h and demold to obtain flame retardant polyurethane foam (PU-FR foam).

3. Results and discussion

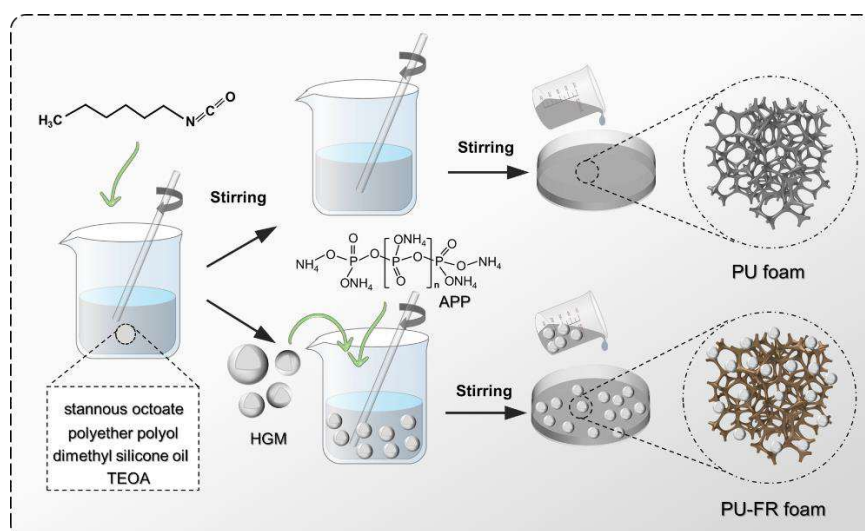


Figure. 1 Schematic illustration of the preparation process and structure of PU foam and PU-FR foam.

The morphology of HGM, PU foam and PU-FR foam were characterized by scanning electron microscope. The scanning electron microscopy (SEM) images of hollow glass microspheres (HGM) are shown in Figures 2A-2C[11]. It can be observed that the HGM exhibit a regular spherical shape, with an uneven particle size distribution and no obvious agglomeration, indicating good dispersibility prior to addition. The presence of a small number of fine particles adhering to the surface of the hollow glass microspheres is due to adsorption of impurities from the air. The SEM images of pure PU foam (Figure 2D-2F) exhibit a typical three-dimensional network structure with interconnected microporous structure, uniform pore size distribution, and smooth and dense pore walls. This structure provides space for the introduction of flame retardants. Compared to pure PU foam, the foam with the addition of hollow glass microspheres and ammonium polyphosphate (Figure 2G-2I) still maintains a three-dimensional network structure, but its microstructure has undergone significant changes. The surface of the pore walls is not smooth, with obvious depressions and roughness, as

shown in Figure 2H. It can be clearly observed that a large number of particles are distributed inside and on the surface of the pore walls, and particle agglomeration has formed in some areas. These structural changes indicate that the flame retardant filler has been successfully introduced into the foam matrix. In addition, the EDS energy spectrum of the PU-FR foam shows that the content of C element is 55.4%, N element is 3.6%, O element is 24.4%, Na element is 0.5%, Si element is 13.1%, and P element is 3.1%. The Si and P elements correspond to the characteristic elements of HGM and APP respectively, demonstrating that both flame retardant components have been successfully incorporated into the system[31-33].

