文章编号： 1008-9357(2025)04-0294-15 DOI： 10.14133/j.cnki.1008-9357.20250410002

苯并噁嗪树脂的高性能化、绿色化与功能化研究进展

谢 琳， 陆 寅， 姚振豪， 盛维琛， 张 侃
（江苏大学材料科学与工程学院，高分子材料研究所，江苏 镇江 212013）

摘 要： 苯并噁嗪树脂作为一类新型的热固性高分子材料，因其具有出色的性能和灵活的结构设计性而备受学术界和产业界的关注。随着高端技术领域的飞速进步以及人类环保意识的不断提高，苯并噁嗪树脂未来的发展趋势必然是以高性能化和多功能化为基石，以可持续绿色化为主导。本团队坚持从新型苯并噁嗪分子的合成出发，通过对分子结构和氢键作用的设计调控，深入探索热固性树脂的单体分子结构与固化机理及固化物性能的关联；创新高性能苯并噁嗪树脂体系，优化可再生生物基热固性树脂结构与性能，设计、制备新型树脂基功能化材料。本文综述了团队近年来在苯并噁嗪树脂高性能化、绿色化与功能化方面的研究进展，并对苯并噁嗪树脂未来的研究方向进行了展望。

关键词： 苯并噁嗪树脂；高性能；功能化；生物基；分子设计
中图分类号： O69 **文献标志码：** A

Research Progress on High Performance, Sustainable and Functional Properties of Benzoxazine Resins

XIE Lin, LU Yin, YAO Zhenhao, SHENG Weichen, ZHANG Kan
（Institute of Polymer Materials, School of Materials Science and Engineering, Jiangsu University, Zhenjiang 212013, Jiangsu, China）

Abstract: Benzoxazine resins, as a novel class of thermosetting polymer materials, have garnered significant attention from both academia and industry due to their unique structural designability. With the rapid advancements in high-end technological fields and the continuous enhancement of environmental awareness among humans, the future development trend of benzoxazine resins is inevitably grounded in high performance and multifunctionality with a predominant focus on sustainability. Our research team insist on the novel synthetic approach to benzoxazine molecules, aiming to explore the relationship between the molecular structure, the curing mechanisms of thermosetting resin monomers and the resulting material properties through the design and regulation of molecular structures and hydrogen bonding. We innovate high-performance benzoxazine resin systems, develop methods for optimizing the performance of sustainable bio-based thermosetting resins, and fabricate new benzoxazine-based functional materials. This paper reviews the recent progress made

收稿日期： 2025-04-10
基金项目： 国家自然科学基金（52073125）；国家重点研发计划（2023 YFB3709700）
作者简介： 谢 琳（1992—），女，山东烟台人，主要研究方向为生物基苯并噁嗪树脂。E-mail: XL15737978779@163.com
通信联系人： 张 侃，E-mail: zhangkan@ujs.edu.cn
引用格式： 谢 琳，陆 寅，姚振豪，盛维琛，张 侃. 苯并噁嗪树脂的高性能化、绿色化与功能化研究进展［J］. 功能高分子学报，2025，38（4）：294-308.
Citation: XIE Lin, LU Yin, YAO Zhenhao, SHENG Weichen, ZHANG Kan. Research Progress on High Performance, Sustainable and Functional Properties of Benzoxazine Resins［J］. Journal of Functional Polymers, 2025, 38（4）: 294-308.

by our team in the high-performance enhancement, greening, and functionalization of benzoxazine resins, while also projecting future research directions for this field.

Key words: benzoxazine resin;　high performance;　functional application;　bio-based;　molecular design

为了满足电工电子和航空航天等先进技术领域的特殊需求，研究者们对高性能材料的开发日趋重视。热固性树脂因其质轻和效优而被认为是高性能聚合物材料基体必要的候选之一。聚苯并噁嗪(PBZ)树脂作为一种较为新型的热固性树脂，由苯并噁嗪单体热开环固化得到，具有较高的热稳定性[1-4]、可调控的力学性能[5,6]、突出的阻燃性[7,8]、较低的表面自由能[9,10]、低介电常数[11-13]、固化过程中近零收缩性[14,15]、低吸水性以及良好的黏附性[12,16,17]等诸多优点，可应用于航空航天、电工电子、涂料和黏合剂等众多技术领域[18](图 1)，被视为传统环氧类、双马来酰亚胺类和酚醛类树脂的有力替代品[19]。然而，苯并噁嗪树脂依然存在高固化温度、低交联密度、质脆低韧以及合成原料化石基来源(煤炭、石油、天然气)占比大的弊端。幸运的是，苯并噁嗪具有灵活的分子结构设计性[20-22]，可通过自然界中广泛存在的生物基酚类(如丁香酚[23,24]、腰果酚[25]、愈创木酚[26,27])、生物基胺(如糠胺[28]、硬脂胺[29]、脱氢枞胺[30])和生物基醛(如糠醛和水杨醛[31])的独特化学结构来调控固化后树脂的性能。然而，开发性能优于普通化石基苯并噁嗪树脂的生物基聚苯并噁嗪热固性材料仍然是一个巨大的挑战。本团队在苯并噁嗪领域深耕多年，通过设计新型化学结构以及构筑苯并噁嗪分子内氢键，在引入不同功能基团的基础上深入探究了苯并噁嗪树脂的构效关系，进一步采用可再生原料合成了新型生物基苯并噁嗪树脂，开发了一系列潜伏催化固化与本征阻燃型生物基树脂，还通过苯并噁嗪树脂的功能化来拓展其在复合材料、润滑油等领域的新应用。

