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

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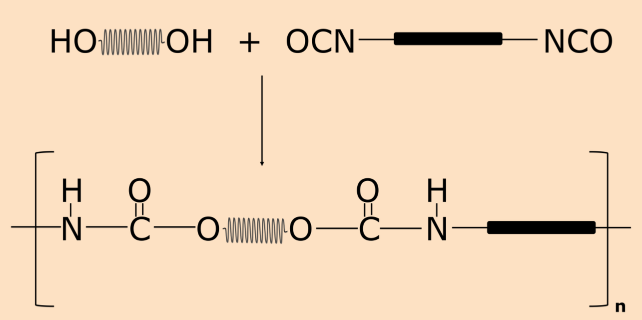
Abstract & Introduction

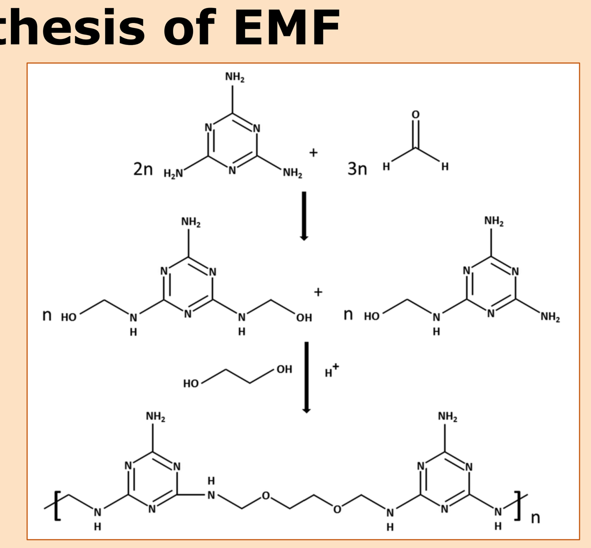
Polyurethane is a synthetic block copolymer made from polyols, polyisocyanates, and chain extenders, and has rapidly evolved into one of the most versatile and diverse plastics since its invention. Amongst, rigid polyurethane foam (RPUF) is a closed-cell plastic. Typically, RPUFs are extensively used as thermal insulation materials due to their excellent chemical resistance for an amorphous material, lower thermal conductivity, and high impact strength than other materials. However, the use of RPUFs is limited in the construction industry because of their high flammability.



Flame retardants (FRs) are essential to slowing the spread of fire or preventing a fire.

In this research, flame-retardant rigid polyurethane foams (FR-RPUFs) was synthesized by combining ethylene glycol-modified melamine−formaldehyde resin (EMF) and phosphorus − nitrogen flame retardants

1. Synthesis of EMF



Scheme 1: This figure shows the synthesis route of Ethylene glycol – modified melamine – formaldehyde resin (EMF) preparation. The molecular structure of EMF were characterized by FTIR spectroscopy, hydroxyl value (383 ± 10 mg KOH/g), and viscosity (9800 ± 100 mPa·s).

