第 39 卷 第 8 期
2026 年 8 月

高 分 子 通 报
POLYMER BULLETIN

Vol. 39, No. 8
August, 2026

·综述·

阻燃硬质聚氨酯泡沫保温材料研究进展

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摘要：硬质聚氨酯泡沫(RPUF)是建筑与工业保温的关键材料，但其由碳、氢、氧元素构成的分子结构使其具有易燃性，带来显著火灾风险，因此发展环境友好型的阻燃技术至关重要。本文综述了主流保温材料的性能特点，明确RPUF在轻质高效保温方面的综合优势。系统分析了RPUF的三大环境友好型的阻燃策略：添加型、反应型与涂层型，阐明其作用机理并比较了前两者的优缺点，涂层型作为新型改性手段在克服传统方法局限方面的独特价值。重点介绍了包括层层自组装、水凝胶、气凝胶、热固化、光固化等在内的涂层实现途径，概述其制备方法、作用机制及研究进展。最后，对高性能多功能一体化涂层、绿色体系及智能响应技术等未来发展前景进行了展望。

关键词：硬质聚氨酯泡沫；保温材料；环境友好型；阻燃；涂层

Research Progress of Flame-retardant Rigid Polyurethane Foam Insulation Materials

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Abstract: Rigid polyurethane foam (RPUF) is a key material for thermal insulation in construction and industry. However, its molecular structure, which comprises carbon, hydrogen, and oxygen, renders it flammable, posing significant fire risks. Therefore, the development of flame-retardant technologies is crucial for ensuring safety. This paper reviews the performance characteristics of mainstream insulation materials and clarifies the comprehensive advantages of RPUF in terms of lightweight and high-efficiency insulation. This review systematically analyzes the three major flame-retardant strategies for RPUF-additive, reactive, and coating types-elucidates their mechanisms of action, and compares the advantages and disadvantages of the first two. Simultaneously, it highlights the unique value of the coating type as an emerging modification method to overcome the limitations of traditional approaches. This review introduces coating implementation methods, including layer-by-layer self-assembly, hydrogels, aerogels, thermal curing, and photocuring, and summarizes their preparation methods, mechanisms of action, and research progress. Finally, we look forward to the future development prospects of high-performance multifunctional integrated coatings, green systems, and intelligent response technologies.

Keywords: Rigid polyurethane foam; Thermal insulation materials; Environmentally friendly type; Flame retardant; Coating

引用：王喆，吴宁晶. 阻燃硬质聚氨酯泡沫保温材料研究进展. 高分子通报，**2026**, 39(8), 1279–1291.

青岛科技大学高分子研究专辑；2026-03-31 收稿，2026-06-01 录用，2026-07-20 网络出版
基金项目：青岛市自然科学基金(基金号 24-4-4-zrjj-200-jch)
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doi: 10.14028/j.cnki.1003-3726.2026.26.087

Citation: Wang, Z.; Wu, N. J . Research progress of flame-retardant rigid polyurethane foam insulation materials. *Polym. Bull.* (in Chinese), **2026**, 39(8), 1279–1291.

在全球范围内节能减排与“双碳”目标的宏大背景下，提升建筑围护结构的热工性能以减少运营能耗，已成为建筑行业的刚性需求与必然选择。作为实现这一目标的关键物理载体，保温材料的性能直接决定了建筑的能耗水平、室内环境质量与长期安全性[1~3]。硬质聚氨酯泡沫(rigid polyurethane foam, RPUF)凭借其极低导热系数(0.018~0.025 W/(m·K))、高闭孔率(>90%)、优异的尺寸稳定性、高强度质量比和成型方式灵活多样等综合性能，在高端建筑、冷链物流和保温管道等领域占据着重要地位。RPUF的极限氧指数(LOI)通常在18%~19%之间，属于易燃材料。在火灾场景下，RPUF不仅燃烧迅速、热释放率高，更伴随着产生大量浓烟和剧毒气体(如CO、HCN等)，严重威胁生命和财产安全[4,5]。因此，对RPUF进行高效阻燃改性，使其在保持优异保温性能的同时满足建筑防火安全规范，已成为学术界与工业界持续关心的核心课题。

本文首先概述保温材料的分类与RPUF的竞争优势，聚焦于其阻燃技术，从作用机理层面深度分析添加型、反应型及涂层型三大途径。文章将着重论述涂层型阻燃技术，详述包括水凝胶、气凝胶、热固化、光固化及辐射固化在内的各类涂层体系的构建方法与研究现状，为研发高性能、多功能、环境友好的新一代安全保温材料提供理论参考。

1 保温材料概览与硬质聚氨酯泡沫的核心优势

1.1 主流保温材料种类与特点

当前市场上的保温材料按其化学本质可分为无机类、有机类和复合类。无机材料如岩棉、玻璃棉及气凝胶毡等，普遍具备不燃、耐高温与耐久性好的特点，但也存在导热系数较高、易吸湿、密度大以及施工复杂等局限。如表1所示，有机材料以发泡聚苯乙烯板(模塑聚苯乙烯泡沫塑料板EPS/挤塑聚苯乙烯泡沫塑料板XPS)[6,7]和RPUF为代表，具有质轻、导热系数低和加工方便的优势，但易燃性是其共性问题。其中EPS/XPS所用卤素阻燃剂面临环境与毒性限制，而酚醛泡沫(PF)[8]虽阻燃性较好却存在脆性大、易粉化等缺点。复合材料则通过结合不同材料的特性，如金属面夹芯板与保温装饰一体板，实现性能的互补与优化。

1.2 硬质聚氨酯泡沫

硬质聚氨酯泡沫因其综合性能优异，在高性能保温市场占据主导。该材料闭孔率高(>90%)，其常温导热系数低至0.018~0.025 W/(m·K)，隔热性能突出[9,10]。其在低密度(30~60 kg/m^3)下仍具高压缩强度与尺寸稳定性，并可通过喷涂或浇注实现与多种基材的化学黏结，形成无缝保温层，有效消除冷桥，兼具防水与隔音功能。

2 硬质聚氨酯泡沫的阻燃改性

提升RPUF的阻燃性，本质上是干扰其燃烧循环——即切断或减弱热分解、可燃气体产生、燃烧反应链传递、热量反馈这一过程。目前主要分为3种策略：添加型、反应型和涂层型阻燃聚氨酯。

2.1 添加型阻燃聚氨酯

将物理阻燃剂通过搅拌混合到发泡体系中。其中含磷阻燃剂(如聚磷酸铵(APP))要起凝聚相阻燃作用[11]。燃烧时生成磷酸或聚偏磷酸，促进聚合物脱水成炭，形成隔热、隔氧的炭层；部分含磷挥发物也可在气相捕获自由基。Li等[12]采用

