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聚氨酯硬质泡沫材料的阻燃改性进展

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摘要：聚氨酯硬泡材料（RPUF）优异的隔热性、低密度和良好的压缩性质使其被广泛用作建筑、汽车、电子电器等领域的隔热保温材料，但RPUF极易燃烧、火焰蔓延速率快、烟毒性大等缺点给人们的生命安全造成了巨大的损失。传统的反应型阻燃聚氨酯硬泡材料阻燃效率低，而添加性阻燃剂与聚氨酯基体不相容而对其制备工艺和力学性能有严重的影响。文中综述了近年来发展的层层自组装（LBL）法、光热固化涂覆法、气凝胶涂覆法等新型的阻燃聚氨酯制备途径，这些方法在保证聚氨酯硬泡材料优异的物理性能基础上能同时提升阻燃效率，制备出高效阻燃RPUF，并展望了未来阻燃聚氨酯的发展趋势与前景。

关键词：硬质聚氨酯泡沫；阻燃改性；阻燃涂层；阻燃机理
中图分类号：TQ328.3 **文献标识码：**A **文章编号：**1000-7555（2024）09-0182-09

聚氨酯（PU）分子结构的可设计性、优异的物理性质和力学性能使其被广泛地应用在服装、汽车、建筑、电子、医疗器材等不同领域[1]。如Fig.1所示，除2020年受疫情影响略有下降外，全球聚氨酯制品的市场规模持续稳步上升，预计到2024年全球聚氨酯市场产值将突破720亿美元[2,3]。由于聚氨酯硬泡材料（RPUF）具有泡孔密度高，导热率低和力学性能良好等特点，因此其作为高层建筑、电子电器、交通运输等领域的保温隔热材料得到广泛应用。聚氨酯的分子结构中含有大量的碳氢结构，极易燃烧，并且会释放出大量有毒和致命的烟雾（如一氧化碳和氰化氢等气体），每年因RPUF建筑保温隔热材料发生火灾导致了大量人员伤亡和巨大的财产损失。据统计，2022年全球因高层建筑火灾导致约6.2万人死亡；全国火灾报告总数约82.5万起，死亡人数超过2000余人，直接经济损失约71.6亿元[4-6]。因此，解决聚氨酯保温材料的火灾隐患，提升RPUF的阻燃性和阻燃效率迫在眉睫。

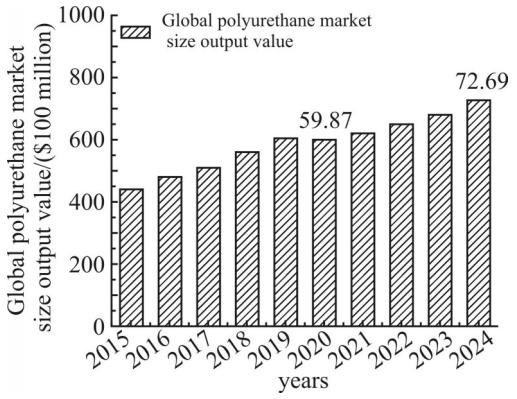


Fig. 1 Market and forecast of the global polyurethane product industry from 2015 to 2024[2]

在过去20年间，提升RPUF阻燃性的主要途径包括反应型阻燃和物理共混法。反应型阻燃剂是对聚氨酯分子链进行阻燃改性，在发泡过程中赋予聚氨酯泡沫阻燃性能，纯RPUF的极限氧指数为18%~19%，通过反应型阻燃的聚氨酯硬泡极限氧指数（LOI）仅提高至23%~24%，垂直燃烧等级为V-1，阻燃效率相对较低[7-9]。添加型阻燃剂通常是将含卤阻