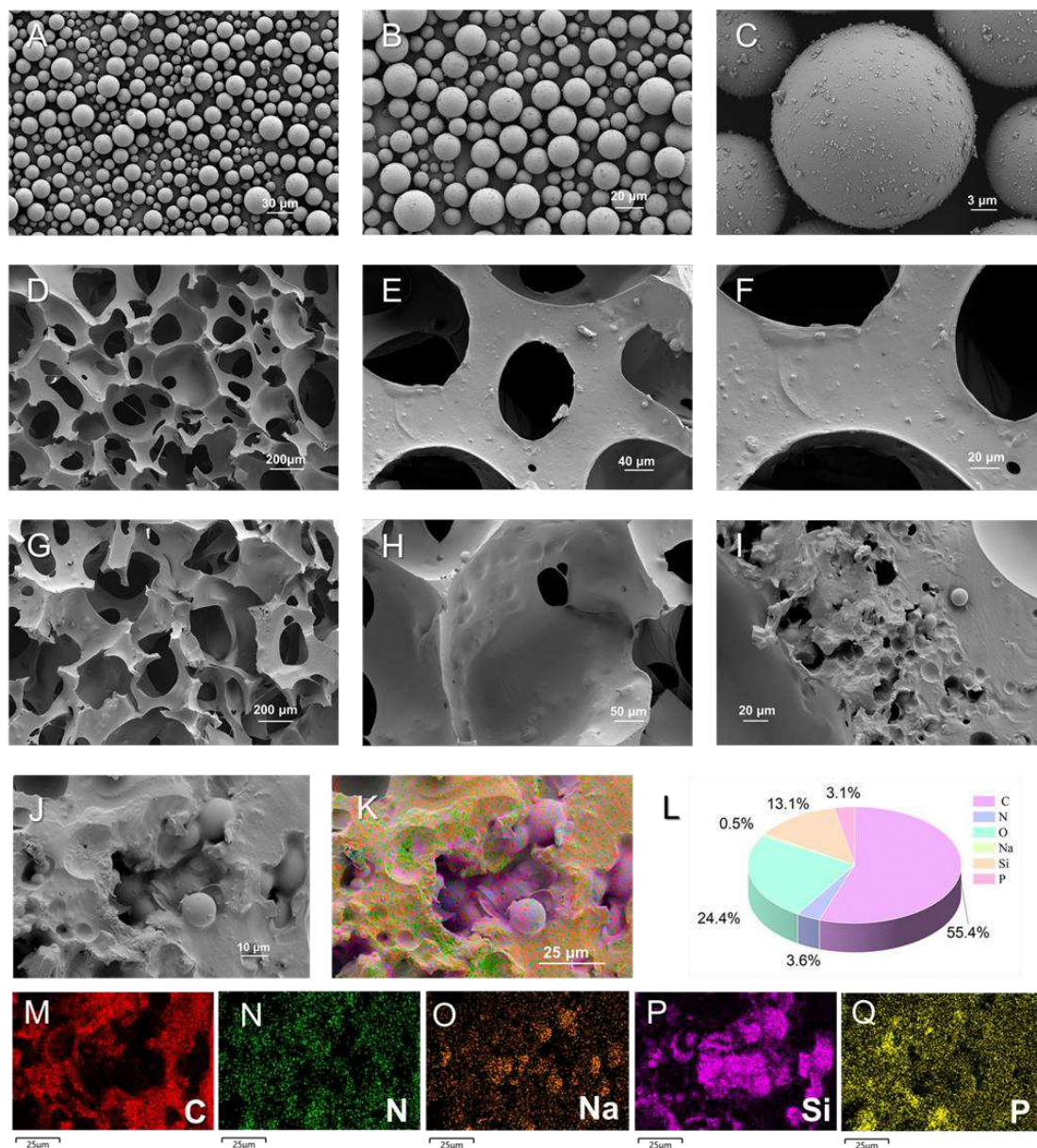


Figure. 2 (A-C) SEM images of HGM. (D-F) SEM images of pure PU foam. (G-I) SEM images of PU-FR foam. (L-Q) Elemental maps of the PU-FR.

The chemical structures of HGM, APP, pure PU, and PU-FR were characterized by FTIR. $1000\text{--}1100\text{ cm}^{-1}$ corresponds to the Si-O-Si stretching vibration of HGM; $3000\text{--}3300\text{ cm}^{-1}$ corresponds to the N-H stretching vibration of APP, $1050\text{--}1280\text{ cm}^{-1}$ corresponds to the P=O and P-O-P characteristic absorption peak, and $500\text{--}600\text{ cm}^{-1}$ corresponds to the P-O bending vibration; For pure PU foam, 3320 cm^{-1} is the N-H

stretching vibration in the amino acid ester, 1720 cm^{-1} is the characteristic peak of the amino acid ester $\text{C}=\text{O}$, and $1050\text{--}1200\text{ cm}^{-1}$ is the C-O-C stretching vibration. Compared with PU sponge, the absorption peak of PU-FR sponge widens at $1000\text{--}1150\text{ cm}^{-1}$, which is due to the stretching of Si-O-Si in HGM and P-O in APP. Therefore, the flame retardants HGM and APP were successfully introduced into the PU foam[10].