表1 主要建筑保温材料的性能对比

Table 1 Performance comparison of main building insulation materials

参数	性能指标			
	RPUF	XPS	EPS	PF
导热系数 (W/(m·K))	0.018~0.0028	0.026~0.032	0.032~0.040	0.018~0.028
密度 (kg/m^3)	30~60	25~45	15~30	40~80
压缩强度 (kPa)	150~300	150~700	70~250	100~200
极限氧指数LOI (%)	18~19	18~19	18~19	35~45
燃烧等级 (GB 8624)	B1/B2	B1/B2	B1/B2	A/B1
长期使用温度 (℃)	−180~110	−180~75	−180~75	−180~150

β-环糊精对APP进行表面修饰得到β-APP，显著提升了其与RPUF基体的相容性。β-APP表面的羟基可与异氰酸酯中的NCO基团反应，从而增强RPUF的交联密度，提高其热稳定性和阻燃性能。添加25 wt% β-APP的阻燃RPUF在700 ℃下的残炭率达到42.8%，LOI提升至24.9%。含氮阻燃剂(如三聚氰胺(MEL))常与磷系协同，释放不燃气体(如NH_3)稀释可燃气体浓度，生成更稳定的交联结构，促进膨胀炭层形成。Liu等利用MEL包覆哌嗪焦磷酸(PAPP)制备了微胶囊阻燃剂(MF-Co@PAPP) (图1)，提升了其在RPUF基体中的相容性，有效抑制了阻燃剂的溶出与迁移，浸水14天后LOI仍达22.1%，总热释放(THR)与总烟释放量(TSP)较纯RPUF分别降低44%和29%。结果表明其能促进体系形成致密炭层，实现凝聚相阻燃，且MF壳层与异氰酸酯反应有助于体系改善力学性能。无机填料如蒙脱土MMT[13]、可膨胀石墨EG[14]等通过吸热分解带走大量热量，降低基体温度，同时释放的水蒸气稀释氧气。Zhang等[15]利用MMT特殊的层状结构和与鸡毛(SF)蛋白反应形成的稳定化学键，制备了MMT与SF共改性RPUF，蒙脱土的加入提高了样品的阻燃性能。当添加3 wt% MMT时，改性RPUF的起始分解温度最高，活化能最大，热稳定性最好。

添加型阻燃剂虽具有工艺简便、成本低廉及易于工业化等优势，但添加型阻燃剂添加过量时，阻燃剂与RPUF基体相容性降低，从而导致物理性能和导热性能下降；发泡时体系黏度过大导致

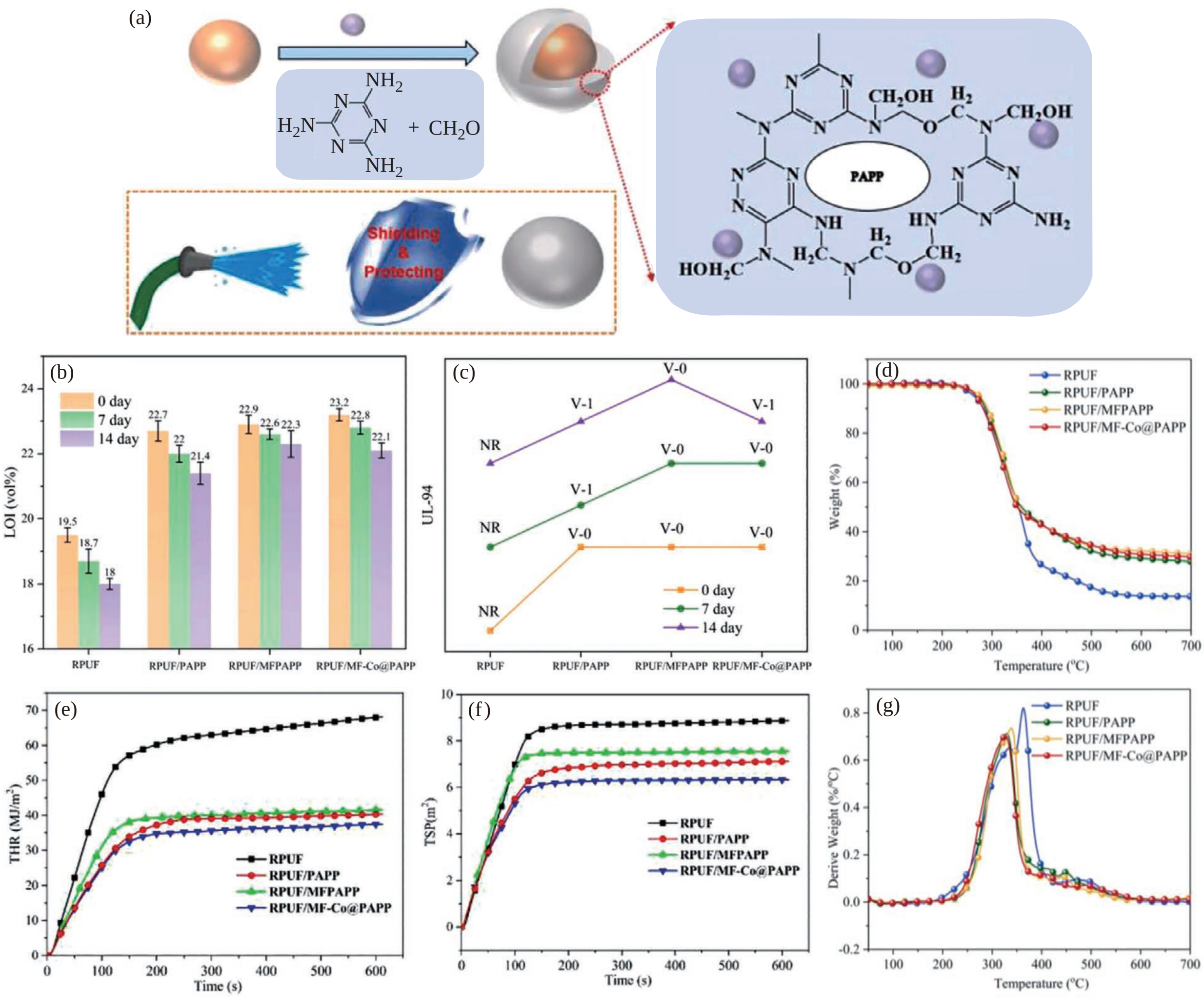


图 1　(a) MFPAPP和MF-Co@PAPP的合成过程；RPUF及复合材料在水中浸泡0、7和14天后的(b) LOI和(c) UL-94等级；(d) TG曲线，(e) THR曲线，(f) TSP曲线，(g) DTG曲线[17] (2024 Elsevier版权许可)

Figure 1　(a) Synthesis process of MFPAPP and MF-Co@PAPP; (b) LOI and (c) UL-94 ratings of RPUF and its composites after immersion in water for 0, 7, and 14 days; (d) TG curves, (e) THR curves, (f) TSP curves, (g) DTG curves (Reprinted with permission from Ref. [17]; Copyright (2024) Elsevier)