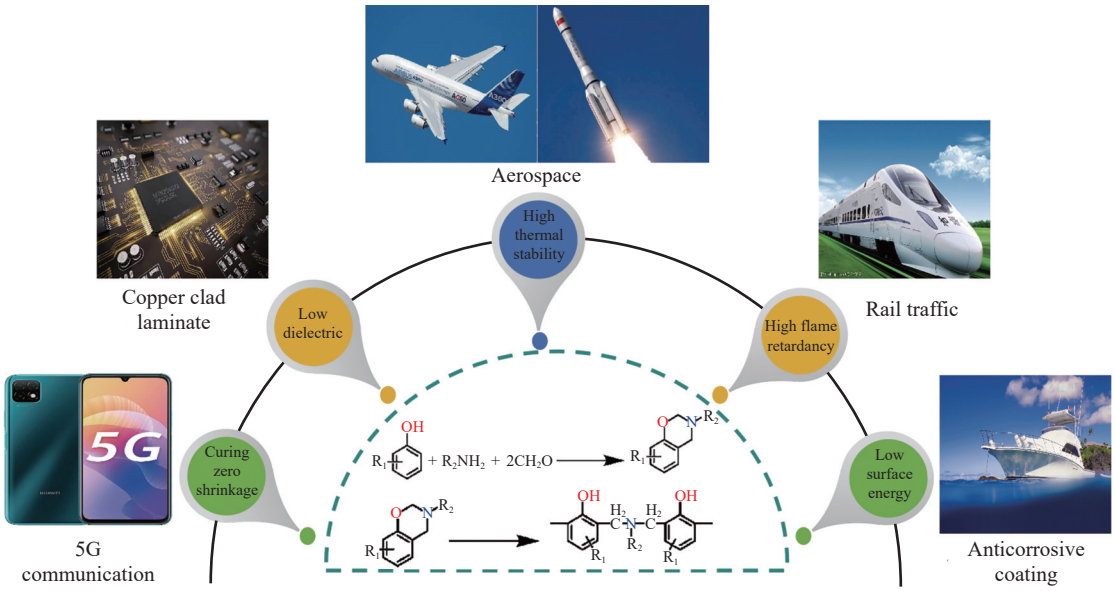

图 1　聚苯并噁嗪树脂的合成及其应用

Fig. 1　Synthesis and application of PBZ resin

本文综述了团队近年来在苯并噁嗪树脂高性能化、绿色化与功能化三方面的工作，具体包括：高性能邻位酰胺/酰亚胺苯并噁嗪的开发；生物质黄酮和香豆素基苯并噁嗪树脂的合成、固化机理与性能研究，尤其详细介绍了分子内氢键的调控机制和潜伏自催化固化机理；以苯并噁嗪为基体制备石墨烯材料，并研究其在热传导、电磁屏蔽和摩擦等领域的应用。

1　高性能苯并噁嗪树脂

苯并噁嗪树脂作为一类极具价值的高分子材料，其独特的分子骨架和可灵活调节的功能基团配置，赋予了材料多变的性能水平。通过对合成原料的精心筛选和对苯并噁嗪结构中取代基的相关改性，可以实现对该材料物理化学性能的精确调控，从而满足多样化的应用场景需求。在苯并噁嗪树脂的开发过程中，分子设

计发挥着核心作用，这是因为分子设计不仅能够塑造树脂的网络结构，还影响着树脂的固化行为以及固化后材料的热学行为和力学特性等。如何通过巧妙的分子设计，弥补苯并噁嗪树脂性能上的短板，合成兼具低固化温度 (易加工) 和高热稳定性 (高性能) 的苯并噁嗪树脂已然成为当前研究的重点。针对这一挑战，本团队以引入耐热基团为切入点，设计合成了以邻位酰胺结构、邻位酰亚胺结构为代表的高性能苯并噁嗪热固性树脂新体系。

1.1 邻位酰胺官能化苯并噁嗪树脂

邻位酰胺官能化苯并噁嗪是由引入了邻位酰胺基团的酚与胺及醛发生曼尼希缩合反应生成[32]，典型结构如图 2(a)所示。邻位酰胺基团与噁嗪环中的氧原子相邻，致使酰胺基团中的 NH 与噁嗪环中的 O 形成分子内氢键(图 2(b))，而酰胺基团若在噁嗪环对位只能形成分子间氢键。这一独特结构促使邻位酰胺苯并噁嗪在热固化过程中能够在较低温度下实现开环聚合，且无需添加引发剂或催化剂[33]。密度泛函理论(DFT)的有关计算与实验阐释了邻位与对位酰胺官能化苯并噁嗪单体的分子结构差异。计算结果表明，分子内氢键的存在显著降低了 O－CH_2 键的总电子密度，进而降低了该键的键能，使邻位酰胺苯并噁嗪更容易发生热开环聚合。实验表征进一步表明，在差示扫描量热(DSC)测试中，相较于对位异构体，邻位酰胺苯并噁嗪的热开环固化峰值温度(T_p)降低约 40 ℃，且基于 Starink 法计算得到的活化能也更低[34]。含有噻吩基团的邻位和对位酰胺苯并噁嗪单体中，噻吩中硫元素可以竞争调控 NH 与噁嗪环中的 O 形成分子内氢键键能，对其分子内可能形成的各种氢键(包括分子内五元环、六元环氢键以及分子间氢键)强度的计算结果(图 2(c))进一步证明，酰胺键中的 NH 与噁嗪环中的 O 形成的分子内氢键越强，相应苯并噁嗪的聚合温度越低[35]。

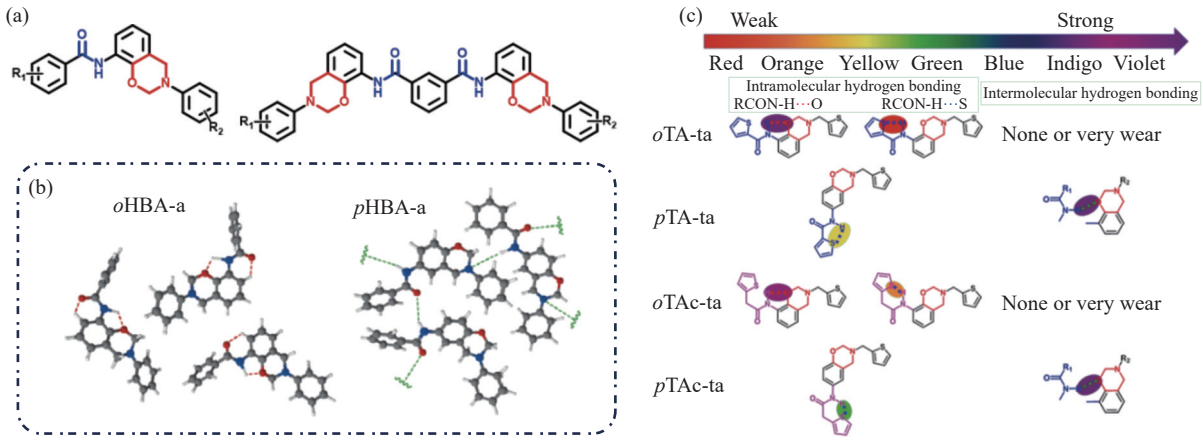

图 2 (a) 典型的邻位酰胺型苯并噁嗪结构式；(b) 邻位酰胺苯并噁嗪(*o*HBA-a)形成分子内氢键，对位酰胺苯并噁嗪(*p*HBA-a)形成分子间氢键[33]；(c) 富含噻吩基团的苯并噁嗪中可能形成各种氢键的强度对比[35]