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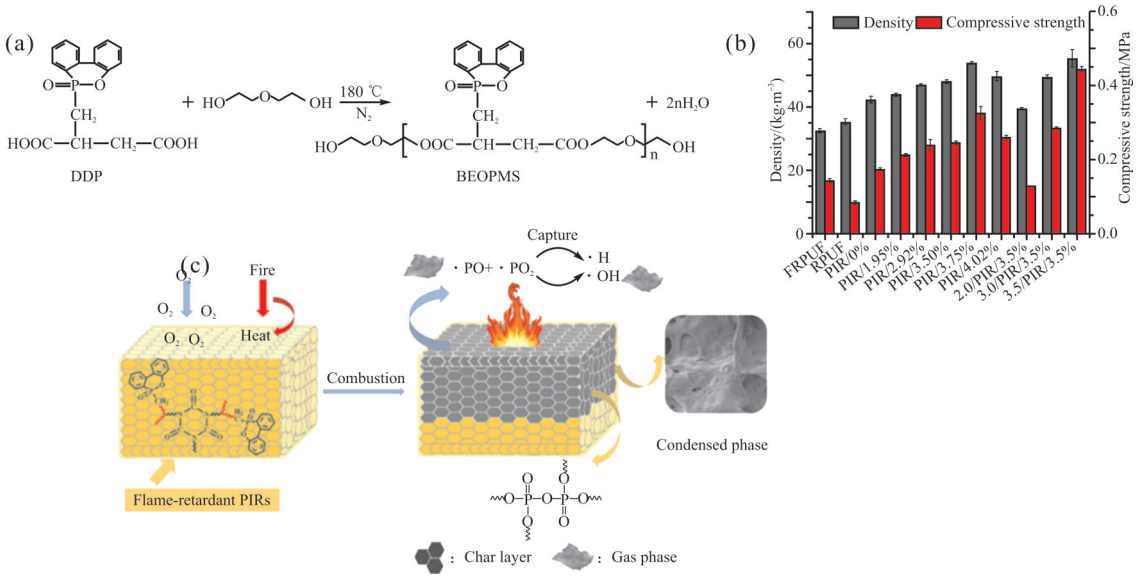


Fig. 2 (a) Synthesis process of BEOPMS; (b) mechanical and physical properties of different contents of flame retardant polyurethane; (c) flame retardant mechanism of modified RPUF [18]

燃剂、无机含磷化合物[10]、膨胀石墨(EG)[11]等阻燃剂通过共混法加入到聚氨酯中提高其阻燃性能。在RPUF体系中添加阻燃剂阻燃效率较高。添加型阻燃剂通常不与RPUF中的异氰酸酯基团反应,阻燃剂和基体之间的相容性较差,使得共混后的RPUF力学性能恶化,严重影响基体固有的性能,且对RPUF的制备工艺有一定的限制[12]。

为使聚氨酯硬泡材料既能实现良好的阻燃性又能保证其原有的力学性能,目前在本领域内提出了层层自组装法(LBL)、光热固化涂层型、气凝胶涂层型等新型的阻燃途径,即在聚氨酯泡沫表面通过层层自组装形成LBL涂层,或在其表面涂覆阻燃预聚体进行光热固化形成阻燃涂层,以达到提高RPUF阻燃性的目的[13]。因此,本文概述了近年来这些新型阻燃涂层对聚氨酯硬泡材料阻燃性和力学性能的影响及其阻燃机理。

1　高效磷氮反应型阻燃改性和复合协效阻燃

传统卤素阻燃剂虽具有较高的阻燃性,但其高毒性限制了其广泛使用,为了迎合绿色可持续发展战略,科学家们开始致力于高效含磷阻燃剂的开发[14]。许冬梅等[15]将聚磷酸铵(APP)和EG添加到RPUF内,与纯RPUF相比,LOI提高了51%,阻燃剂与基体之间的不相容性使得整体的力学性能发生了恶化。将含有磷等阻燃元素的化合物通过化学反应引入RPUF分子链内进行改性,可使改性后的RPUF具有一定的阻燃性,如Melissa等[16]采用四(羟甲基)硫酸磷(THPS)对环氧大豆油(ESO)进行磷酸化改性处理,合成了磷酸化环氧化大豆油(PESO)(如Fig.2),将PESO与聚氨酯原料反应形成含磷聚氨酯硬泡材料P-RPUF,PESO的加入促进了P-RPUF的炭化能力,形成了一层保护屏障层,可以抑制燃烧过程中的热量释放和烟雾排放;与纯RPUF相比,含有12.3% PESO的阻燃RPUF的峰值放热率、总放热率和总烟雾产生量分别下降了40%,35%和49%。Zhou等[17]合成了3种含磷桐油基多元醇,用于制备阻燃P-RPUF,其中阻燃效果最好的P-RPUF的LOI达到26.2%。此外,将带有刚性分子结构的含磷反应型阻燃剂引入RPUF分子链中,改性后的RPUF不但具有一定的阻燃性,而且其力学性能也会有一定程度的提高,如Qian等[18]通过9,10-二氢-10-[2,3-二(羟基羰基)丙基]-10-磷杂菲-10-氧化物(DDP)与二甘醇反应合成了反应性阻燃二元醇(BEOPMS),而后将BEOPMS与多元醇发泡制备了P-RPUF,当P-RPUF的磷含量为3.5%时,改性后的RPUF的LOI值从