发泡不充分，从而进一步影响产品性能；小分子阻燃剂可能从RPUF基体中迁移或溢出，造成体系阻燃性能衰减并影响其表面处理[16]。

2.2 反应型阻燃聚氨酯

反应型阻燃剂是将含阻燃元素的化合物作为反应单体，通过化学键合到聚氨酯分子链上。Wang等[18]通过将9,10-二氢-9-氧杂-10-磷杂菲-10-氧化物(DOPO)依次与马来酸酐(MA)、二乙醇胺(DEA)及硅烷偶联剂(KH-561)反应，合成了一种反应型磷/硅阻燃剂，再与可膨胀石墨(EG)复配构建多组分阻燃体系，并应用于植物油基RPUF中。所制备的复合材料LOI质量分数达30.0%，达到UL-94 V-0等级，其峰值热释放(pHRR)、THR及TSP较纯RPUF分别显著降低47.5%、57.9%和62.8%。同时，含5 wt% EG与20 wt%该阻燃剂的RPUF体系仍保持良好的机械性能，体现了阻燃与力学性能的较好平衡。Wang等[19]采用一种新开发的含磷多元醇及其超支化产物作为传统聚醚多元醇(LY-4110)的替代品(图2)，制备阻燃RPUF。LOI增加到24%。pHRR、THR和烟释放速率(TSR)分别下降了65.5%、72.3%和63.0%。

反应型阻燃聚氨酯的效率有限，常需引入EG[20]或GO[21]等无机物协同提升，但此类大量添加会导致力学性能下降，且存在分散不均问题，制约阻燃抑烟功能的发挥。因此，开发兼具高效阻燃、低烟毒性与优良力学性能的新型阻燃方法是当前研究的迫切需求[22,23]。

3 涂层型阻燃聚氨酯材料

通过在聚氨酯表面涂覆低含量阻燃涂层，可在基本不影响基体性能的前提下实现高效阻燃，并同步赋予材料防水、耐候、隔热等多功能特性。目前，RPUF阻燃涂层的制备主要包括层层自组装(LBL)、水凝胶涂层、气凝胶涂层、光固化、热固化和辐射固化等多种方法。

3.1 LBL层层自组装

LBL技术通过在聚合物表面有序沉积阻燃组分，如酸源、碳源与气源，实现其在涂层中的优化分布与协同阻燃效应。燃烧过程中能促进形成致密稳定的膨胀炭层，有效隔绝热传递[24]。该方法具备成膜均匀、厚度可控、工艺温和且适用于复杂表面等特点，是一种高效且环境友好的表面阻燃改性策略[25]。

Sun等[26]利用单宁酸(TA)、壳聚糖(CS)及乙

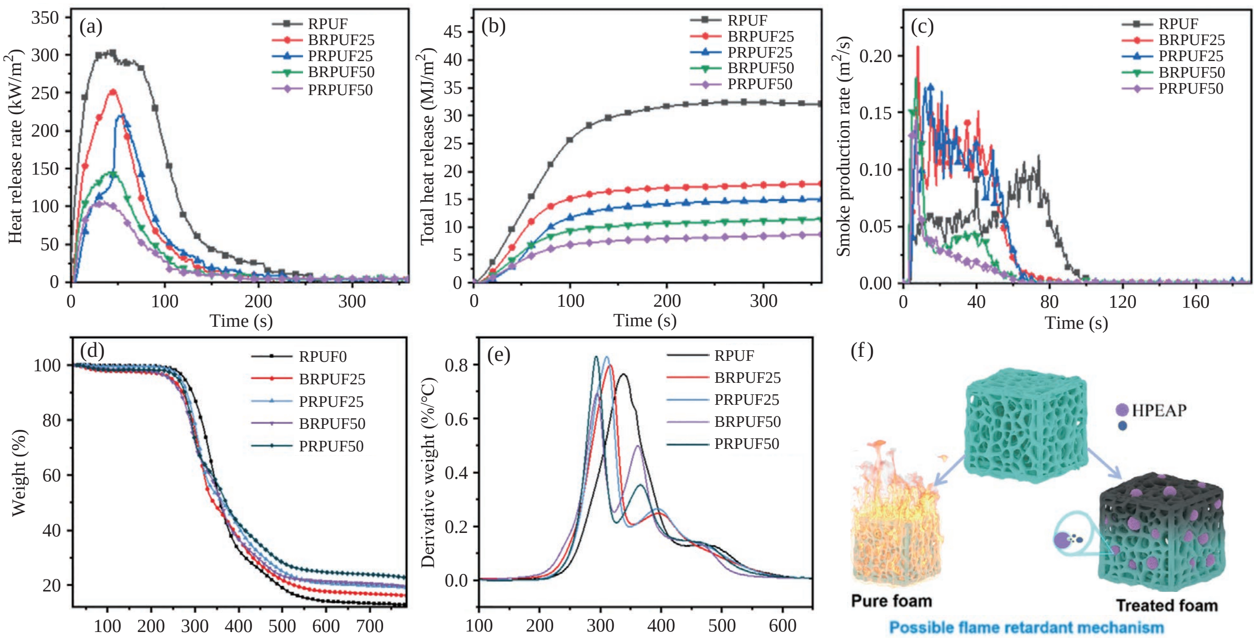


图2 CCT测试的(a) HRR曲线，(b) THR曲线，(c) SPR曲线，(d) TGA曲线，(e) DTG曲线；(f) FR RPUF的阻燃机理示意图[19] (2024 Elsevier版权许可)

Figure 2 (a) HRR curves, (b) THR curves, (c) SPR curves of the CCT test, (d) TGA curves, (e) DTG curves of the thermal degradation test; (f) Schematic diagram of the flame retardation mechanism of FR RPUF (Reprinted with permission from Ref. [19]; Copyright (2024) Elsevier)