Fig. 2 (a) Typical structural formulae of *ortho*-amide type benzoxazine; (b) Intramolecular hydrogen bonding in *o*HBA-a and intermolecular hydrogen bonding in *p*HBA-a[33]; (c) Qualitative strength of hydrogen bonding in thiophene rich benzoxaiznes[35]

此外，邻位酰胺型苯并噁嗪在后固化阶段，酚羟基和其邻位酰胺基团之间会发生分子内热环化反应，脱去水分子形成苯并噁唑环贯穿于树脂网络结构中(图 3(a))[32]，不但热稳定性进一步提升，介电性能也得到优化。基于邻位酰胺苯并噁嗪的苯并噁唑热环化反应并结合苯并噁嗪灵活的分子设计性，将多种功能基团引入邻位酰胺苯并噁嗪单体可以实现性能调控：(1)引入三氟甲基使树脂的介电常数 (ε_r) 降至 2.42～2.19，介电损耗 (tan δ) 降至 0.012～0.008，而玻璃化转变温度(T_g)高达 354 ℃，且热稳定性显著提升，质量损失 5% 温度 (T_{d5}) 和 10% 质量损失温度 (T_{d10}) 分别达到 417 ℃ 和 512 ℃[36]；(2)引入炔基可在聚合过程中环化形成苯环从而改善综合性能，树脂的介电常数降至 2.55～2.31，介电损耗降至 0.008～0.004，且 T_{d10} 为 445 ℃，800 ℃ 下的残碳率(Y_c)为 66%[37]；(3)引入乙烯基可以与硅氧烷发生硅氢加成反应进而制备含硅氧烷链的主链型苯并噁嗪树脂，结合苯并噁唑热环化处理，树脂也展现出优异的介电性能(介电常数为 2.52～2.13，介电损耗为 0.056～0.008)和热稳定性(T_g 高达 400 ℃，T_{d10} 为 445 ℃)(图 3(b))[38]。以上结果表明，邻位酰胺苯并噁嗪在赋予树脂单体低固化温度的同时，能进一步通过后固化过程苯并噁唑化提升树脂的综合性能。该系列树脂在电子封装领域展现出良好的应用潜力。

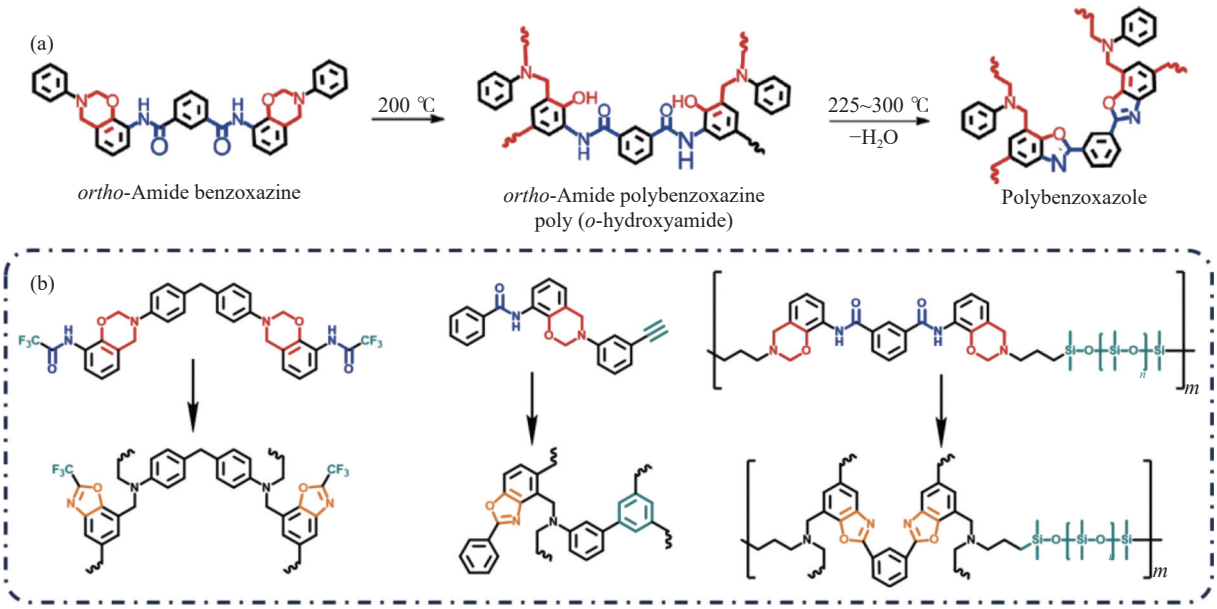

图 3　(a) 邻位酰胺苯并噁嗪的热固化机理[32]; (b) 含三氟甲基、炔基和硅氧烷的邻位酰胺苯并噁嗪的结构式

Fig. 3　(a) Thermal curing mechanism of *ortho*-amide benzoxazine[32]; (b) Strutural formulae of *ortho*-Amide benzoxazine with trifluoromethyl, alkynyl and siloxane functionalities

1.2　邻位酰亚胺官能化苯并噁嗪树脂

本团队首次观察到邻位酰亚胺型苯并噁嗪中的噁嗪环负电荷氧原子与酰亚胺功能团之间存在分子内排斥作用, 从而导致 C−N 键旋转受抑制而产生阻转异构, 该异构体特征在核磁共振(NMR)测试中得到充分验证, 在 DFT 计算中也有体现(图 4(a))[39]。本团队进一步合成了多种具有阻转异构特征的邻位酰亚胺型苯并噁嗪单体, 并通过 DFT 模拟计算对其空间结构进行了深入研究(图 4(b))[40]。

