Preparation of Flame-Retardant Rigid Polyurethane Foams by Combining Modified Melamine–Formaldehyde Resin and Phosphorus Flame Retardants

Heng Zhu and Shiai Xu*

ABSTRACT: In this work, ethylene glycol-modified melamine–formaldehyde resin (EMF) was synthesized from ethylene glycol, paraformaldehyde, and melamine, and then rigid polyurethane foams (RPUFs) were prepared using EMF, polyols and polyisocyanate. The effects of ammonium polyphosphate (APP) and dimethyl methylphosphonate (DMMP) on the flame retardancy, mechanical properties, thermal stability, and morphology of the prepared RPUFs were studied. It is shown that the flame-retardant performance of EMF-filled RPUFs can be enhanced by the addition of APP and DMMP. Thus, APP and DMMP can synergistically improve the flame retardancy of RPUFs. APP has good smoke suppression, while DMMP can increase the total smoke production and CO/CO₂ weight ratio during the combustion of RPUFs.

1. INTRODUCTION

Polyurethane (PU) is a synthetic block copolymer prepared from polyols, polyisocyanates, and chain extenders, and it has rapidly developed into one of the most versatile and diverse plastics since its invention in 1937. PU products are widely used in home furnishing, clothing leather, mechanical accessories, and sports equipment. Foams are one of the most important commercial products of PU, and they can be classified into flexible, semi-rigid, and rigid foams based on their mechanical properties and apparent density.

Rigid polyurethane foams (RPUFs) are widely used in the construction of external walls owing to their excellent chemical resistance, high strength-to-weight ratio, and low density. Nevertheless, RPUFs are highly flammable with a low limiting oxygen index (LOI) of about 19.0%, and they often burn rapidly with a high heat release rate and a large amount of dense smoke, leading to many fire casualties and economic losses. Attempts have been made to improve the flame retardancy of RPUFs by adding flame retardants. Phosphorus flame retardants are extensively used in RPUFs for their excellent catalytic effect on the formation of a carbon layer during combustion or at high temperatures. Among the phosphorus flame retardants, dimethyl methylphosphonate (DMMP) is an environmentally friendly flame retardant that can effectively increase the flame retardancy of polymers.

However, it is often impractical to improve the flame retardancy of polymers by increasing the loadings of DMMP because DMMP is an additive flame retardant and thus it may migrate to the foam surface and therefore cause spontaneous loss of the flame retardant. More importantly, DMMP is quite expensive, and thus the desired flame retardancy would be achieved at high economic costs. For this reason, DMMP is often compounded with some cheaper flame retardants to reduce cost, such as montmorillonite and vermiculite. Ammonium polyphosphate (APP) contains both phosphorus and nitrogen, and it is often applied as an intumescent flame retardant in a variety of polymer materials. APP acts as a flame retardant mainly in the condensed phase. However, APP decomposes to produce polyphosphoric acids at high temperatures, and char is formed from catalytic dehydration of polymers, and N₂ and NH₃ are also released to promote the formation of the porous intumescent char. The intumescent phosphorus-rich char can act as a barrier against heat and O₂.

Melamine is often used in polyurethane foams due to its steady structure and rich nitrogen, which can increase the fire resistance of RPUFs and decrease the smoke density during incineration. Melamine can also release nitrogen-containing gases when heated, which will dilute the flammable gases released during the degradation of the matrix. The self-
condensation of melamine at high temperatures can result in the formation of melam, which enables the carbon layer to be more compact after burning. However, the mechanical strength of RPUFs decreases with the addition of melamine. Recently, Cao et al. reported that melamine resin and phosphorus-based flame retardants demonstrated a significant synergistic effect. Nevertheless, high water content limits the applications of amino resins in RPUFs. In our previous reports, ethylene glycol-modified urea-formaldehyde resin and ethylene glycol-modified urea-melamine-formaldehyde resin were synthesized and applied in RPUFs, which could increase the smoke suppression and flame retardancy of RPUFs. In the present study, ethylene glycol-modified melamine–formaldehyde resin (EMF) was synthesized from melamine, paraformaldehyde, and ethylene glycol. The synergistic effects of EMF, APP, and DMMP on the thermal stability and combustion performance of RPUFs were studied, and the thermal degradation characteristics of foams under a nitrogen atmosphere were characterized by thermogravimetric analysis–Fourier transform infrared (TG-FTIR) spectroscopy.