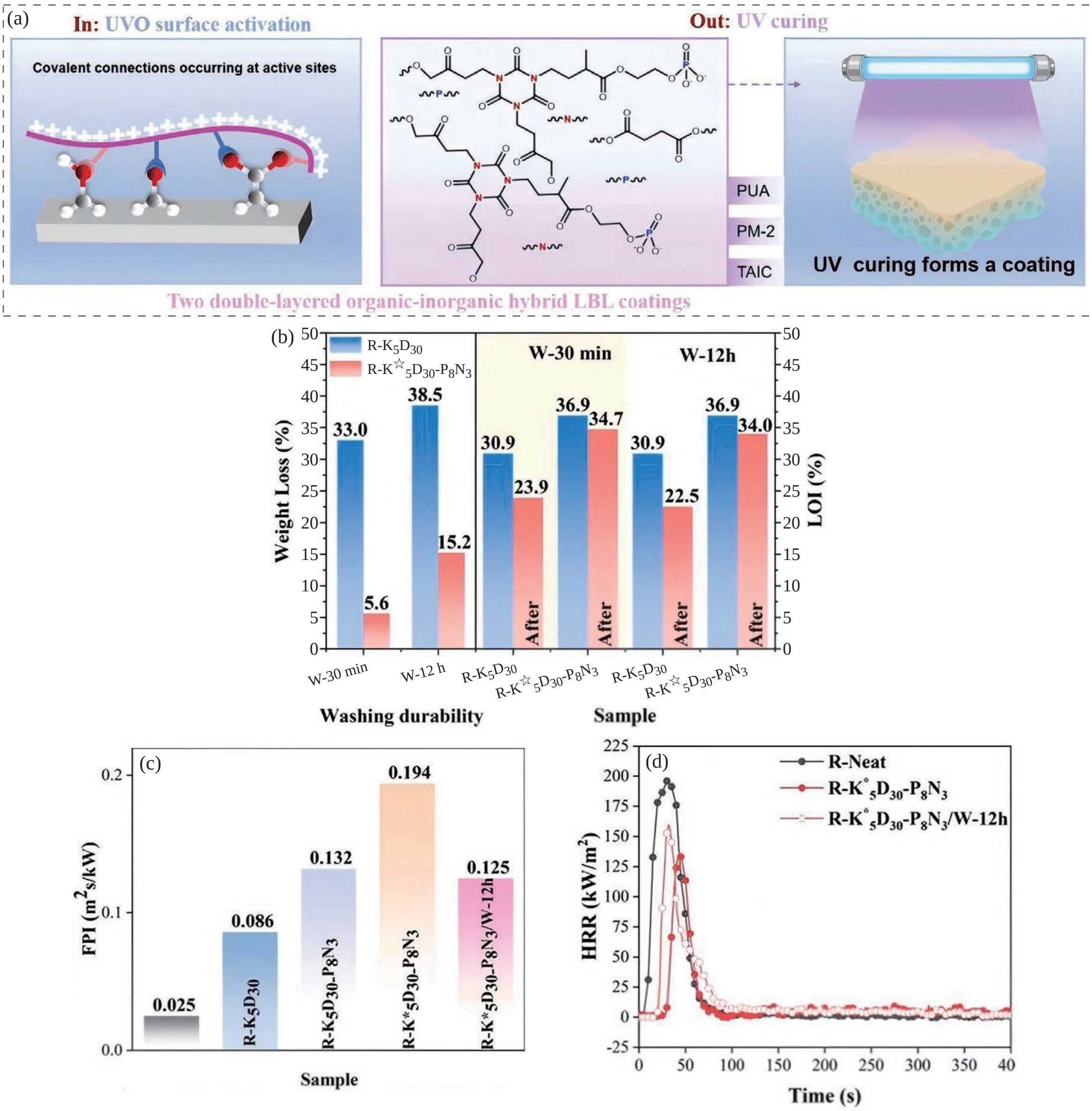
烯二胺四甲基膦酸(EDTMPA)，在RPUF表面通过层层自组装的方法构建了阻燃涂层。当EDTMPA作为最外层(T/C/E-3BL)时，其快速分解促进形成致密炭层，体系LOI达23.2%，通过UL-94 V-0等级，残炭率增加10.4%，平均热释放率下降10.1%，且涂层力学与抗刮擦性能优良。Jin等在紫外臭氧活化后的RPUF表面，通过共价接枝与交替沉积技术，结合*L*-丝氨酸改性高岭土与磷酸盐阻燃剂，最终覆以磷/氮紫外光固化涂层，形成致密防护网络(图3)。优化体系(R-K*$_5$D$_{30}$-P$_8$N$_3$)的LOI为36.9%，达到UL-94 V-0等级，pHRR与TSP较纯RPUF分别降低31.8%和30.0%，并表现出优异的耐水性能。

3.2　水凝胶涂层

水凝胶阻燃涂层是一种基于高含水聚合物网络的表面防护体系。涂覆于RPUF后，通过水分蒸发吸热降温及脱水成炭形成隔热屏障的双重机制，显著降低热释放峰值并提升残炭率，为实现高效环保的表面阻燃提供了新途径。Wang等[28]通过构建MXene@HNT复合物，并采用层层自组装技术结合双网络水凝胶(DH)将其稳固负载于RPUF表面，制备了RPUF/M@H/DH阻燃体系(图4)。该体系表现出优异的阻燃性能，达到UL-94 V-0级，LOI提升至30.5%，pHRR与TSP分别降低29.3%和15.0%，成炭率提高了151.1%，且保持了良好的力学性能。