邻位酰亚胺型苯并噁嗪树脂经固化后同样可进一步后固化形成聚苯并噁唑树脂。然而, 邻位酰亚胺进行苯并噁唑热环化的机理与邻位酰胺苯并噁嗪有所差异[41]: 酰亚胺基团会先与苯并噁嗪开环生成的酚羟基反应, 释放出二氧化碳分子, 进而形成苯并噁唑基团(图 4(c)), 且该反应温度显著高于邻位酰胺苯并噁嗪树脂的后固化温度。

此外, 引入包括马来酰亚胺[42-45]、降冰片烯[4,43,46-51]、炔基[4,52]、氰基[47,53,54]、邻苯二甲腈[51,55]、环丁烯[46]等具有交联反应活性的基团到苯并噁嗪单体结构中, 树脂的热学和力学性能进一步提高。以降冰片烯和炔基同时引入邻位酰亚胺苯并噁嗪单体为例, 炔基有效降低了单体的固化温度, 降冰片烯则显著提升了树脂的交联密度(图 4(d)), 最终获得的高性能树脂具有 250 ℃ 的 T_g 和 458 ℃ 的 T_{d10}[4]。

综上, 邻位酰胺和邻位酰亚胺型苯并噁嗪树脂以及相应的后固化得到的聚苯并噁嗪的性能数据均汇总于表 1 中。

2　生物基高性能苯并噁嗪热固性树脂

当前, 化学工业的原料大多源于化石基资源。化石基资源不仅面临枯竭的困扰, 还给生态环境造成破坏。因此, 为推动高性能苯并噁嗪热固性树脂朝着可持续方向发展, 借助第四代化工路线的生物质平台化合物来制备苯并噁嗪树脂刻不容缓。在生物基苯并噁嗪树脂的开发过程中, 原料的筛选与分子设计至关重要。通常, 相较于脂肪族原料, 采用酚和芳香族或类芳香族胺合成的苯并噁嗪树脂在性能上更具优势。基于上述认知, 本团队系统开展了生物基高性能苯并噁嗪树脂的研究工作。

2.1　黄酮类生物基苯并噁嗪树脂

黄酮类化合物是一类广泛存在于蓝莓、蔬菜、茶叶、香料以及豆制品中的有机酚化合物[56-59], 按结构可分为二氢黄酮(如橙皮苷和柚皮素(NAR))、黄酮醇(如槲皮素和山奈酚)、黄酮(如芹菜素(API)和木犀草素)、异黄酮(如大豆素和染料木素)以及花色素(如飞燕草素和芍药素)[60]。该类化合物含有一种类似于脱氧安息

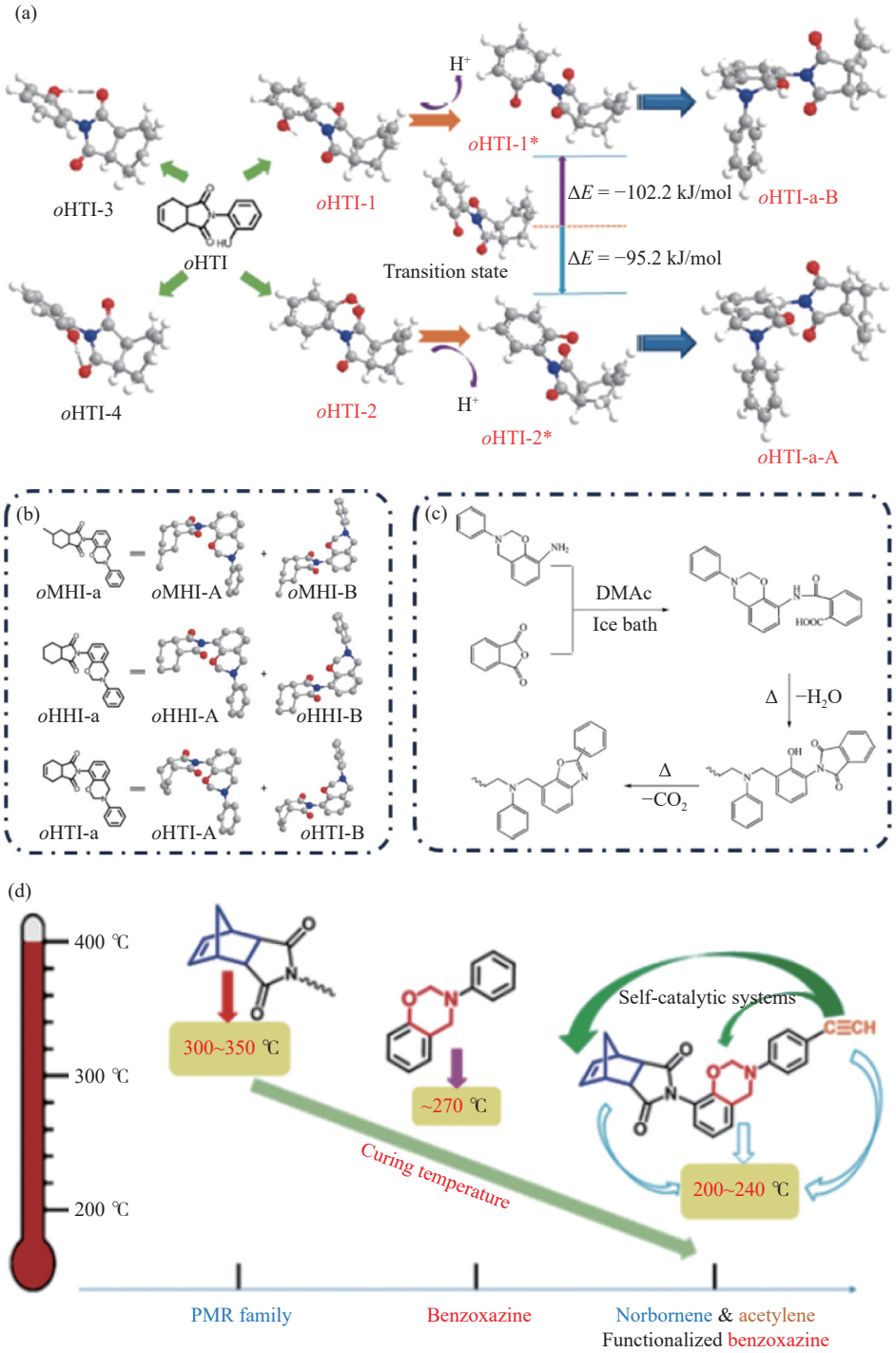

图 4 (a) 邻位酰亚胺苯并噁嗪的阻转异构机理[39]; (b) 多种含有阻转异构构象的邻位酰亚胺苯并噁嗪单体[40]; (c) 邻位酰亚胺苯并噁嗪的固化与后固化行为[41]; (d) 含有降冰片烯和炔基的邻位酰亚胺苯并噁嗪树脂[4]