2. EXPERIMENTAL SECTION

2.1. Materials. LCN-403 polyether polyol (viscosity at 25 °C: 20000–50,000 mPa·s, hydroxyl value: 730–780 mg KOH/g) was obtained from Lianchuang New Materials Company Limited. LY-4110 polyether polyol (viscosity at 25 °C: 2500 mPa·s, hydroxyl value: 430 mg KOH/g) was obtained from Luyuan New Material Company Limited. APP (degree of polymerization: >1000, average particle diameter: 1–45 μm, 31% P, 15% N) was obtained from Shandong Taixin Chemical Company Limited. AK-8805 silicone surfactant was obtained from Jiangsu Meiside Chemical Company Limited. Polyarylpolyamethyleneisocyanate (PAPI) (average functionality: 2.8, NCO (%): 34.0–35.0) was obtained from Wanhua Chemical Company Limited. Ethylene glycol, melamine, paraformaldehyde, DMMP, dimethylcyclohexylamine (PC-8), ammonium chloride (NH₄Cl), diethanolamine (DEA), and tris(2-hydroxyethyl) amine (TEOA) were obtained from Sinopharm Chemical Reagent Company Limited.

2.2. Synthesis of EMF. As illustrated in Scheme 1, EMF with a paraformaldehyde/ethylene glycol/melamine mass ratio of 1:2:4.2 was prepared by the neutral-acid–base procedure. Briefly, appropriate amounts of melamine, ethylene glycol, and paraformaldehyde were added to a 500 mL four-neck round-bottom flask equipped with a mechanical stirrer, a reflux condenser, and a thermometer, and the system was heated up to 105 °C. Thirty minutes later, the pH of the system was adjusted to 4.0–4.5 with NH₄Cl. Once the predetermined degree of polycondensation was achieved, the pH value of the system was readjusted to 9.0–9.5 with triethanolamine and the resin was matured at 80 °C for 1 h. Finally, the resin was cooled and stored for future use. The parameters of EMF resin are illustrated in Table 1.

| parameters                          | values  |
|-------------------------------------|---------|
| hydroxyl value (mg KOH/g)           | 383 ± 10 |
| viscosity (mPa·s)                   | 9800 ± 100 |
| free formaldehyde (%)               | 0.11    |

2.3. Preparation of RPUFs. As shown in Scheme 2, the free-foaming method was applied to prepare RPUFs according to the formulations shown in Table 2. First, polyols, EMF, and phosphorus flame retardants were mixed and stirred at 200 rpm for at least 2 h, and then the surfactant, blowing agent, and catalyst were fed and stirred for 2 min using a homogenizer. PAPI was fed and mixed for 10 s at 2000 rpm, and then poured out for free foaming. Finally, the RPUFs were matured at 70 °C for 36 h.
2.4. Characterizations. The molecular structures of EMF and melamine were characterized by Fourier transform infrared (FTIR) spectroscopy on a Nicolet 6700 FTIR spectrometer from KBr pellets in a wavenumber range of 400−4000 cm\(^{-1}\) at an optical resolution of 4 cm\(^{-1}\) with 32 scans.

The apparent density and compression strength were measured according to GB/T 6343-2009 and GB/T 8813-2008 with samples of 50×50×50 mm\(^3\), respectively. The samples were compressed in a direction parallel to the growth direction of the foam.

The LOI value was measured using a JF-3 oxygen index instrument with test bars of 127×10×10 mm\(^3\) according to GB/T 2406.2-2009. Each sample was examined under a nitrogen flow (50 mL/min) on a NETZSCH STA 409 PC instrument at a heating rate of 10 °C/min in a nitrogen atmosphere (30 mL/min).