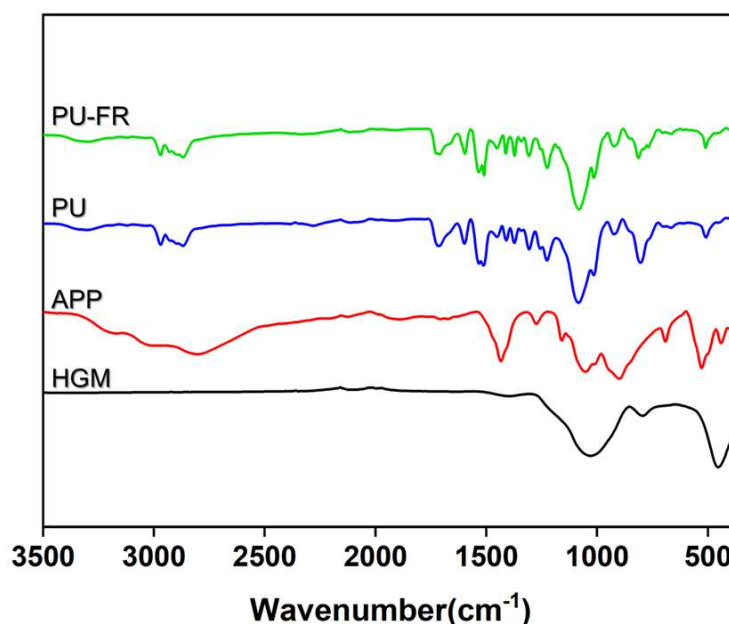


Figure. 3 Fourier transform infrared spectrum of HGM, APP, pure PU and PU-FR.

The surface wettability of PU-FR foam was characterized using a contact angle measuring instrument, as shown in Figure 4. Water droplets remained on the surface of the PU-FR foam in a spherical shape with a contact angle of 125.9° . Water could not penetrate into the porous channels inside the foam, indicating that HGM successfully constructed a hydrophobic surface after flame retardant modification of the foam, solved the problem of poor water resistance of the foam, and expanded the application of polyurethane foam in humid environments.

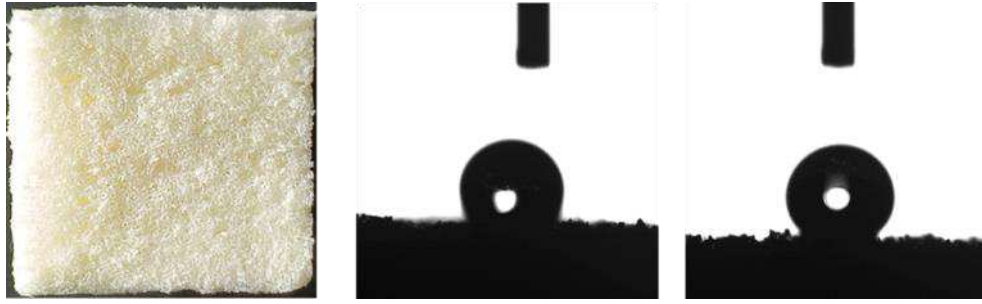


Figure. 4 Water contact angle of PU-foam.

The flame retardancy of PU foam and PU-FR foam was investigated by using cone calorimeter. As shown in Figure 5A, the pure PU foam completely burned without a complete carbon layer, indicating that the pure PU foam was difficult to form an effective barrier layer during the combustion process[34, 35]. In contrast, the PU-FR foam formed a dense carbon layer after combustion (Figure 5B), indicating that the synergistic effect of hollow glass microspheres and ammonium polyphosphate promotes the carbonization process of the PU matrix and inhibits further thermal decomposition and combustion spread of the matrix. The HRR curves of pure PU foam and PU-FR foam are shown in Figure 5C. At 90 s, the peak heat release rate (pHRR) of pure PU foam is 432.35 kW m^{-2} , and then the heat release rate drops rapidly, indicating that pure PU foam burns intensely and releases a large amount of heat in a short period of time. In contrast, the pHRR value of PU-FR foam is 376.64 kW m^{-2} , which is 12.9% lower than that of pure PU foam, indicating that the addition of HGM and APP improves the flame retardancy of pure PU foam. The total heat release (THR) curve reflects the total heat release of the material throughout the entire combustion process. As shown in Figure 5D, the THR of pure PU foam is 76.76 MJ m^{-2} , and the THR of PU-FR foam is 61.28 MJ m^{-2} , which is 20% lower than that of pure PU foam. This decrease is