Fig. 4 (a) Mechanism of atropisomerization in *ortho*-imide benzoxaizne[39]; (b) Different types of *ortho*-imide benzoxazine atropisomers[40]; (c) Curing and post curing behavior of *ortho*-amide benzoxazine[41]; (d) *ortho*-Imide benzoxazine containing norbornene and alkynyl[4]

香的独特化学结构，能够在燃烧中迅速碳化成致密的碳层，因此有助于提升苯并噁嗪树脂的热稳定性和阻燃性[61]。此外，黄酮类化合物结构中含有羟基、羰基、醚等基团，不仅具有构建氢键的潜力，还赋予其抗菌、抗炎、抗病毒、抗氧化等多种生理活性，在医学和健康领域有着广阔的应用前景[62-65]。

基于黄酮类化合物的特点，本团队首先以二氢黄酮类三酚——柚皮素为酚源合成了生物基苯并噁嗪单体(NAR-fa)，研究表明柚皮素中的羰基可与其邻位羟基形成稳定的分子内氢键，赋予该苯并噁嗪潜伏自催化固化的特性，固化温度低至 166 ℃；将其作为改性剂添加到商业化双酚 A 型苯并噁嗪及白藜芦醇基苯并噁嗪

表 1　邻位酰胺和邻位酰亚胺聚苯并噁嗪和聚苯并噁唑的热性能与介电性能

Table 1　Thermal and dielectric properties of *ortho*-amide and *ortho*-imide polybenzoxazine and polybenzoxazole

Polybenzoxazine and polybenzoxazole	Sample	T_p/℃	T_g/℃	T_{d5}/℃	T_{d10}/℃	Y_c/%	ε_r (1 Hz～1 MHz)	tan δ (1 Hz～1 MHz)	Ref.
Amide type	*ortho*-amide-poly(benzoxazine)	212	212	—	—	—	—	—	[32]
	para-amide-poly(benzoxazine)	259	—	—	—	—	—	—	[32]
	poly(*o*TA-ta)	193	—	287	307	45	—	—	[35]
	poly(*p*TA-ta)	233	—	298	353	42	—	—	[35]
	poly(*o*TAc-ta)	204	—	296	341	55	—	—	[35]
	poly(*p*TAc-ta)	229	—	299	329	44	—	—	[35]
	poly(*o*TFA-ddm)	207	—	—	—	—	3.19～2.84	0.032～0.019	[36]
	cFPBO	—	354	417	512	65	2.42～2.19	0.012～0.008	[36]
	poly(Pp-apa)	220	—	337	383	50	3.06～2.72	0.014～0.005	[37]
	PBO-Pp-apa	—	—	418	445	66	2.55～2.31	0.008～0.004	[37]
	poly(AI-al-PDMS)	243	315	302	342	—	3.01～2.64	0.108～0.011	[38]
	PBO-AI-al-PDMS	—	>400	393	445	—	2.52～2.13	0.056～0.008	[38]
Imide type	poly(*o*HTI-a)	231	233	—	—	—	—	—	[39]
	poly(*o*HTI-ac)	179	276	396	—	62	—	—	[39]
	poly(*o*HTI-ch)	245	198	—	—	—	—	—	[39]
	poly(*o*HTI-cy)	246	217	—	—	—	—	—	[39]
	poly(*o*MHI-a)	258	173	327	367	26	—	—	[40]
	poly(*o*HHI-a)	254	180	340	375	28	—	—	[40]
	poly(*o*HTI-a)	252	233	342	382	48	—	—	[40]
	poly(*o*PP-a)	234	174	319	358	60	—	—	[40]
	poly(BZaa)	223	265	—	—	—	—	—	[41]
	cPI	—	308	410	515	70	—	—	[41]
	cPBO	—	>400	511	567	71	—	—	[41]

树脂中, 可显著降低树脂固化温度, 同时有效提升树脂的耐热性与阻燃性[66]。鉴于芹菜素与柚皮素结构相似且兼具碳碳双键及分子内氢键的特征, 将芹菜素与糠胺(fa)合成了新型全生物基双苯并噁嗪(API-fa)[67]。苯并吡酮和 API-fa 中的碳碳双键以及呋喃环能够形成额外的交联网络, 可显著提高生物基苯并噁嗪聚合物的热性能和阻燃性能: 其 T_g 高达 376 ℃, 在 800 ℃ 下的残碳率(Y_c)为 66%, 微型量热燃烧法(MCC)测试数据显示该材料的放热速率(HRR) 仅为 20.2 J/(g·K), 总释放热(THR)为 9.4 kJ/g。研究表明, 基于白杨素(CHR)制备的生物基聚苯并噁嗪中存在显著的分子内氢键作用[68], 特别是 OH···N 键可以保护－OH 基团不与水相互作用, 使聚合物涂层展现出优异的疏水性[69,70]。本团队另一项研究表明, 白杨素与炔胺合成的生物基苯并噁嗪作为绿色添加剂具有显著优势: 可以有效降低环氧树脂和双马来酰亚胺体系的聚合温度, 同时提升其热稳定和阻燃性能[71]。作为一种结构独特的黄酮类化合物, 山奈酚(KAE)与芹菜素相比具有显著差异: 其 4 个羟基中有 2 个与酮基相邻且其中一个为非酚羟基, 与糠胺结合后会形成五元或六元氢键环, 进而合成富含氢键的苯并噁嗪树脂。基于该树脂基体制备的碳纤维增强复合材料展现出优异的性能, 与化石基苯并噁嗪复合材料相比, 其 T_g、抗拉强度和杨氏模量分别提提升 108%、28% 和 82.7%, 在交通运输和航空航天领域显示出巨