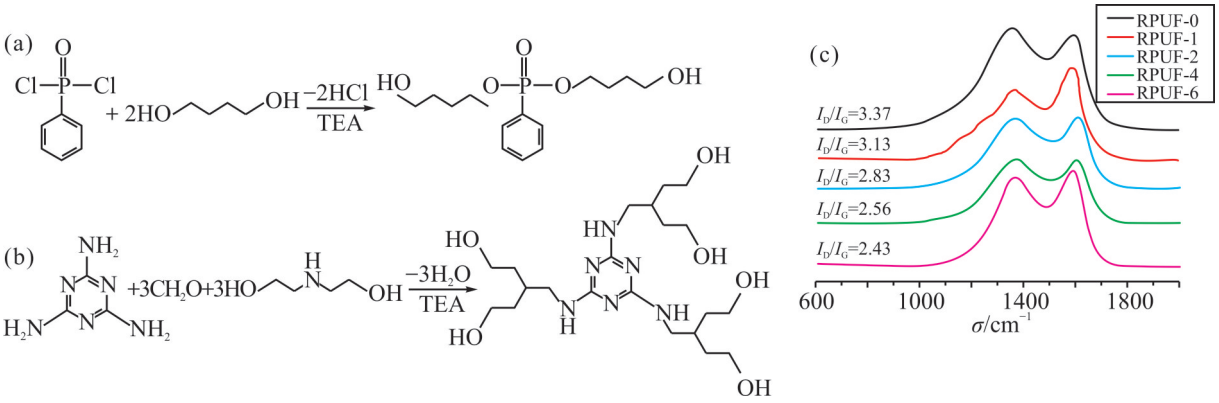


Fig. 3 Synthesis route of reactive flame retardant polyols (a) BHPP and (b) MADP; (c) Raman spectra of residual char[22]

22.0 %增加到26.5%，并在UL-94可燃性测试中达到V-0等级。在燃烧过程中，阻燃剂的P—C键断裂会在凝聚相中形成磷酸和聚磷酸，并释放一氧化磷（PO）和二氧化磷（PO_2）自由基，其中，磷酸和聚磷酸可以促进基质脱水和羧化，提高残炭的产率，PO和PO_2自由基可以捕获空气中的氢自由基和羟基，提高RPUF的阻燃效率（如Fig.2所示）；而且随着BEOPMS的引入，异氰酸酯基/羟基（NCO/OH）比值的提升，阻燃RPUF的密度提高，压缩强度从0.13 MPa提高到0.45 MPa[19~21]。

当RPUF分子链中引入阻燃元素后，反应型含磷P-RPUF仍存在阻燃效率较低的缺点。针对这一问题，对RPUF进行复合协效改性可大幅度提高RPUF的阻燃性能，Yao等[22]合成了双(4-羟基丁基)苯基膦酸酯（BHPP）和三聚氰胺衍生多元醇（MADP），如Fig.3所示，在RPUF/EG体系内，当BHPP/MADP的质量比为1:1时，阻燃剂内的C＝P—O分解有助于形成紧密和连续的残炭，三嗪环基团热释放产生NH_3，从残炭的拉曼光谱可知残炭的石墨化程度逐步提高，与RPUF/EG相比，LOI值从27.0%增加到33.5%，UL-94测试达到V-0等级[23]。笔者课题组[24]通过苯基磷酰胺二氯（PPDCl）与乙二醇反应形成苯基磷酰二醇醚低聚物（PPGE），并将PPGE与多苯基多亚甲基多异氰酸酯（PAPI）共混发泡制备了P-RPUF。当P-RPUF燃烧时，PPGE受热分解产生的含P自由基可捕捉H•和OH•等断链自由基以延缓RPUF的分解；而且，燃烧后形成的连续焦渣一定程度上抑制了可燃气体的扩散和热量传递。在2%P-RPUF体系内加入EG后，与纯RPUF相比，LOI值从20.0%增加到34.5%，UL-94等级达到了V-0；由于RPUF分子链中含刚性苯环结构的PPGE链段的存在，P-RPUF的压缩模量从初始的0.28 MPa增加至0.78 MPa，阻燃RPUF获得超高阻燃效率的同时其力学性能得到大幅度提升[25,26]。