3.3　气凝胶涂层

气凝胶涂层凭借纳米多孔结构赋予的极低热导率(<0.020 W/(m·K))，为RPUF提供了以高效隔热为核心的阻燃新途径[29]。该涂层在火灾中不仅



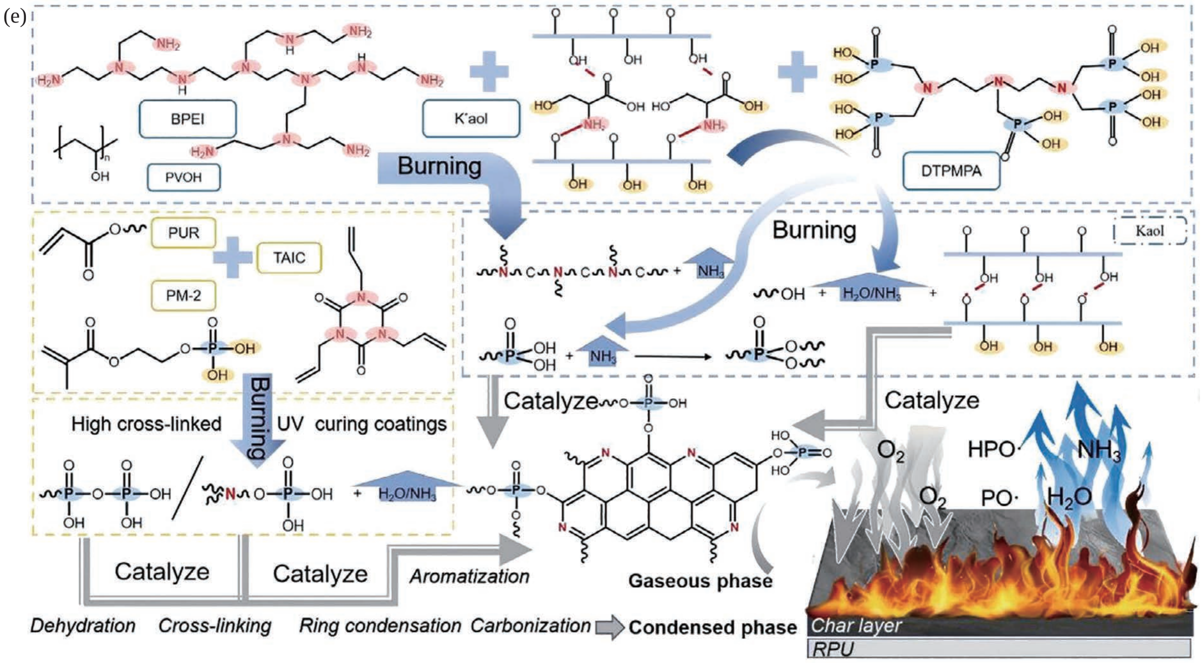


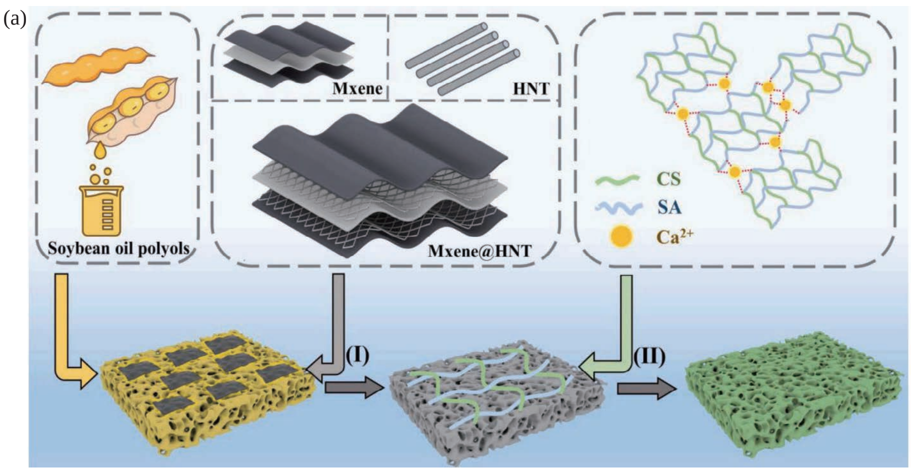
图 3 (a)样品的失重和LOI；(b，c) RPUF样品在浸出后的CCT测试数据；(d) RPUF样品的制备过程；(e)自组装和紫外线固化涂层的RPUF样品的阻燃机理示意图[27] (2026 Applied Surface Science版权许可)

Figure 3 (a) Weight loss and LOI; (b, c) CCT test data of RPUF samples after leaching; (d) The preparation process of RPUF samples; (e) Proposed flame-retardant mechanism of RPUF samples containing self-assembly and UV curing coatings (Reprinted with permission from Ref. [27]; Copyright (2026) Elsevier)

能大幅延缓热流传递，其稳定的多孔骨架还能有效阻隔热解气体扩散与可燃气体渗透，高温下可进一步形成持久隔热屏障[30,31]。Xu等[32]开发了一种木质素增强型阻燃RPUF复合材料，通过引入木质素作为增强与阻燃双功能填料，并协同甲基磷酸二甲酯(DMMP)与EG阻燃体系，再经表面SiO_2气凝胶层后处理，构建了Ct-RPUF/L/FR复合材料。该材料在保持与纯RPUF相当的隔热性能同时，抗压强度由132.4 kPa提升至178.3 kPa，极限氧指数达25.3%，并通过UL-94 V-0级，燃烧时热释放与烟生成显著降低，且表现出良好的耐老化性与环境友好性，满足建筑保温材料的阻燃标准。Gao等在研究中采用真空冻干法在RPUF表面构建了气凝胶阻燃涂层(APP/SA/TEOS) (图5)，显著提升了材料的热稳定性，700 ℃下残炭率较纯RPUF提高了198.0%，LOI达到60%，涂层能有效延长点火时间，降低总热释放率。同时，涂层RPUF保持了优异的隔热性能，导热系数仅为0.0281 W/(m·K)。

3.4 热固化阻燃涂层

热固化阻燃涂层以环氧、酚醛或有机硅树脂为



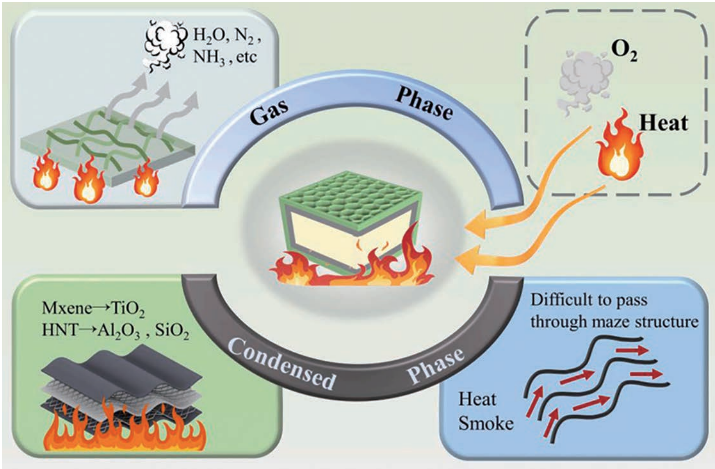
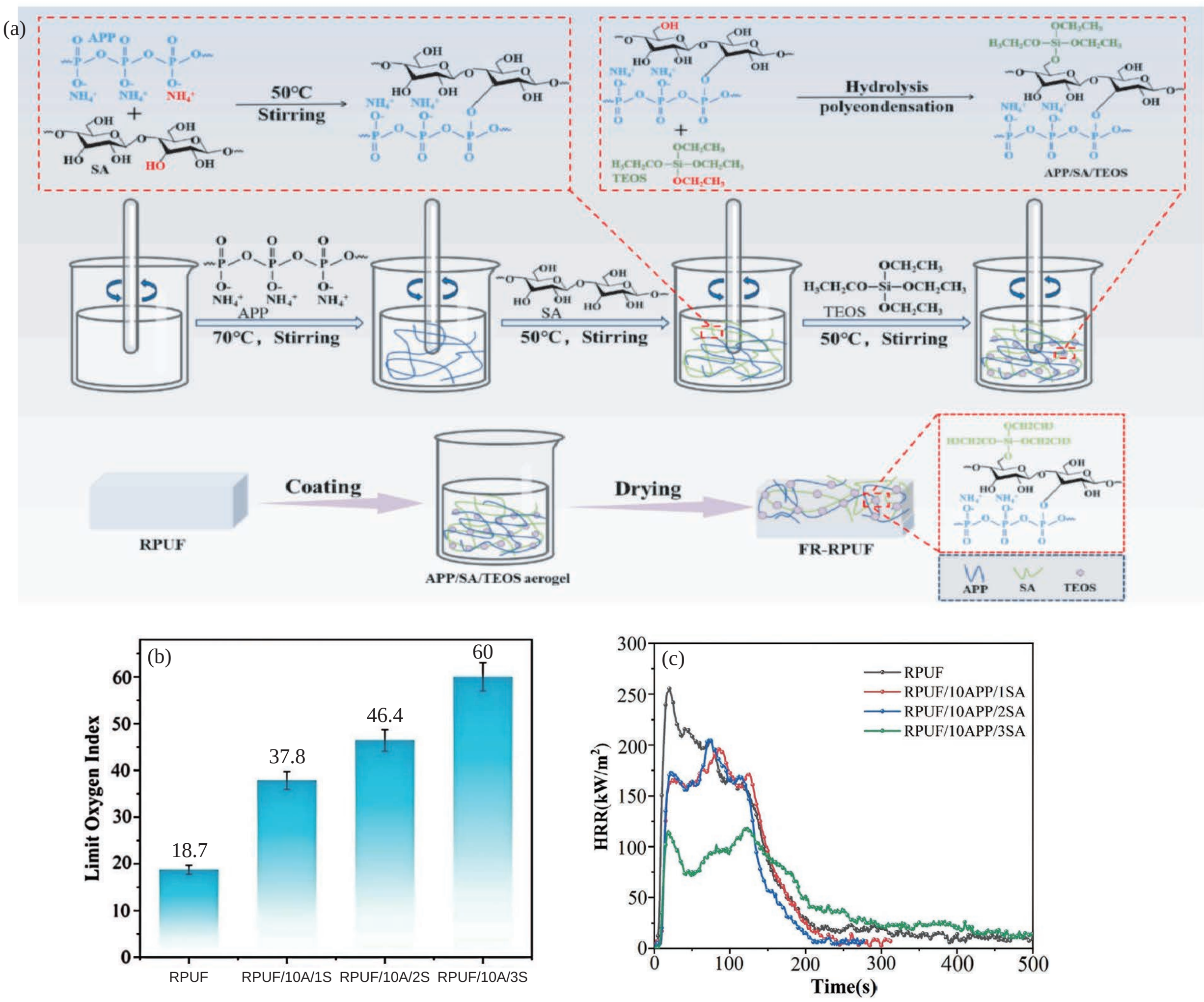