大的应用潜力[72]。本团队最近以 7-羟基黄酮(HYD)、白杨素、芹菜素、木犀草素(LUT)等合成单、双以及三官能苯并噁嗪单体,探究了噁嗪环数量和氢键对聚合物固化机理和热性能的影响,进一步证明含有分子内氢键的黄酮基苯并噁嗪具有潜在的自催化作用,从而能够降低固化温度,且其固化温度与苯并噁嗪单体中噁嗪数量成反比[73]。典型的含分子内氢键的黄酮基苯并噁嗪单体的结构和相应的潜伏催化固化机理如图 5 所示,相关的热性能与阻燃性能数据汇总于表 2。

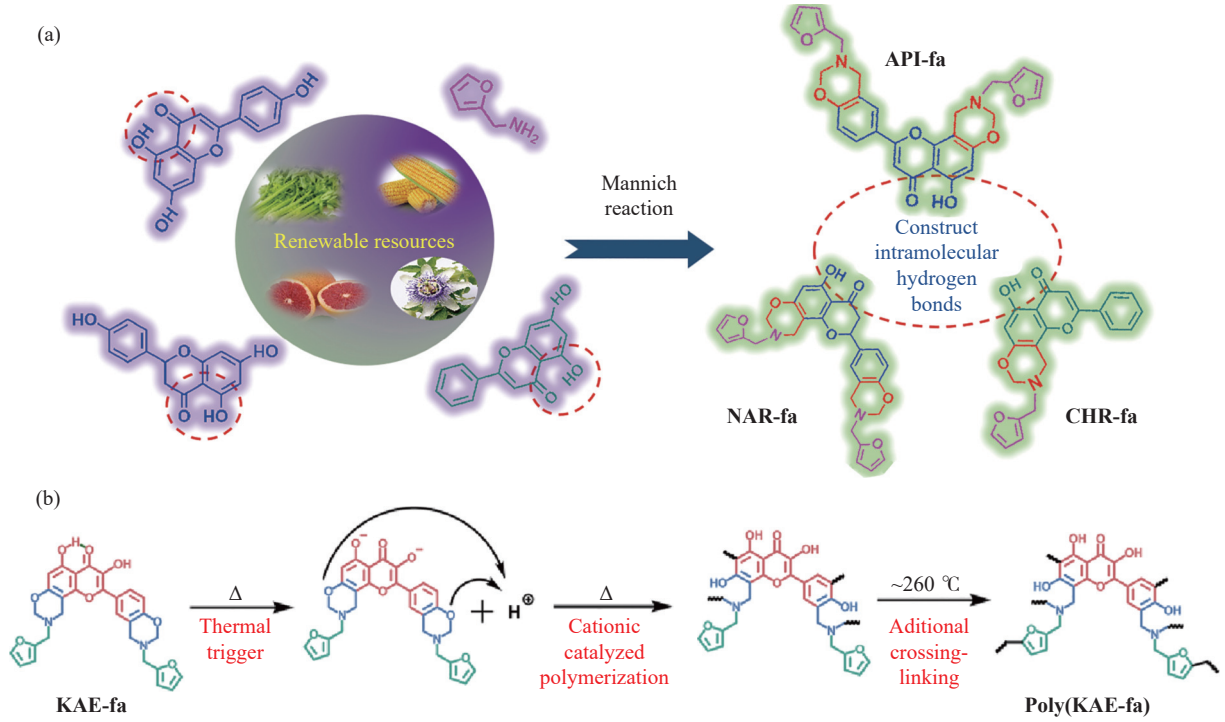

图 5 (a) 含分子内氢键的黄酮基苯并噁嗪单体结构示意图; (b) 以山奈酚基苯并噁嗪单体为例的分子内氢键潜伏催化固化机理[72]

Fig. 5 (a) Structural diagram of flavonoid-based benzoxazine monomers containing intramolecular hydrogen bond; (b) Intramolecular hydrogen bond latent catalytic curing mechanism of kaempferol-based benzoxazine monomer[72]

表 2 黄酮基苯并噁嗪树脂的热性能与阻燃性能

Table 2 Thermal properties and flame retardancy of flavonoid-based benzoxazine resins

Flavonoid bio-based phenol	Sample	T_p/℃	T_g/℃	T_{d5}/℃	T_{d10}/℃	Y_c/%	HRC/(J·g^{-1}·K^{-1})	THR/(kJ·g^{-1})	Ref.
Naringenin	poly(NAR-fa)	166	286	361	404	64	31.9	6.6	[66]
	poly(REs-fa-NARE-fa)	217	313	353	412	65	28.0	6.7	[66]
	poly(BA-a-NARE-fa)	238	178	311	344	36	150.0	21.1	[66]
Apigenin	poly(API-fa)-1	189	295	301	429	63	22.5	11.2	[67]
	poly(API-fa)-2		376	384	448	66	20.2	9.4	[67]
Chrysin	poly(CHR-fa)	180	_	335	366	48	43.3	7.4	[68]
Chrysin	poly(CHR-ac)	184	248	327	350	57	18.5	5.2	[71]
Kaempferol	poly(KAE-fa)	184	304	390	436	63	10.1	3.4	[72]
7-Hydroxyflavone	poly(HYD-a)	213	213	331	360	54	65.0	9.6	[73]
Chrysin	poly(CHR-a)	224	224	321	347	51	61.0	8.0	[73]
Apigenin	poly(API-a)	266	266	390	438	62	11.4	2.2	[73]
Luteolin	poly(LUT-a)	246	246	339	373	65	37.8	7.5	[73]