2 新型含磷/硅涂层的制备与阻燃改性

涂层型阻燃剂仅需要在聚氨酯表面涂敷较低含量的阻燃剂就可以实现聚氨酯泡沫材料所需的阻燃性而不会改变RPUF本身的性能，目前，RPUF阻燃涂层的制备方法主要分为逐层组装法、直接涂覆法、光固化法和热固化法等。

2.1 LBL法

LBL是采用无机物或有机-无机混合纳米涂层作为阴阳离子，通过静电作用层层自组装制备的多层无卤阻燃涂层，LBL法制备的阻燃涂层能够抑制燃烧后聚氨酯泡沫熔体的滴落，并大幅降低热释放速率和烟释放量[27]。Lee等[28]在PU泡沫上成功沉积了云母基复合涂层，仅需2层壳聚糖阳离子/聚(丙烯酸)阴离子云母（CHM/PAAM）涂层，即可使聚氨酯泡沫热释放速率峰值降低43%，总烟雾释放量降低70%，大幅削减了聚氨酯泡沫的烟雾释放量；并且随着涂层层数增加可进一步降低烟雾释放量。Pan等[29]在PU泡沫表面沉积了由壳聚糖、钛酸纳米管和藻酸盐制成的阻燃涂层，如Fig.4(a)所示，涂覆后的PU泡沫的质量仅增加5.65%，其峰值放热率、峰值发烟率和烟释放总量分别降低了70.2%，62.8%和40.9%，形成的高石墨化程度的焦渣提供了有效的保护，抑制了可燃气体的扩散(Fig.4(b,c))，使其阻燃性