3. RESULTS AND DISCUSSION

3.1. FTIR Spectra of Melamine and EMF. The structures of melamine and EMF were characterized by FTIR. As shown in Figure 1, the absorption bands at approximately 3470, 3420, 3330, and 3130 cm\(^{-1}\) are attributed to the \(\text{−NH}_2\) stretching vibration, while those at approximately 1650 and 814 cm\(^{-1}\) are attributed to the triazine ring of melamine.\(^{37}\) After the synthesis of EMF, the peaks at approximately 1550 and 814 cm\(^{-1}\) are assigned to the triazine ring; those at approximately 1180 and 1230 cm\(^{-1}\) are assigned to C−O−C and −CH\(_2\)− of −CH\(_2\)−O−CH\(_2\)− groups, respectively; and the absorption peaks at approximately 3340 cm\(^{-1}\) are attributed to
−NH−. These results indicate that EMF is successfully synthesized in the system.

3.2. Forming Behavior, Cell Morphology, and Compressive Strength of RPUFs. The microstructure of

Figure 2. SEM images and cell size distributions of RPUFs: (a) RPUF-1, (b) RPUF-2, (c) RPUF-3, and (d) RPUF-4.
RPUDs was characterized by SEM. All RPUFs with different flame-retardant systems show a closed cell structure but quite different cell morphology. As shown in Figure 2, a large number of irregular cells with thin walls can be observed in the original polyurethane foam, and the introduction of APP causes no notable changes in cell morphology. However, Figure 2d shows that the integrity of foam cells is improved with increasing DMMP loading, which can be attributed to a decrease in the viscosity of the foaming system.

The pore size distributions of RPUFs are also shown in Figure 2. It is observed that the pore size of RPUF-1 ranges from 25 to 400 μm but mostly in the range of 100–225 μm. Compared with RPUF-1, phosphorous-flame-retardant foams show a smaller mean cell size and a narrower distribution. For example, the pore size of RPUF-4 ranges from 25 to 325 μm, while that of RPUF-3 ranges from 25 to 300 μm with a narrow pore distribution. The cell aspect ratio of RPUFs decreases with the participation of APP and DMMP and reaches a minimum of 1.13 in RPUF-3 due to the heterogeneous nucleation action and the decreased viscosity of the forming system. During the free forming of RPUFs, reduced viscosity equalizes the force acting on the cell wall and uniform cells are obtained.

As shown in Table 3, the foaming behavior of RPUFs is described by the cream time and tack-free time of free foaming.

| samples | $T_a^a$ (s) | $T_b^b$ (s) | density (kg/m$^3$) | compressive strength (kPa) compared with RPUF-1 (%) |
|---------|-------------|-------------|-------------------|--------------------------------------------------|
| RPUF-1  | 18          | 60          | 50.53 ± 0.69      | 215.7 ± 12.1                                     |
| RPUF-2  | 18          | 65          | 50.91 ± 0.55      | 228.1 ± 23.8                                     |
| RPUF-3  | 19          | 64          | 51.15 ± 0.73      | 242.9 ± 12.7                                     |
| RPUF-4  | 18          | 64          | 51.33 ± 0.43      | 258.7 ± 18.6                                     |

* $T_a$: cream time  
* $T_b$: tack-free time.

In this study, the cream time and tack-free time of all RPUFs are shorter than that of common RPUFs due to the presence of the catalytic tertiary amine moiety in EMF, leading to an increase in cell aspect ratio, as shown in Figure 2. The cream times of RPUFs are all within 18–19 s, which means that the phosphorous flame retardants show no reactivity with isocyanate.

The compressive strength of RPUFs is also shown in Table 3. As illustrated in Table 3, increasing the DMMP loading helps to improve the mechanical behavior, which is mainly attributed to the regular cellular structure.