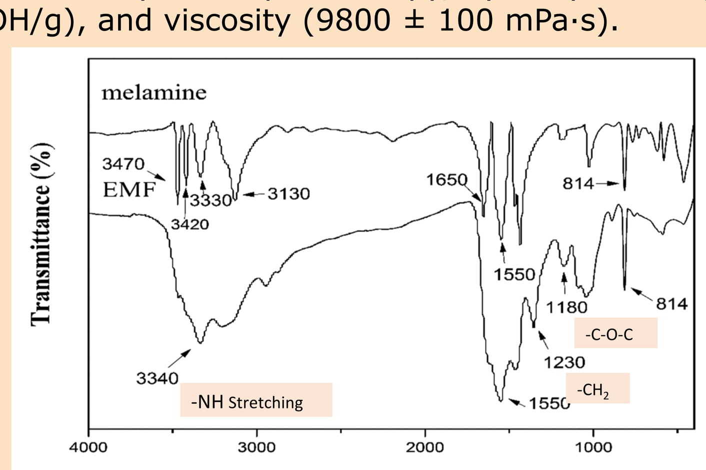
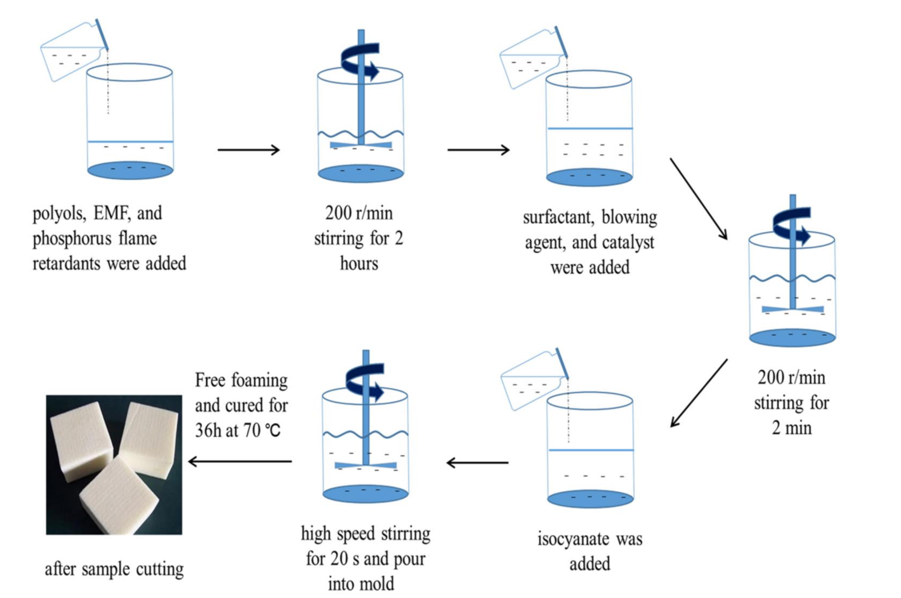


Figure 1: The absorption bands at approximately 3470, 3420, 3330, and 3130 cm^{-1} in spectra 1 are attributed to the $-NH_2$ stretching vibration, while those at approximately 1650 and 814 cm^{-1} are attributed to the triazine ring of melamine. The peaks at approximately 1550 and 814 cm^{-1} in spectra 2 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−.

Experimental, Results, Discussion

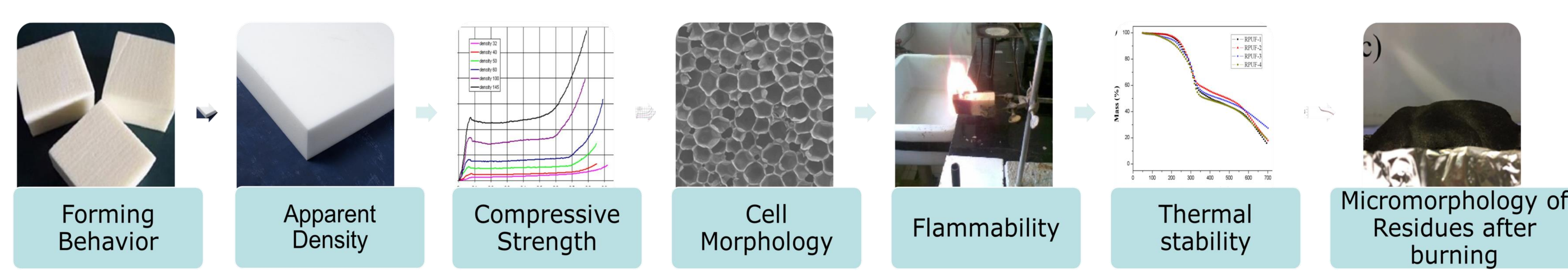
2. Preparation of flame-retardant RPUFs by combining EMF, ammonium polyphosphate (APP) and dimethyl methylphosphonate (DMMP) flame retardant



Content	RPUF-1	RPUF-2	RPUF-3	RPUF-4
EMF	100	100	100	100
Polyether polyol	50	50	50	50
APP		20	10	
DMMP			10	20
Silicon surfactant	4.5	4.5	4.5	4.5
Catalyst	1.0	1.0	1.0	1.0
Isocyanate	176	176	176	176
Water	1.5	1.5	1.5	1.5

Scheme 2 and Table 1: Preparation of RPUFs using free-foaming method according to the formulations shown in Table 1. The effect of EMF, APP, and DMMP on flame retardancy, mechanical properties, thermal stability, and morphology were studied.