attributed to the dense char layer, which blocks heat and gas exchange, thereby reducing the thermal decomposition of the polyurethane matrix[36, 37].

The flame retardant mechanism of PU-FR foam is as follows: ammonium polyphosphate decomposes upon heating to generate polyphosphate, which catalyzes the dehydration and carbonization of polyurethane. At the same time, inert gases are released to promote the expansion of the carbon layer, relying on the dense carbon layer to achieve thermal insulation and oxygen isolation in the condensed phase flame retardant. In addition, the inert gases such as ammonia produced by decomposition dilute the combustible mixture to achieve gas phase flame retardant. Hollow glass microspheres, as inorganic flame retardants, enhance the carbon layer skeleton with a rigid hollow structure, delay the inward conduction of external heat, and slow down the thermal decomposition of PU foam. The combination of HGM and APP can effectively reduce the heat release rate and total heat release of PU foam, significantly improving the flame retardant performance of PU foam[38].

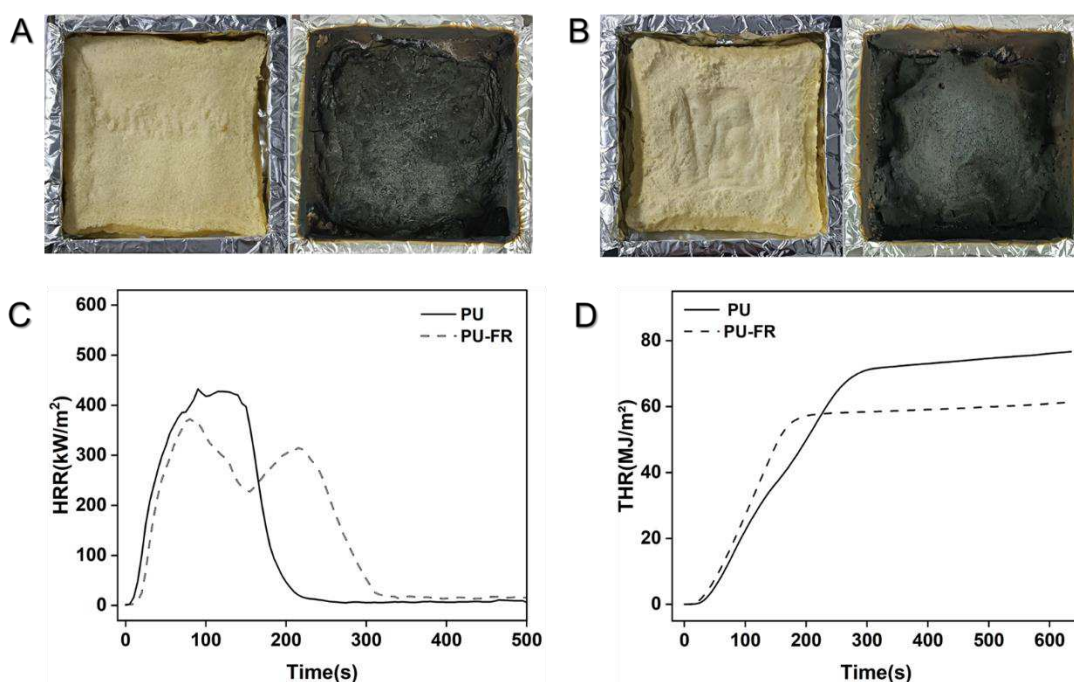


Figure. 4 Digital photographs of the (A) pure PU, (B) PU-FR before (left) and after (right) the cone calorimetry tests. (C) HRR curves of pure PU and PU-FR. (D) THR curves of pure PU and PU-FR.