### 3.3. Flammability of RPUFs

LOI was applied to evaluate the flammability of RPUFs. As shown in Table 4, due to the presence of melamine in EMF, the LOI of RPUF-1 (24.8%) is higher than that of usual RPUFs (about 19%). The highest LOI of 29.1% is achieved in RPUF-3 containing 10 phr APP/10phr DMMP. Thus, the incorporation of both APP and DMMP has a synergistic flame-retardant effect, which is probably due to their different flame-retardant mechanisms. The vaporization or decomposition of DMMP occurs at about 181 °C, and it exhibits a flame retardant mechanism of gas-phase action. DMMP can release gaseous phosphorus-containing fragments at the initial stage of foam combustion. The phosphorus-containing radical scavengers can effectively trap H• and OH• radicals in the gas phase, prevent the chain reaction of the flame, and thus effectively suppress the flame strength. On the other hand, APP shows a flame retardancy effect mainly in the condensed phase. APP is an intumescent flame retardant containing both nitrogen and phosphorus, and thus it can promote the formation of a phosphorus-containing carbon layer at high temperatures. The addition of 20 phr one-component flame retardant in the formulations leads to an increase in LOI to 26.6 and 26.9% for APP- and DMMP-filled RPUFs, respectively.

### 3.4. Fire Behaviors of RPUFs

The CCT was performed to characterize the fire behaviors of RPUFs. The heat release rate (HRR) and peak heat release rate (PHRR) are recognized as indicators of fire intensity. As shown in Figure 3a, two peaks are observed in the HRR curves for all foams. In the initial
combustion stage of RPUFs, carbamate groups are degraded in a short time, resulting in the release of a large number of volatile combustible fragments and consequently an increase in the flame strength. As the combustion proceeds, a thermally stable carbon layer is formed to protect the inner polymer and the first HRR peak is formed. Meanwhile, it is observed that the incorporation of phosphorus-containing flame retardants results in an earlier appearance of the first peak in the HRR curves. Given the incessant heat flow, further degradation takes place in the above char layer, leading to formation of new protective chars in some formulations and therefore the second peak.23 However, the second peaks of phosphorus-containing RPUFs are significantly lower than that of the original foam, which is mainly due to the formation of a thicker carbon layer. As shown in Figure 3b, the total heat release (THR) of RPUFs containing 20 phr APP, 10 phr APP/10 phr DMMP, and 20 phr DMMP are about 10.7, 22.4, and 18.1% lower than that of RPUF-1, respectively.

The total smoke production (TSP), smoke production rate (SPR), total smoke release (TSR), and rate of smoke release (RSR) are applied to characterize the smoke emission of RPUFs.16 As illustrated in Table 5, the lowest TSP (2.4 m^2) and TSR (272.1 m^2/m^2) are observed in RPUF-2 containing 20 phr APP, indicating that APP performs well in smoke suppression. This is because APP promotes the formation of an expansion carbon layer and prevents further degradation of the inner polymer during combustion. However, the TSPs and TSRs of RPUFs gradually increase as DMMP loading increases in RPUFs, which is due to the low flame-retardant effects in the condensed phase. In Figure 4, the second SPR and RSR peaks of the phosphorus-containing RPUFs are observed at about 120 s, which occur later than that of the original foam (about 100 s). Moreover, the intensity of the second peak in the SPR and RSR curves of APP- and DMMP-filled RPUFs is higher than that of the original foam, which is mainly due to the degradation of the thick phosphorus-containing carbon layer during the later burning.

The CO/CO2 weight ratio stands for the level of complete combustion. Thus, the higher the CO/CO2 weight ratio, the less complete the combustion, and therefore, the more toxic the smoke generated. It is found that the CO/CO2 weight ratios of the original foam and RPUF-2 are 0.071 and 0.052, respectively, which are lower than those of the foam containing 10 phr APP/10 phr DMMP (0.074) and RPUF-4 containing 20 phr DMMP (0.087). All these results suggest that APP is better able to suppress CO generation than DMMP, which even has a negative effect.

3.5. Thermal Stability of RPUFs. Figure 5 shows the TGA and derivative thermogravimetric (DTG) curves of the foams, and the test results are summarized in Table 6. As shown in Figure 5, the initial degradation temperature of RPUFs is lower than that of nonflame-retardant polyurethane foams (about 250 °C) because EMF can be decomposed more easily.7 The addition of EMF leads to the generation of melamine, HCN, HNCO, polyols, isocyanates, NH3, and some stable intermediates during the first decomposition stage of RPUF-1. Melamine can be self-condensed into melem at high temperatures, making the carbon layer more compact; inert gases released by EMF can dilute the concentration of polymer fragments. As a result, RPUF-1 has better flame retardancy than nonflame-retardant polyurethane foams. The second decomposition stage corresponds to the degradation of substituted urea and imidodicarbonic diamide generated during the reaction between polyols and isocyanates.41 Owing to further decomposition of residues, the third decomposition stage begins at around 500 °C.