2.2　香豆素类苯并噁嗪树脂

存在于种子、根和叶的次生代谢物中的香豆素及其衍生物是用于制备荧光化学传感器[74]和防污涂料[55]等高分子材料的家族型天然化合物, 4-甲基-7-羟基香豆素[75,76]和 7-羟基香豆素[77]合成单官的苯并噁嗪树脂的相关研究工作此前也有报道。Sini 等[78]研究表明, 相比于双官或者多官的苯并噁嗪树脂, 单官的苯并噁嗪树脂往往交联密度低, 存在大量的结构缺陷, 故而在热稳定性方面稍逊一筹。本团队以秦皮乙素 (6, 7-二氢香豆素) 制备了双官生物基苯并噁嗪单体, 经高温固化后形成的树脂体系交联密度增大, T_g 可以达到 261 ℃, 热稳定性得到显著提升(T_{d10} 和 Y_c 分别为 407 ℃ 和 57%[79]), 而且新获得的苯并噁嗪树脂在无卤、无磷的条件下也表现出 UL-94 V-0 级别的优异阻燃性, 尤其最高 HRR 仅为 2.51 J/(g·K)(图 6(a))。此外, 二氢香豆素凭借异常灵活的分子设计能力与酪胺制得了生物基双苯并噁嗪[80]。该方法不仅简单环保, 而且得到的富含氢键的生物基聚苯并噁嗪具有优异的热稳定性, 其黏附强度(图 6(b))和低表面能特性也极为出色。此外, 含香豆素的苯并噁嗪在 365 nm 波长紫外光照下能诱导产生 [2π+2π] 环加成反应, 产生新的光聚体(图 6(c)), 进而增强材料的耐热性能[81]。

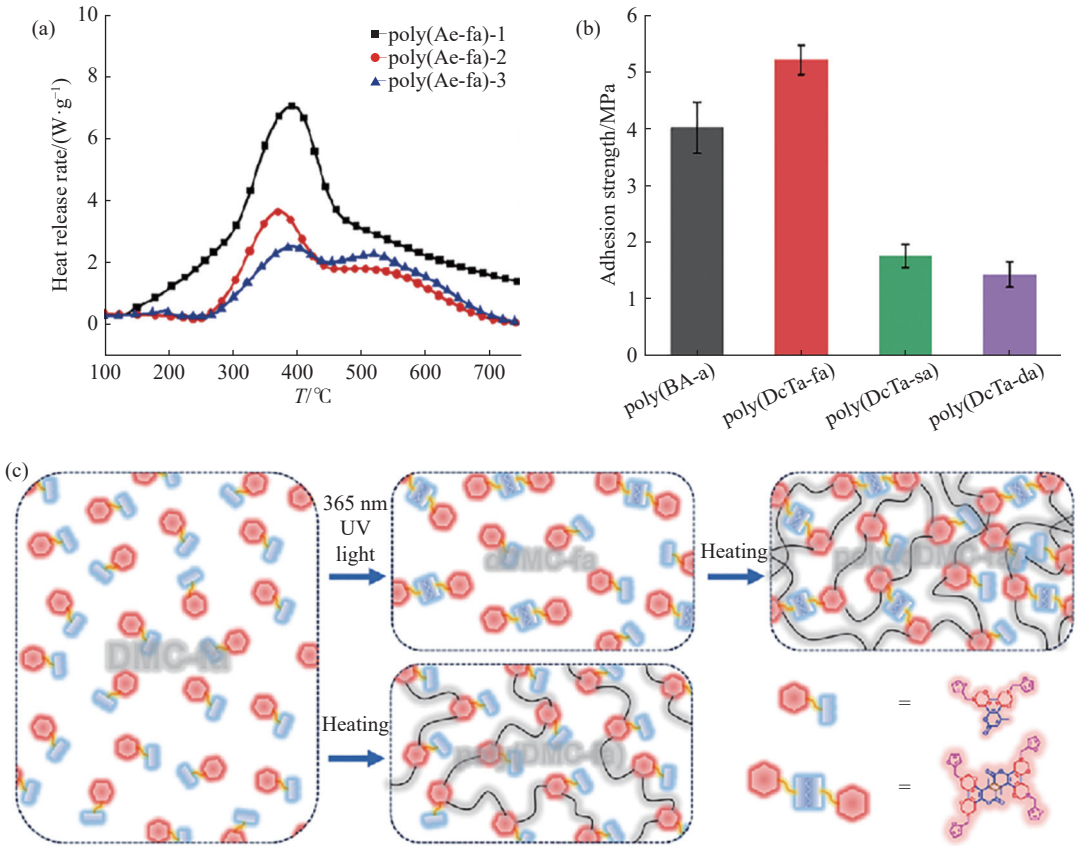

图 6　香豆素类苯并噁嗪树脂优异的 (a) 阻燃性[79], (b) 黏附强度[80] 以及 (c) 光、热固化机理[81]

Fig. 6　Excellent (a) flame retardant [79], (b) adhesion strength[80] and (c) light, thermal curing mechanism of coumarin benzoxazine resins[81]

3　苯并噁嗪树脂的功能化应用

近年来, 研究者们已成功开发了一系列适用于不同领域的功能性苯并噁嗪材料, 涵盖阻燃材料[3]、抗菌材料[82]、高效碳吸附材料[83]以及高性能摩擦材料[84]等。

3.1　苯并噁嗪/石墨烯复合材料

聚苯并噁嗪本身存在脆性高、电绝缘性强以及热传导性能差等问题[85-87], 因而仅依靠调控苯并噁嗪单体结构和聚合方法难以满足其在导电、导热等应用中的性能需求。目前, 通过化学或物理手段将相应功能性纳米材料引入苯并噁嗪基体以构筑复合材料, 是一种提升其传导性能的有效途径。

受到砖泥结构的启发, 本团队在一种含有邻位酰胺结构单体的基础上引入呋喃基团增强基体与石墨烯

之间的结合力，即利用呋喃官能团中的共轭二烯与石墨烯上的碳碳双键发生 Diels-Alder 反应并通过真空过滤技术实现石墨烯与苯并噁嗪复合材料的有效组装，成功制备出如图 7(a)所示的层状结复合薄膜，几乎每一层石墨烯均平行于复合薄膜片材的表面，且相邻石墨烯层沿面内方向呈现高度取向性[83]。这种排列方式显著增大了接触面积，同时固化后聚合物支撑的石墨烯结构促进了致密网络的形成，为声子传播提供了低热阻路径，极大地提升了热传导效率。含有邻位酰胺结构的苯并噁嗪化合物在热活化固化过程中能够发生独特的结构重排，生成具有较低介电常数和损耗因子的聚苯并噁唑[44]，显著增强聚合物基质的刚性(图 7(b))。当石墨烯质量分数仅为 46.8% 时，复合薄膜的面内热导率可高达 39.2 W/(m·K)，显著优于纯苯并噁嗪树脂的热导率(0.31 W/(m·K))。此外，复合薄膜还具有优异的电磁屏蔽性能，层层堆叠的石墨烯片显著增强了电磁波的层间反射，而致密的砖/砂状微观结构则大幅提升了材料的有效表面积，从而构建了一道高效的电磁波屏障(图 7(c))，因此，聚苯并噁嗪/石墨烯薄膜展现出高达 1.04 dB/μm 的电磁干扰(EMI)屏蔽效率。