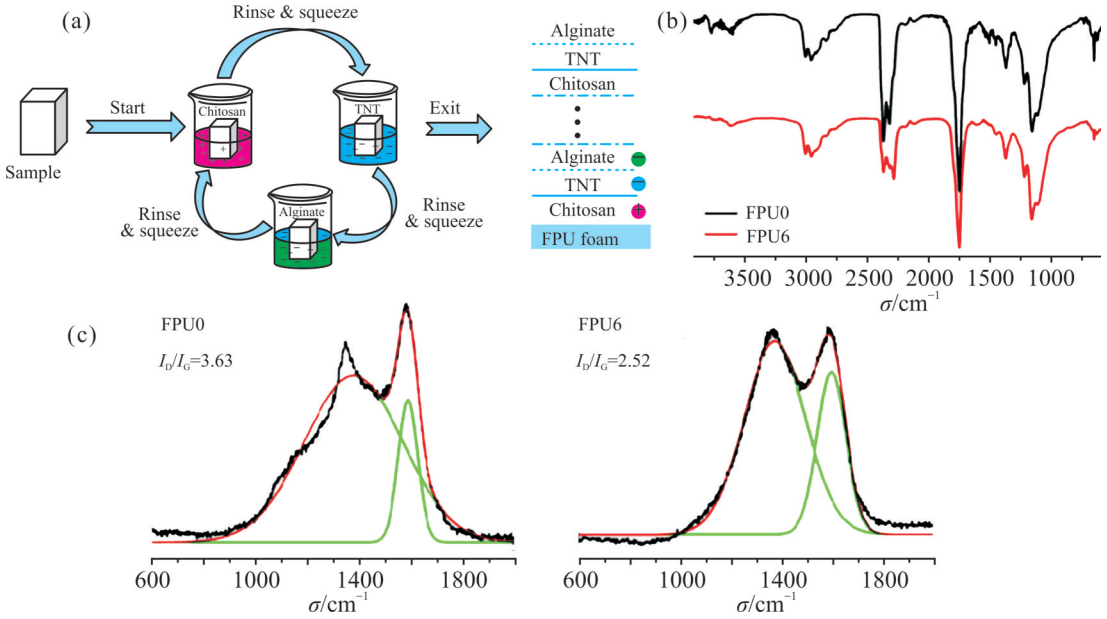


Fig. 4 (a) Schematic diagram of layer by layer assembly of flame retardant coating; (b) FT- IR spectra of thermal decomposition products of FPU0 and FPU6; (c) Raman spectra of residual char of FPU0 and FPU6[29]

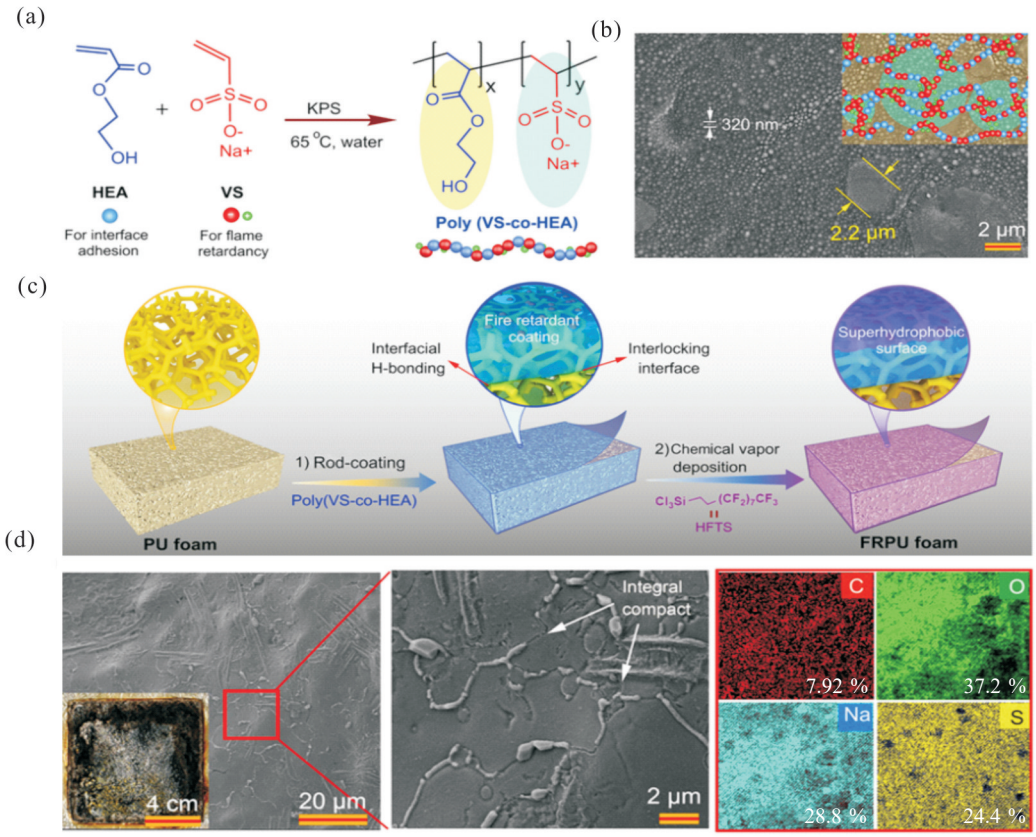


Fig. 5 (a) Synthesis of flame-retardant poly(VS-*co*-HEA) coating; (b) typical phase separation micro/nano structure of poly(VS50-co-HEA50); (c) schematic diagram of the preparation process of flame-retardant rigid polyurethane foam (FRPU); (d) SEM images of the residue of FRPU[34]