图 4　(a)环保型阻燃RPUF/M@H/DH的制备示意图；(b) RPUF/M@H/DH的阻燃机理示意图[28] (2024 Elsevier版权许可)

Figure 4　(a) Schematic diagram of the preparation of environmentally friendly flame-retardant RPUF/M@H/DH; (b) Schematic diagram of the flame-retardant mechanism of RPUF/M@H/DH (Reprinted with permission from Ref. [28]; Copyright (2024) Elsevier)

基体，在RPUF表面经加热固化构建交联网络，实现高效防火保护层。其阻燃机理主要依赖于涂层受热后形成高强度炭层，该炭层可有效隔绝热量与可燃气体。固化后的涂层具有良好的附着力与耐久性，为RPUF提供了长效且稳定的阻燃解决方案。

Wang等通过开环反应制备了含磷预聚物(HEMAP-*co*-GMA)，并如图6所示，经由涂覆和热固化在RPUF表面形成交联涂层，显著提升了材



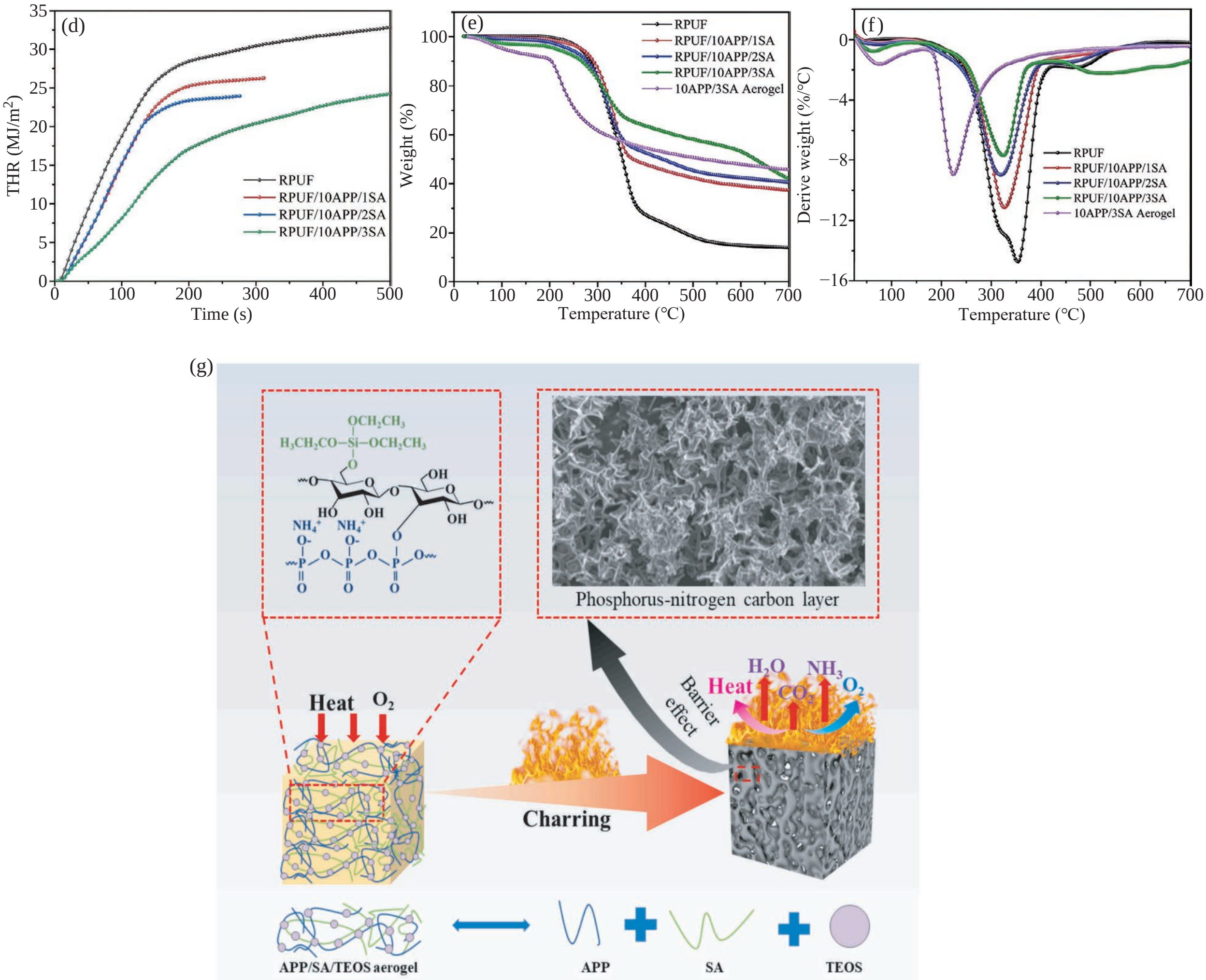
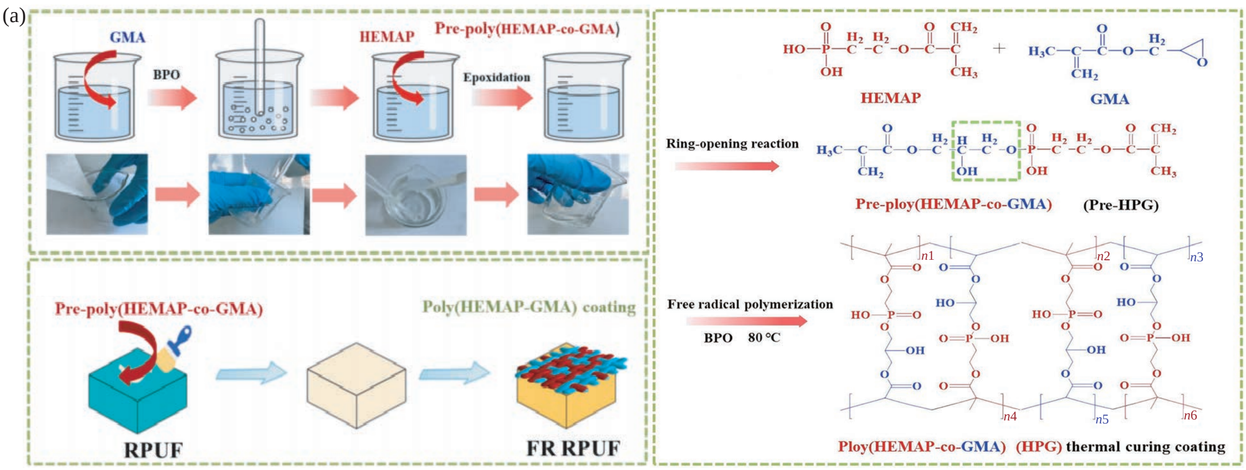