4. Conclusions

In summary, we demonstrated a method for preparing flame retardant polyurethane foam through a simple “one pot method”. The prepared PU-FR has rich macroporous structure and elasticity. In addition, the water contact angle of flame retardant foam is 125.9° , which is super hydrophobic. Notably, PU-FR foam has excellent flame retardancy, the pHRR value of PU-FR foam is 376.64 kW m^{-2} , which is 12.9% lower than that of pure PU foam, and the THR of PU-FR foam is 61.28 MJ m^{-2} , which is 20% lower than that of pure PU foam. Based on the above results, the disadvantages of traditional polyurethane foam being flammable have been effectively solved through a simple and green preparation method, expanded the application scope of polyurethane foam.

CRedit authorship contribution statement

Ye Niu: Formal analysis, Writing—original draft, Investigation, Methodology. Yiyang Liu: Visualization. Haoli Wang: Writing—review & editing. Shuo Wang: Writing—review & editing,

Conflict of Interest

The authors declare no conflict of interest.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

The authors are grateful to the Natural Science Basic Research Program of Shaanxi (No. 2025ZC-YYDP-34), Scientific Research Program Funded by Education Department of Shaanxi Provincial Government (No. 25JK0291), High-level Talents Foundation of Ankang University (No. 2023AYQDZR11).

References

1. L. Gu, Z. Ren, S. Li, R. Song, H. Wu, L. Zhang, X. Liu, F. Sun, Raw materials, preparation methods, flame retardant properties and applications of bio-based flame retardant polyurethanes: Research progress and challenges, *European Polymer Journal*, 232 (2025).
2. R. Lubczak, D. Broda, M. Kus-Liśkiewicz, D. Szczęch, E. Bobko, B. Dębska, M. Szpiłyk, J. Lubczak, Flame retardant polyurethane foams with starch unit, *Polymer Testing*, 104 (2021).
3. V.K. Mishra, R.H. Patel, Synthesis and characterization of flame retardant polyurethane: Effect of castor oil polyurethane on its properties, *Polymer Degradation and Stability*, 175 (2020).
4. J. Wang, B. Xu, X. Wang, Y. Liu, A phosphorous-based bi-functional flame retardant for rigid polyurethane foam, *Polymer Degradation and Stability*, 186 (2021).
5. X. Zhang, Y. Huang, J. Zhang, B. Liao, J. Men, L. Wang, J. Yang, D. Chen, Self-Foaming, Oil-Absorbable, Flame Self-Extinguishing and Thermal Insulation POSS/PDMS Foams, *Small*, 21 (2025).
6. E. Akdogan, M. Erdem, M.E. Ureyen, M. Kaya, Rigid polyurethane foams with halogen-free flame retardants: Thermal insulation, mechanical, and flame retardant properties, *Journal of Applied Polymer Science*, 137 (2019).
7. Y. Chen, L. Li, X. Wu, Construction of an efficient ternary flame retardant system for rigid polyurethane foam based on bi-phase flame retardant effect, *Polymers for Advanced Technologies*, 31 (2020) 3202-3210.

8. P. Kopczyńska, T. Calvo-Correas, A. Eceiza, J. Datta, Synthesis and characterisation of polyurethane elastomers with semi-products obtained from polyurethane recycling, *European Polymer Journal*, 85 (2016) 26-37.
9. L. Liu, Z. Wang, M. Zhu, Flame retardant, mechanical and thermal insulating properties of rigid polyurethane foam modified by nano zirconium amino-tris-(methylenephosphonate) and expandable graphite, *Polymer Degradation and Stability*, 170 (2019).
10. Y. Niu, S. Wang, Z. Zhu, M. Su, Y. Wang, L. Yan, Y. Ma, H. Sun, W. Liang, A. Li, Hollow glass microspheres modified polyurethane sponge with enhanced flame retardancy, *Journal of Applied Polymer Science*, 139 (2022).
11. S. Wang, Y. Chen, J. Zhang, T. Wang, Y. Niu, J. Wang, Enhanced flame retardancy of polyurethane foam with alginate-based flame-retardant coating, *International Journal of Biological Macromolecules*, 289 (2025).
12. W. Yao, D. Zhang, Y. Zhang, T. Fu, D. Guan, Y. Dou, Synergistic Flame Retardant Effects of Expandable Graphite and Ammonium Polyphosphate in Water-Blow Polyurethane Foam, *Advances in Materials Science and Engineering*, 2019 (2019) 1-8.
13. R. Yang, B. Wang, X. Han, B. Ma, J. Li, Synthesis and characterization of flame retardant rigid polyurethane foam based on a reactive flame retardant containing phosphazene and cyclophosphonate, *Polymer Degradation and Stability*, 144 (2017) 62-69.
14. S.-D. Jiang, G. Tang, J. Chen, Z.-Q. Huang, Y. Hu, Biobased polyelectrolyte multilayer-coated hollow mesoporous silica as a green flame retardant for epoxy resin,