能得到大幅提升。Chen等[30]通过LBL法将壳聚糖和六偏磷酸钠涂覆在RPUF表面，涂覆后的RPUF可在高温下抵抗火焰的穿透，使火焰增长率、热释放速率峰值和最大平均放热率分别降低了55%，43%和38%。虽然LBL处理技术具有诸多优势，但其在实际应用中存在一定挑战，特别是大规模生产具有一定的技术难度[31]。针对这个问题，Bethany等[32]利用两步沉积工艺将带有相反电荷的聚乙烯亚胺、聚磷酸铵和埃洛石黏土组成的聚电解质复合涂层（PECs）成功应用于RPUF。这种涂层工艺不仅简便实用，而且利用这种技术制备出的阻燃涂层与RPUF结合后热释放速率峰值降低了52%以上，该无卤涂层阻燃聚氨酯泡沫更加环保，并提升了安全性[33]。

2.2 直接涂覆法

采用LBL法制备的阻燃涂层虽在一定程度上提高了PU的阻燃性能，但其阻燃效率未能达到预期要求，且阻燃涂层与基体的黏结性较差；而且，LBL法的涂覆工艺过于繁琐，使该法的工业化应用受到了极大的限制。Ma等[34]通过蜗牛和树蛙黏附力机制原理，首先将丙烯酸羟乙酯（HEA）和乙烯基磺酸钠（VS）进行自由基共聚，将得到的聚合物(Poly(VS-*co*-HEA))涂覆在聚氨酯硬泡材料表面，成功设计出了具有相分离微/纳米结构的阻燃聚合物涂层(如Fig.5所示)，对该涂层阻燃RPUF体系进行阻燃测试表明：LOI值达到了35.5%，而且UL-94测试达到V-0，燃烧后产生的焦炭产率高达80.3%，阻燃涂层RPUF的焦炭层完整且紧凑，该涂层使用氟硅烷对表面进行CVD法处理后，该涂层被赋予超疏水的效果，极大提高了该涂层的耐用性[35]。

2.3 光、热固化阻燃涂层

在RPUF表面直接涂覆阻燃剂制得阻燃RPUF，其工艺虽然简便，但对RPUF力学性能的改善较小。通过光固化或热固化制备阻燃涂层可以在RPUF表面形成三维交联的网络结构，可以大大增加聚氨酯

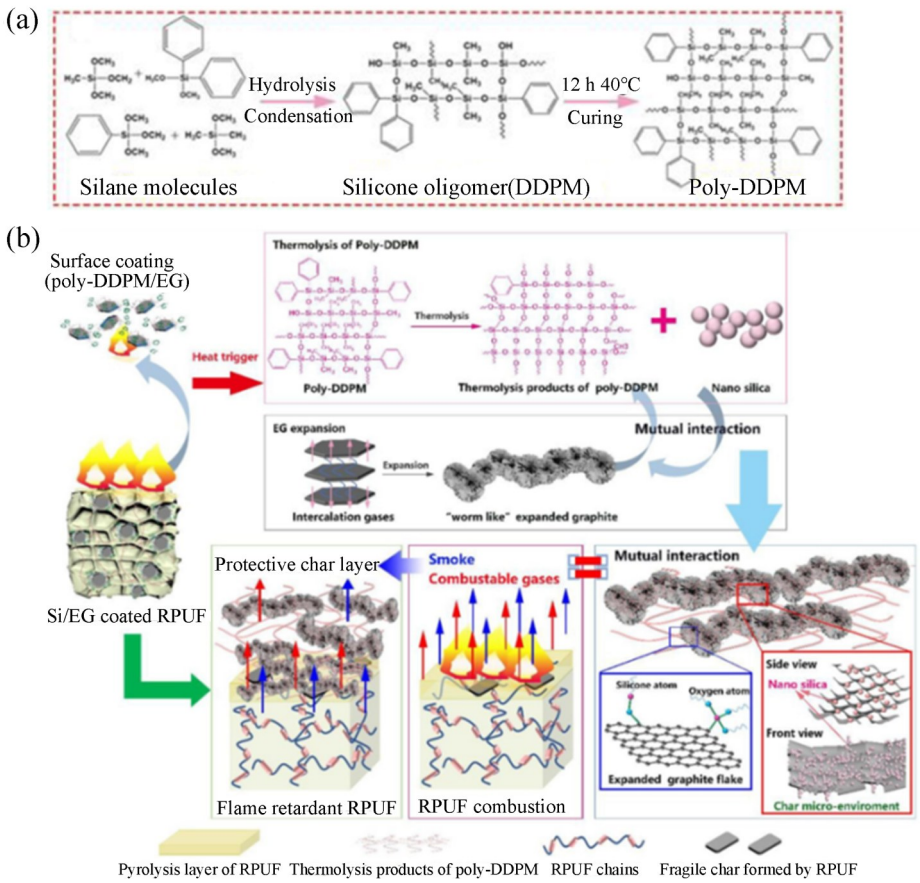


Fig. 6 (a) Schematic diagram of the synthesis route of DDPM and curing process of polyDDPM; (b) schematic diagram of the flame retardant mechanism of Si/EG coating RPUF[36]