3. Characterization of RPUFs



3.1 Forming Behavior, Apparent density, Compressive Strength, and Cell Morphology

samples	T_c[a] (s)	T_{tc}[b] (s)	density (kg/m³)	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	+5.7
RPUF-3	19	64	51.15 ± 0.73	242.9 ± 12.7	+12.6
RPUF-4	18	64	51.33 ± 0.43	258.7 ± 18.6	+19.9

[a]T_c: cream time [b]T_{tc}: tack-free time.

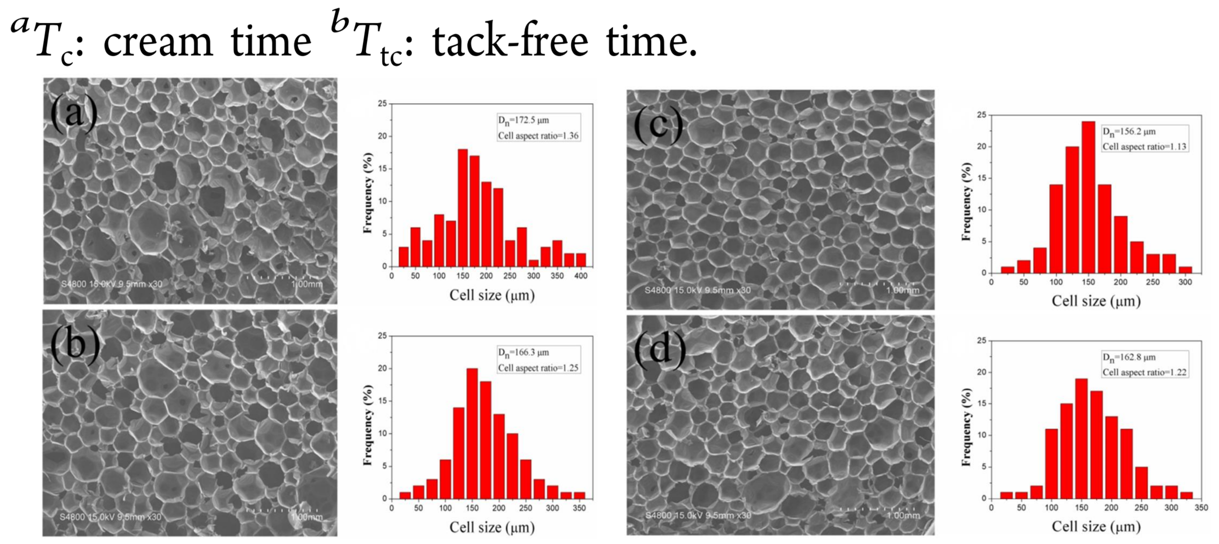


Table 2 and Figure 2: The foaming behavior of RPUFs is described by the cream time and tack-free time of free foaming. SEM images show that the introduction of APP does not cause significant changes in cell morphology, and that the integrity of the foam cells improves as the DMMP load increases. Increasing the DMMP percentage shows an increase in the compressive strength of the RPUF.

3.2 Flammability, Thermal Stability and Morphology of Residues After Burning

Parameter	RPUF-1	RPUF-2	RPUF-3	RPUF-4
LOI (%) (±0.2)	24.8	26.6	29.1	26.9
Total smoke production (m^2)	3.8	2.4	3.1	3.6
Total smoke release (m^2/m^2)	431.5	272.1	353.0	405.5

Table 3: The highest LOI was achieved in RPUF-3 containing EMF/APP/DMMP due to their different flame-retardant mechanisms.