Journal of Hazardous Materials, 342 (2018) 689-697.

15. S. Wang, W. Liu, D. Yang, X. Qiu, Highly Resilient Lignin-Containing Polyurethane Foam, *Industrial & Engineering Chemistry Research*, 58 (2018) 496-504.

16. Y. Niu, S. Wang, Z. Zhu, M. Su, Y. Wang, L. Yan, Y. Ma, H. Sun, W. Liang, A. Li, Robust composite aerogels with excellent flame retardant and thermal insulation properties based on modified hollow glass microspheres, *Polymer Degradation and Stability*, 202 (2022).

17. Y. Niu, Q. Zhou, S. Ma, X. Du, H. Zhang, S. Wang, Janus film based on konjac glucomannan with excellent flame retardancy enhanced by hollow glass microspheres, *International Journal of Biological Macromolecules*, 330 (2025).

18. Y. Niu, X. Du, S. Ma, H. Zhang, X. Meng, S. Wang, Flame Retardancy Konjac Glucomannan Based Aerogel Enhanced by Aluminum Hydroxide Coated Hollow Glass Microspheres, *Journal of Applied Polymer Science*, 143 (2025).

19. N. Wang, G. Xu, Y. Wu, J. Zhang, L. Hu, H. Luan, Q. Fang, The influence of expandable graphite on double-layered microcapsules in intumescent flame-retardant natural rubber composites, *Journal of Thermal Analysis and Calorimetry*, 123 (2015) 1239-1251.

20. M. Li, Z. Zhu, Y. Chen, Y. Pan, X. Cao, Y. Jing, R. Jiao, H. Sun, J. Li, A. Li, Preparation of composite aerogels with excellent flame retardant and thermal insulation properties based on modified hollow glass microspheres, *Polymer Degradation and Stability*, 228 (2024).

21. S. Wang, Y. Niu, L. Yan, Y. Jing, Z. Zhu, H. Sun, J. Li, W. Liang, A. Li, Recyclable

solar evaporator based on hollow glass microspheres for water purification and desalination, *Journal of Environmental Chemical Engineering*, 10 (2022).

22. S. Wang, Y. Niu, X. Ye, F. Liu, M. Su, Z. Zhu, H. Sun, J. Li, W. Liang, A. Li, Robustly Inorganic Solar Steam Generator Derived from Hollow Glass Microspheres Based Composites for Desalination, *Solar RRL*, 5 (2021).

23. S. Wang, Y. Niu, W. Mu, Z. Zhu, H. Sun, J. Li, W. Liang, A. Li, Robust hollow glass microspheres-based solar evaporator with enhanced thermal insulation performance for efficient solar-driven interfacial evaporation, *Materials Today Chemistry*, 26 (2022).

24. J. Ding, Q. Liu, B. Zhang, F. Ye, Y. Gao, Preparation and characterization of hollow glass microsphere ceramics and silica aerogel/hollow glass microsphere ceramics having low density and low thermal conductivity, *Journal of Alloys and Compounds*, 831 (2020).

25. H. Yang, Y. Jiang, H. Liu, D. Xie, C. Wan, H. Pan, S. Jiang, Mechanical, thermal and fire performance of an inorganic-organic insulation material composed of hollow glass microspheres and phenolic resin, *Journal of Colloid and Interface Science*, 530 (2018) 163-170.