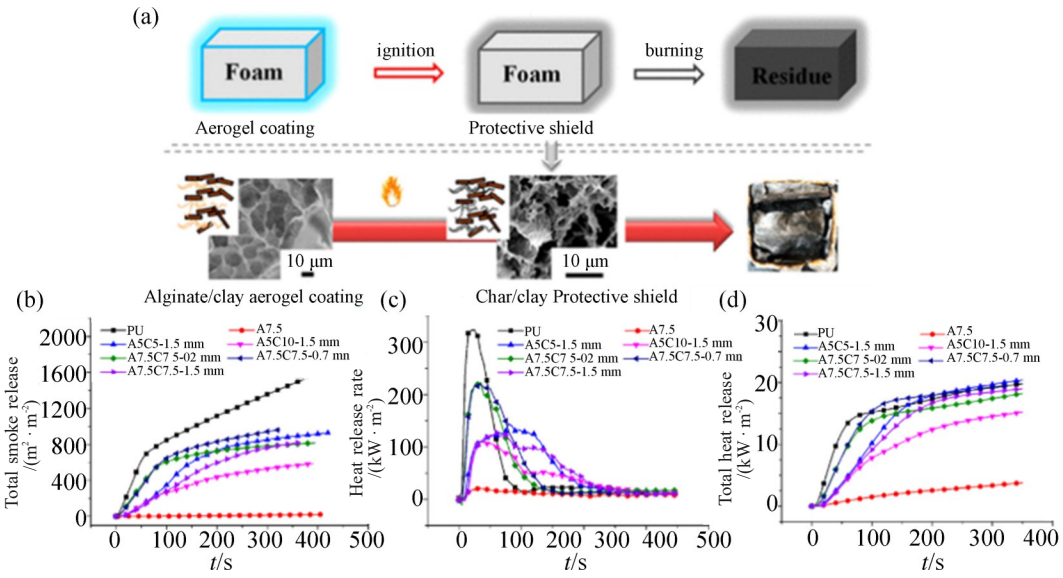


Fig.7 (a) Flame retardant mechanism of polyurethane coated with alginic acid/clay aerogel; (b) TSR, (c) HRR and (d) THR curves of flame retardant RPUF coated with aerogel[43]

硬泡材料的力学性能，并且阻燃效率较高。Wang等[36]合成了一种有机硅低聚物（DDPM），将DDPM预聚液与EG共混形成新的阻燃涂料，如Fig.6所示，通过刷涂的方式将其均匀涂覆在RPUF表面，采用低温加热在RPUF表面形成热固化阻燃涂层。在燃烧过程中，EG和ploy-DDPM可形成保护性炭层，与纯RPUF样品相比，其阻燃性能大幅提高，LOI值从18%增加到32.3%，UL 94等级提高到V-0级别，热释放速率峰值降低了55%。该涂层不仅有良好的耐久性，而且将ploy-DDPM与EG薄片结合时，EG与聚DDPM之间的CH-π和π-π相互作用，使得Si/EG涂层RPUF的压缩强度提高到290 kPa。Huang等[37]通过紫外光（UV）固化的方式将开发的新型无卤素自熄涂层应用于RPUF表面，获得了表面阻燃的RPU泡沫系统（SFR-RPUF）。当SFR-RPUF泡沫涂层厚度为25 μm时，燃烧时SFR涂层会形成致密炭层，并释放多种惰性气体以防止RPUF泡沫进一步燃烧并减少火焰蔓延，其中SFR-RPUF与纯RPUF相比，平均热释放速率降低了33.2%，大大提升了防火安全性。此外，由于光固化涂层的自支撑作用，与纯RPUF相比，压缩强度略有提升[38]。