图 5 (a) APP/SA/TEOS/RPUF的合成过程;RPUF与阻燃RPUF样品的阻燃性能:(b) LOI,(c) HRR 曲线,(d) THR曲线;热失重测试的(e) TG曲线和(f) DTG曲线;(g) APP/SA/TEOS膜涂覆的RPUF的阻燃机理示意图[30] (2024 Elsevier版权许可)

Figure 5 (a) The synthesis process of APP/SA/TEOS/RPUF; Flame retardancy of RPUF and flame-retardant RPUF samples: (b) LOI, (c) HRR curves, (d) THR curves; (e) TG curves and (f) DTG curves of CCT test; (g) Schematic diagram of the flame retardancy mechanism of RPUF coated with APP/SA/TEOS film (Reprinted with permission from Ref. [30]; Copyright (2024) Elsevier)



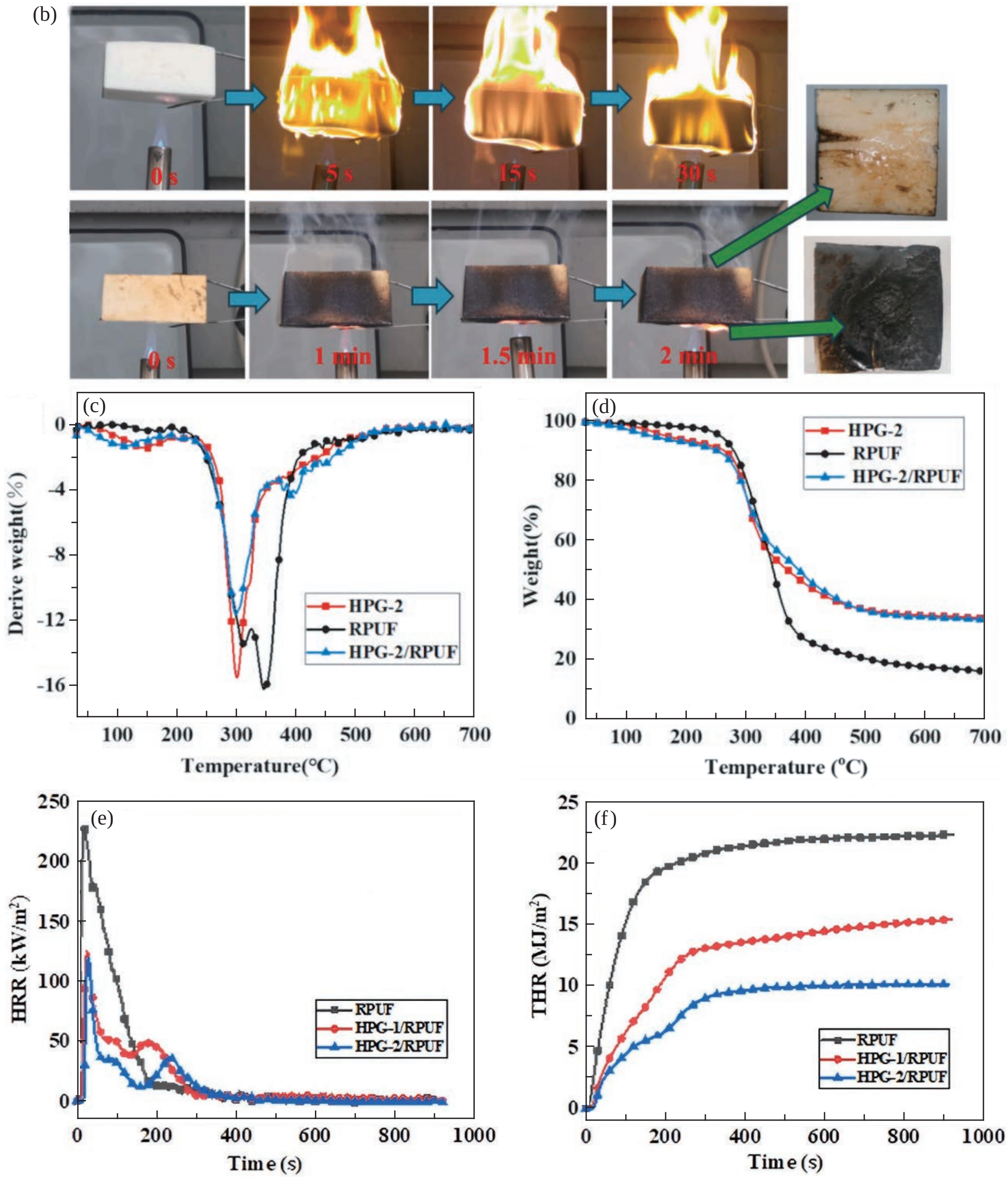


图 6　(a) HPG涂层和阻燃RPUF的制备过程；(b) RPUF和HPG-2/RPUF连续燃烧测试的视频截图，HPG-2/RPUF上下表面的照片；HPG-2, RPUF和HPG-2/RPUF样品的(c) TG 曲线，(d) DTG 曲线，(e) HRR 曲线，(f) THR曲线[33] (2024 Elsevier版权许可)

Figure 6　(a) Preparation process of HPG coating and flame-retardant RPUF; (b) Video screenshots of the continuous combustion test of RPUF and HPG-2/RPUF, photographs of the top and bottom surfaces of HPG-2/RPUF; (c) TG curves, (d) DTG curves, CCT curves (e) HRR curves and (f) THR curves of HPG-2, RPUF, and HPG-2/RPUF samples (Reprinted with permission from Ref. [33]; Copyright (2024) Elsevier)

料的阻燃性能，LOI提高至27.8%，达到UL-94 V-0等级，THR和pHRR分别降低79.6%和54.6%。阻燃机制主要归因于致密炭层的物理屏障与含磷自由基的化学抑制协同作用。此外，该三维交联涂层还进一步改善了RPUF的疏水性、抗压强度与隔热性能。

3.5　光固化涂层

紫外光固化阻燃涂层是一种通过光引发聚合反应在RPUF表面快速形成交联网络的高效阻燃技术。该技术利用含磷、氮等阻燃元素的活性单体，在紫外光照射下于数秒内固化成膜[34,35]。阻燃机制结合了涂层的致密物理屏障作用与阻燃元素的气相自由基捕获及凝聚相成炭催化协同效应。该技术具有高效节能、环境友好、涂层硬度高及附着力强等优点，同时优异的可设计性便于实现多功能集成，为RPUF的先进阻燃防护提供