Figure 3

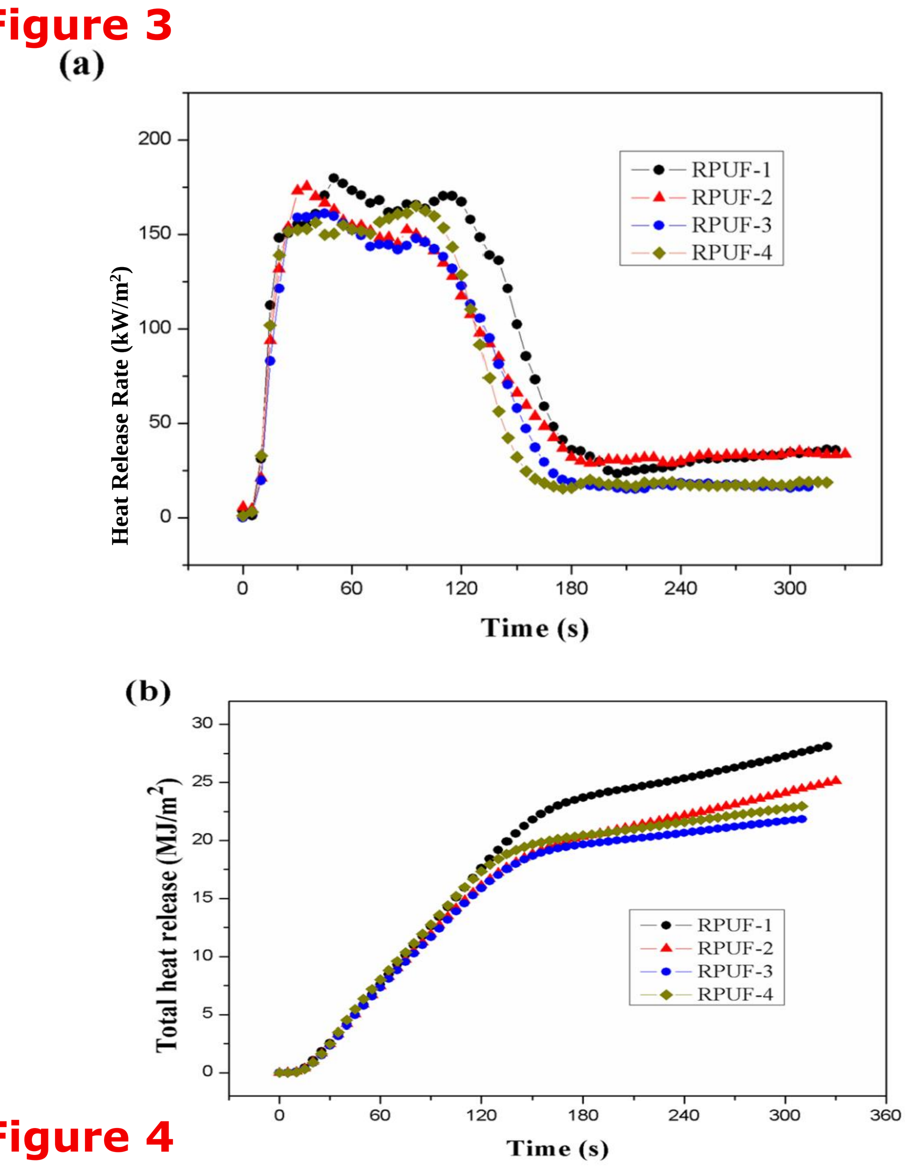
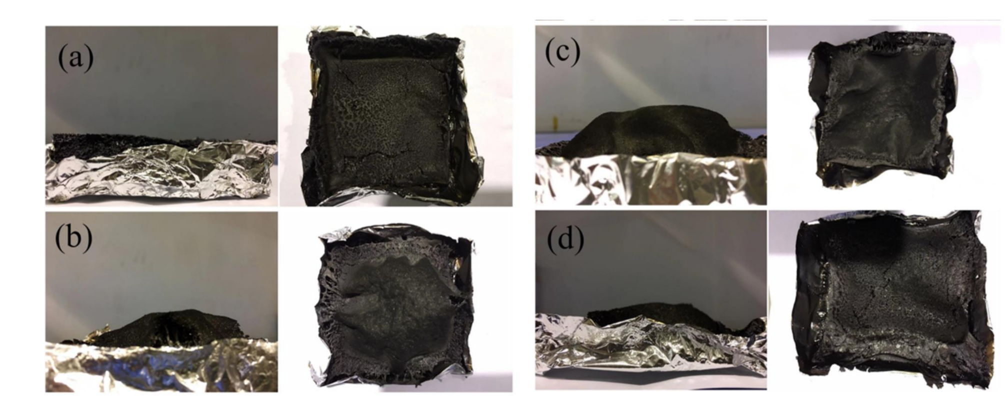


Figure 3a and b: Cone calorimetric test (CCT) was performed to characterize the fire behaviors of RPUFs.Two peaks are observed in the HRR curves for all foams. 1st peak, carbamate groups are degraded in a short time. As the combustion proceeds, a thermally stable carbon layer is formed to protect the inner polymer. Meanwhile, the incorporation of P-containing flame retardants results in an earlier appearance of the 1st peak in the HRR curves. However, the 2nd 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.