The incorporation of DMMP into RPUFs enables the initial degradation temperature of RPUF-3 and RPUF-4 to be lower than that of RPUF-1 and RPUF-2 due to the low volatilization temperature of DMMP (about 181 °C). However, the

Table 5. Flammability and Smoke Emission Behaviors of RPUFs

| samples | RPUF-1 | RPUF-2 | RPUF-3 | RPUF-4 |
|---------|--------|--------|--------|--------|
| TTI (s) | 3      | 4      | 4      | 4      |
| PHRR (kW/m²) | 179.7 | 175.4  | 161.1  | 165.1  |
| THR (MJ/m²) | 28.1  | 25.1   | 21.8   | 23.0   |
| PSPR (m²/s) | 0.050 | 0.037  | 0.041  | 0.043  |
| TSP (m³) | 3.8    | 2.4    | 3.1    | 3.6    |
| PRSR (m³/s) | 5.67  | 4.21   | 4.63   | 4.84   |
| TSR (m²/m²) | 431.5 | 272.1  | 353.0  | 405.5  |
| CO (kg/kg) | 0.09  | 0.06   | 0.08   | 0.09   |
| CO₂ (kg/kg) | 1.27  | 1.16   | 1.08   | 1.04   |
| CO/CO₂ weight ratio | 0.071 | 0.052  | 0.074  | 0.087  |

“PSPR is the peak smoke production rate. “PRSR is the peak smoke release rate.

Figure 4. (a) SPR and (b) RSR curves of RPUFs.
incorporation of APP and DMMP into RPUFs results in a higher residue rate after TGA, indicating that APP and DMMP display significant flame retardancy in EMF-filled polyurethane foams. This is because the addition of APP and DMMP forms a thick phosphorous-rich char layer that provides better protection for the inner polymer and thus prevents more in-depth degradation of foams.

3.6. Micromorphology of Residues after CCT. It is known that the morphology of the char can have an effect on the flame retardancy of materials during burning. Figure 6 shows the photographs of residual chars of RPUFs after CCT. As shown in Figure 6a, the char after CCT of RPUF-1 shows no expansion action but some obvious cracks and pores on the char surface. Figure 6b,c shows that the addition of APP results in an increase in char height due to the expansion effect but no obvious cracks and pores on the surface of char. The addition of DMMP shows a less expansion effect compared with APP, as shown in Figure 6d.

To further verify the effect of the char layer during combustion, the morphology of RPUFs after CCT was characterized by SEM. As shown in Figure 7a, a compact and thin char layer is generated, which makes it hard to insulate mass and heat transfer. The residual char layers of APP-filled RPUFs (Figure 7b) and DMMP-filled RPUFs (Figure 7d) are thicker than that of the original foam due to the formation of phosphonic or phosphate acids from the combustion of APP and DMMP. The acids dehydrate the foam to form a dense carbonized zone, which can react with melamine to form salt that covers the surface of the char layer. A thick char layer can slow down the heat and mass transfer between the gas and the condensed phases and prevent the underlying polymer from further combustion. However, when both APP and DMMP are incorporated, the carbon layer of RPUF-3 is thicker and denser than that of single phosphorus-based flame retardant, which can be attributed to the synergistic effect of APP and DMMP.

3.7. TG-FTIR Analysis of RPUFs. The thermal degradation of RPUFs under a nitrogen atmosphere was determined using TG-FTIR. As shown in Figure 8a, the broad peaks at 2300–2400 cm\(^{-1}\) are attributed to CO\(_2\). The peaks at 1652 cm\(^{-1}\) are

![Figure 5](image-url)  
**Figure 5.** (a) TGA and (b) DTG curves of RPUFs.