了创新解决方案[36,37]。

Ding等合成了含磷预聚物(HSP)，并利用紫外光固化技术在RPUF表面构建了交联阻燃涂层(图7)，使材料LOI提高至26.8%并通过UL-94 V-0等级；阻燃机理源于高致密炭层的物理屏障与含磷组分的自由基捕获协同作用，同时高度交联的HSP网络不仅提升了涂层机械性能和疏水性，还借助动态二硫键赋予其自修复与可回收特性。Yu等[38]采用植酸、山梨醇与甘氨酸开发了生物基膨胀型阻燃涂层，并通过紫外光固化将其应用于RPUF表面，LOI提升至39.7%且通过UL-94 V-0等级。该涂层将复合材料点火时间延长3 s，pHRR降低约60%，并显著抑制了烟气释放，阻燃机理主要归因于燃烧过程中形成的致密炭层与不可燃气体的协同效应。

3.6 其他辐射固化方式

辐射固化阻燃涂层(如电子束固化)通过高能辐射引发活性树脂体系(常含磷、氮等阻燃单体)在RPUF表面快速聚合，形成高交联密度的保护层[40]。该技术具有穿透力强、无需引发剂、可固化厚涂层且适用于复杂形状的表面阻燃[41]。Cai等[42]将氧化铁(Fe_2O_3、$Fe_2O_3 \cdot H_2O$、Fe_3O_4)与多孔结构复合，结合硅改性聚磷酸铵(Si-APP)，开发了兼具阻燃、辐射冷却与高反射功能的聚氨酯涂层。燃烧过程中氧化铁的催化作用与Si-APP的脱水成炭协同促进形成致密膨胀炭层，提升防火安全性。

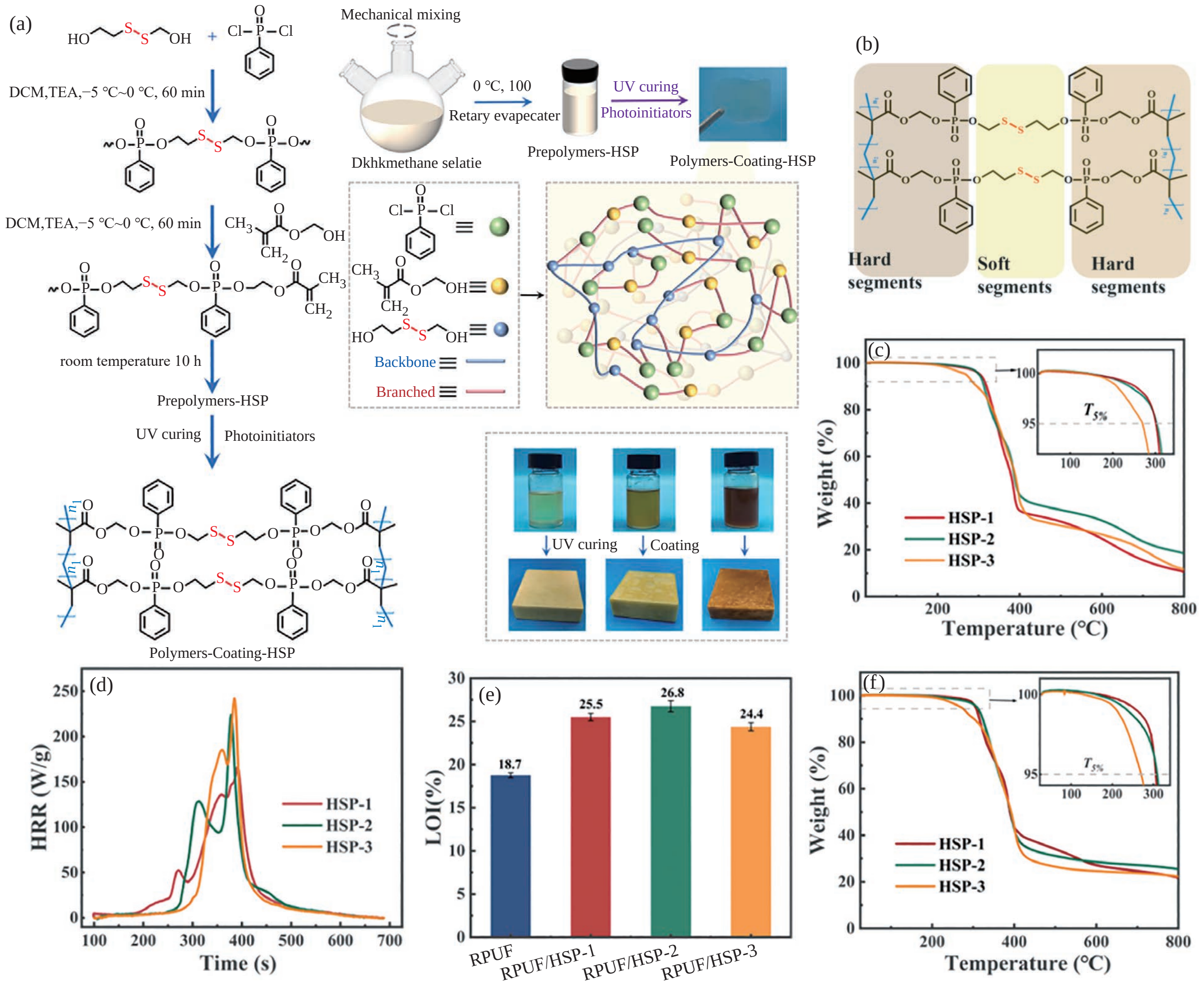


图7 (a) HSP的合成示意图；(b) HSP聚合物的软硬段链结构；(c) HSP在空气中的TG曲线；(d) CCT测试的HRR曲线；(e)阻燃RPUF的LOI；(f) HSP在N_2中的TG曲线[39] (2025 Elsevier版权许可)

Figure 7 (a) Schematic diagram of HSP synthesis; (b) Hard and soft segments structure of HSP polymer; (c) TG curve of HSP in air; (d) HRR curve of CCT test; (e) the LOI of flame-retardant RPUF; (f) TG curves of HSP in r nitrogen (Reprinted with permission from Ref. [39]; Copyright (2025) Elsevier)

4　总结与展望

总结了近年来提高RPUF阻燃性能的技术，并体现了从初期的简单机械共混，逐步演进至阻燃剂结构设计，并向着表面功能构筑方向发展。涂层型阻燃技术作为一种先进的表界面工程技术，成功地将材料的保温性能与防火功能共存，代表了未来高性能安全保温材料发展的重要方向。未来的研究将集中于以下几个方面：一是开发集高效阻燃和长效耐候等多功能于一体的高性能涂层技术；二是致力于绿色可持续，推动基于生物基的无卤低毒阻燃体系发展；三是探索涂覆工艺创新与响应型阻燃，实现涂层对火险的感知与自主强化防护。

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