3　气凝胶阻燃改性聚氨酯泡沫

近年来，开发的新型多孔材料——气凝胶因具有低密度、高表面积和低热导率等优点被广泛用于生物医疗、超级电容器和催化剂载体等领域[39,40]。气凝胶的纳米孔及三维网状结构延长了基质的热量传导路径，所以将气凝胶作为阻燃涂层不仅能提升聚氨酯泡沫的阻燃性能[41,42]，还可以改善泡沫材料的隔热性能。Chen等[43]利用冷冻干燥法制备了具有海藻酸盐/黏土气凝胶涂层的高效阻燃聚氨酯泡沫，如Fig.7所示，在A7.5C7.5-0.7 mm的组分中，LOI值高达60%，远超市面上绝大部分阻燃剂，其热释放速率、烟释放总量、CO释放量和CO_2释放量等都有不同程度的降低。其阻燃机理主要是燃烧的气凝胶隔绝了热量及可燃气体的输送，进而降低了火焰传播速率。由于气凝胶的固体骨架是由三维网络结构的纳米颗粒组成，这些微观颗粒之间可以形成强大的链接力，当气凝胶与聚氨酯硬泡材料结合后，可使阻燃RPUF的压缩强度有一定的提升。

4　前景与展望

本文总结了近年来提高RPUF阻燃性能的方法，并探讨了这些阻燃方法对RPUF性能的影响及其阻燃机理。在RPUF中引入添加型阻燃剂会对RPUF的制备与加工性能造成严重影响，含磷反应型阻燃改性体系虽对RPUF的加工性能没有明显影响，但其阻燃效率较低。针对以上问题，在反应阻燃剂中引

入其它阻燃元素进行协效阻燃，并将含刚性基团的反应阻燃剂引入RPUF分子链内，可以同时提高RPUF的阻燃效率和力学性能。反应性与添加性阻燃剂进行复合改性可提高RPUF的阻燃效率；通过不同的方式在RPUF表面形成阻燃涂层，可以提升RPUF本身的阻燃效率，而且还可赋予聚氨酯硬泡材料高压缩性能，疏水性等，这些多功能性为扩大聚氨酯硬泡材料的应用领域提供更多的可能。

气凝胶阻燃涂层可以提高RPUF的阻燃效率和隔热性，但由于气凝胶涂层繁琐的操作和复杂的工艺，气凝胶阻燃涂层难以得到大规模的商业应用。尽管当前气凝胶涂层的成本较高，但考虑到其出色的性能和潜在的市场需求，可以相信随着未来气凝胶涂层制备工艺的持续改进和优化，气凝胶涂层的生产成本将得到降低，使其具备推广应用的可能。总之，阻燃RPUF的发展趋势更加注重可持续、环保、高效节能等阻燃剂的开发，提高聚氨酯材料的阻燃效率和综合物理性能，并降低RPUF燃烧中的烟毒性，以扩大RPUF在建筑、电子电器和交通运输等领域的应用。

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Progress of Flame Retardant Modification for Rigid Polyurethane Foam Materials

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ABSTRACT: Rigid polyurethane foam (RPUF) materials are widely used as thermal insulation material in buildings, automobiles, electronic applications, and other fields because of their excellent thermal insulation, low density, and good compressive properties. However, RPUF is very easily burnt when it is ignited, the flame spread rate is fast and the smoke toxicity is large, which cause huge loss to people's life safety. The traditional reactive flame retardant RPUF has low flame retardant efficiency. Whereas the addition of flame retardants has serious influence on the preparation technology and mechanical properties because of the incompatibility between additive flame retardant and polyurethane matrix. In this paper, new flame retardant routes on the improvement in the flame retardancy of RPUF have been developed in recent years, and different flame retardant coatings by layer-by-layer assembly (LBL) method, photo and thermal curing, aerogel coating, etc. were reviewed. The highly efficient flame retardant RPUFs have not only maintained the mechanical performance of RPUFs, but also improved the flame retardant efficiency. The development trend and prospect of flame retardant RPUFs in the future were prospected.

Keywords: rigid polyurethane foam; flame retardant; flame retardant coating; flame retardant mechanism