Residual char photographs of RPUFs after CCT

Figure 4

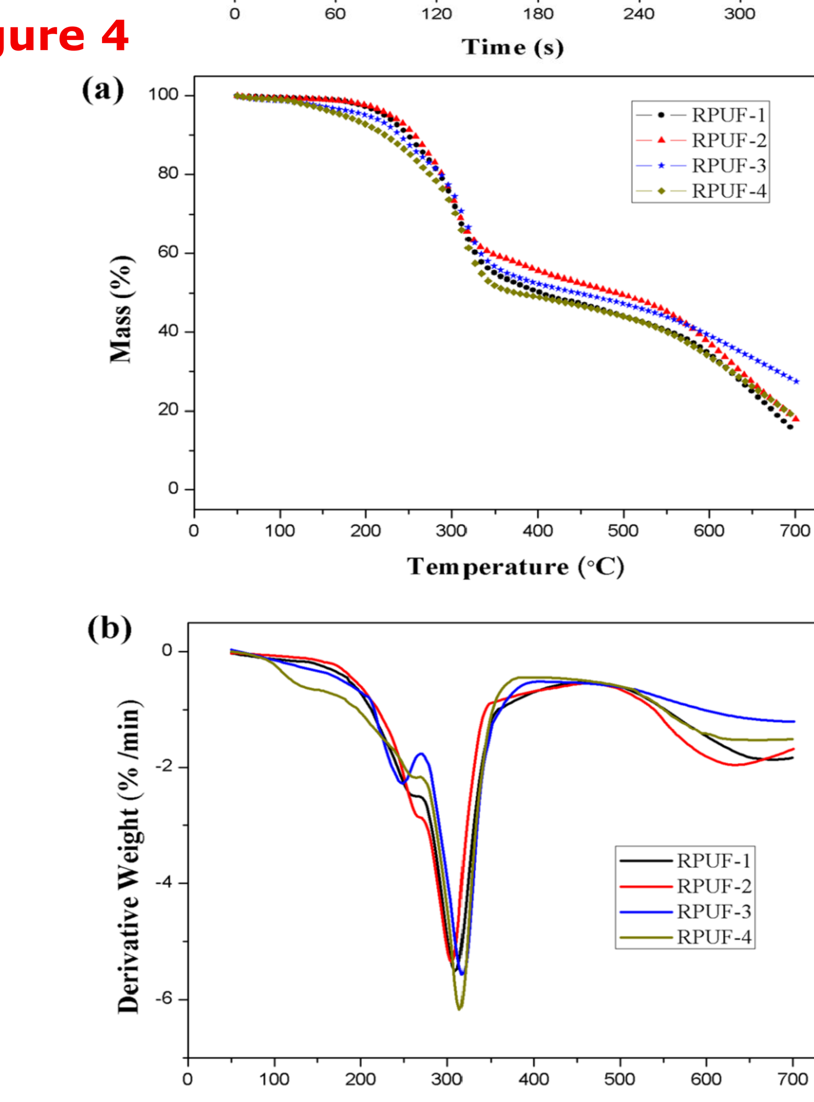


Figure 4 a and b: Thermogravimetric analysis shows the initial degradation peak of RPUFs is lower than that of nonflame-retardant polyurethane foams (about 250 °C). Because EMF can be decomposed more easily to form stable intermediates during first decomposition stage. The incorporation of DMMP into 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. In addition, the incorporation of APP and DMMP into RPUFs results in a higher residue rate after TGA.

Conclusion & Future work

- The flame-retardant performance of EMF-filled RPUFs can be enhanced by the incorporation of phosphorus and nitrogen flame retardants.
- EMF, APP and DMMP have a significant effect on the mechanical strength, flammability, thermal stability and residue rates.
- This research drives it possible to develop sustainable polyurethane materials that ensure optimal thermal parameters for equipment and buildings.

Reference

Zhu, H. & Xu, S. Preparation of Flame-Retardant Rigid Polyurethane Foams by Combining Modified Melamine-Formaldehyde Resin and Phosphorus Flame Retardants. ACS Omega 5, 9658–9667 (2020)