26. H.-B. Chen, P. Shen, M.-J. Chen, H.-B. Zhao, D.A. Schiraldi, Highly Efficient Flame Retardant Polyurethane Foam with Alginate/Clay Aerogel Coating, *ACS Applied Materials & Interfaces*, 8 (2016) 32557-32564.

27. H. Wang, C. Jiao, L. Zhao, X. Chen, Preparation and characterization of TiO₂-coated hollow glass microsphere and its flame-retardant property in thermoplastic polyurethane, *Journal of Thermal Analysis and Calorimetry*, 131 (2017) 2729-2740.

28. S. Zhang, F. Chu, Z. Xu, Y. Zhou, Y. Qiu, L. Qian, Y. Hu, B. Wang, W. Hu, The improvement of fire safety performance of flexible polyurethane foam by Highly-efficient P-N-S elemental hybrid synergistic flame retardant, *Journal of Colloid and Interface Science*, 606 (2022) 768-783.
29. E. Çalışkan, T.Ç. Çanak, M. Karahasanoğlu, I.E. Serhatlı, Synthesis and characterization of phosphorus-based flame retardant containing rigid polyurethane foam, *Journal of Thermal Analysis and Calorimetry*, 147 (2021) 4119-4129.
30. S. Wang, X. Yang, Z. Li, X. Xu, H. Liu, D. Wang, H. Min, S. Shang, Novel eco-friendly maleopimaric acid based polysiloxane flame retardant and application in rigid polyurethane foam, *Composites Science and Technology*, 198 (2020).
31. H. Wei, Z. Zhu, H. Sun, P. Mu, W. Liang, A. Li, Graphene and poly(ionic liquid) modified polyurethane sponges with enhanced flame-retardant properties, *Journal of Applied Polymer Science*, 134 (2017).
32. S. Wang, Y. Niu, C. Wang, F. Wang, Z. Zhu, H. Sun, W. Liang, A. Li, Modified Hollow Glass Microspheres/Reduced Graphene Oxide Composite Aerogels with Low Thermal Conductivity for Highly Efficient Solar Steam Generation, *ACS Applied Materials & Interfaces*, 13 (2021) 42803-42812.
33. S. Wang, Y. Niu, L. Yan, W. Chan, Z. Zhu, H. Sun, J. Li, W. Liang, A. Li, Polyimide-based superhydrophilic porous membrane with enhanced thermal insulation for efficient interfacial solar evaporation, *Composites Science and Technology*, 228 (2022).
34. Z. Zhu, Y. Niu, S. Wang, M. Su, Y. Long, H. Sun, W. Liang, A. Li, Magnesium hydroxide coated hollow glass microspheres/chitosan composite aerogels with

excellent thermal insulation and flame retardancy, *Journal of Colloid and Interface Science*, 612 (2022) 35-42.

35. Z. Zhu, S. Wu, C. Liu, P. Mu, Y. Su, H. Sun, W. Liang, A. Li, Ionic liquid and magnesium hydrate incorporated conjugated microporous polymers nanotubes with superior flame retardancy and thermal insulation, *Polymer*, 194 (2020).

36. H. Wei, F. Wang, X. Qian, S. Li, Z. Hu, H. Sun, Z. Zhu, W. Liang, C. Ma, A. Li, Superhydrophobic fluorine-rich conjugated microporous polymers monolithic nanofoam with excellent heat insulation property, *Chemical Engineering Journal*, 351 (2018) 856-866.

37. H. Wei, F. Wang, H. Sun, Z. Zhu, C. Xiao, W. Liang, B. Yang, L. Chen, A. Li, Benzotriazole-based conjugated microporous polymers as efficient flame retardants with better thermal insulation properties, *Journal of Materials Chemistry A*, 6 (2018) 8633-8642.

38. S. Wu, Z. Zhu, C. Liu, Y. Su, F. Wang, W. Bai, H. Sun, W. Liang, A. Li, Facile preparation of composite flame retardant based on conjugated microporous polymer hollow spheres, *Journal of Colloid and Interface Science*, 586 (2021) 152-162.