![Figure 6](image-url)  
**Figure 6.** Residual char photographs of RPUFs after CCT: (a) RPUF-1, (b) RPUF-2, (c) RPUF-3, and (d) RPUF-4.

![Table 6](image-url)  
**Table 6.** TGA Data of RPUFs

| samples  | \(T_{\text{initial}}^a\) (°C) | \(T_{\text{max}}^a\) (°C) | \(W_1^a\) (%) | \(T_{\text{max}}^b\) (°C) | \(W_2^b\) (%) | \(T_{\text{max}}^c\) (°C) | \(W_3^c\) (%) | (%) compared with RPUF-3 (%) |
|----------|------------------|------------------|------------|------------------|------------|------------------|------------|------------------|
| RPUF-1   | 222              | 259              | 85.8       | 309              | 69.0       | 677              | 15.0       | −45.3            |
| RPUF-2   | 228              | 266              | 89.3       | 306              | 71.9       | 633              | 30.6       | −34.7            |
| RPUF-3   | 201              | 249              | 87.9       | 316              | 68.1       | 659              | 35.2       | 27.4             |
| RPUF-4   | 174              | 256              | 80.6       | 314              | 64.5       | 659              | 24.7       | 18.6             |

\(^a\)\(T_{\text{initial}}\) is the initial degradation temperature (temperature at 5.0% weight loss). \(^b\)\(T_{\text{max}}\) is the maximum-rate degradation temperature. \(^c\)\(W\) is the weight remaining percentage at the maximum-rate degradation temperature.
attributed to the aromatic ring, while those at 1530 cm\(^{-1}\) can be assigned to the absorption of HNC\(\equiv\)O. Due to the decomposition of EMF, CH\(_3\)OH (O–H deformation, 676 cm\(^{-1}\)) and CH\(_2\)O (1743 cm\(^{-1}\)) are detected. However, the absorption intensity of phosphorus-containing foams is gradually reduced. The characteristic bands of compounds containing P–O (817 cm\(^{-1}\)) and NH\(_3\) (927 cm\(^{-1}\)) are observed, which correspond to the pyrolysis products from APP in Figure 8b.\(^{20,21}\) As shown in Figure 9, for the foams

Figure 7. SEM images of RPUFs residues after CCT: (a) RPUF-1, (b) RPUF-2, (c) RPUF-3, and (d) RPUF-4.

Figure 8. FTIR spectra of the gas products at different temperatures during thermal degradation: (a) RPUF-1 and (b) RPUF-2.

Figure 9. FTIR spectra of the gas products at different temperatures during thermal degradation: (c) RPUF-3 and (d) RPUF-4.
containing DMMP, the peak at 1275 cm\(^{-1}\) is attributed to the absorption of the P−C group of DMMP and it can be detected below 250 °C, which confirms the degradation of DMMP at high temperatures. The absorption intensity of RP-UF-3 is weaker than that of other samples at above 500 °C, which is mainly due to the thick and dense carbon layer, as shown in Figure 7c.

4. CONCLUSIONS

A series of halogen-free flame-retardant RPUFs were prepared from EMF and phosphorus flame retardants in this paper, and the effects of APP/DMMP contents on the compressive strength, cell morphology, flammability, thermal stability, and flame retardancy of RPUFs were studied. The results show that the flame-retardant performance of EMF-filled RPUFs can be enhanced by the incorporation of phosphorus flame retardants. APP and DMMP have a significant synergistic effect on the LOI and residue rates. Furthermore, APP shows well smoke suppression, while DMMP can increase the TSP, TSR, and CO/CO\(_2\) weight ratio during the combustion of RPUFs.

Author Information

Corresponding Author

Shuai Xu — Shanghai Key Laboratory of Advanced Polymeric Materials, Key Laboratory for Ultrathin Materials of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, China; School of Chemical Engineering, Qinghai University, Xining 810016, China; orcid.org/0000-0002-7003-5255; Phone: 86-021-64253353; Email: saxu@ecust.edu.cn

Author

Heng Zhu — Shanghai Key Laboratory of Advanced Polymeric Materials, Key Laboratory for Ultrathin Materials of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.9b03659

Notes

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