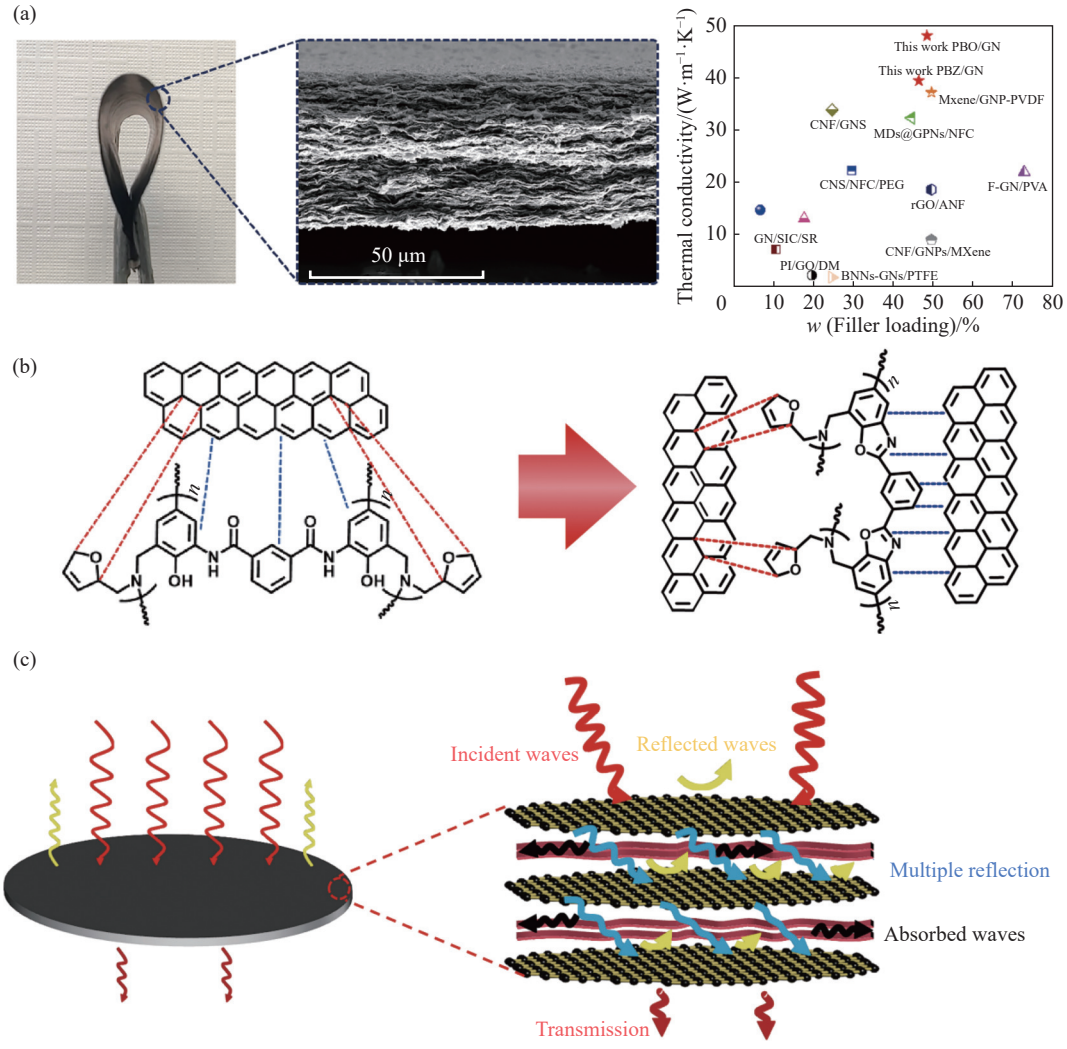

图 7 基于真空过滤的聚苯并噁嗪/石墨烯导热复合材料：(a) 复合材料薄板的导热系数；(b) 后固化过程中聚苯并噁嗪结构到聚苯并噁唑结构的转换；(c)EMI 屏蔽机理[83]

Fig. 7 Polybenzoxazine/graphene thermal conductivity composite based on vacuum filtration: (a) Thermal conductivity of composite sheet; (b) Conversion of polybenzoxazine structure to polybenzoxazole structure during postcuring; (c) EMI shielding mechanism[83]

聚苯并噁嗪/石墨烯薄膜经进一步热处理后，聚苯并噁嗪成功完成了结构重排并转变为高度共轭的聚苯并噁唑[83]。这一转变显著增强了聚合物与石墨烯之间的 π-π 相互作用，从而使复合薄膜的面内热导率从 39.2 W/(m·K) 进一步提升至 47.8 W/(m·K)。此外，该转化过程中形成了更密集交联的网络结构和更小的石墨烯层间距，这种结构变化不仅强化了电磁波的反射与散射效应，而且显著提高了能量损耗，实现了更高的电磁屏蔽性能，从而使得聚苯并噁唑/石墨烯薄膜的电磁干扰屏蔽效率进一步提升至 1.19 dB/μm。

3.2　苯并噁嗪基激光诱导石墨烯

随着机械系统对能效和耐用性的要求不断提高, 越来越多的润滑剂被应用于减少摩擦和磨损。润滑剂的应用不仅可以显著提高机械系统的能源利用效率, 还能有效延长部件的使用寿命。石墨烯材料因其独特的低摩擦特性和优异的抗磨损性能而备受关注, 其高导热性能够快速散失滑动产生的热量, 从而进一步提升系统的稳定性。然而, 对于油基润滑剂而言, 如何在无需复杂化学改性的前提下实现超细碳质颗粒的良好分散仍然是一个亟待解决的问题。

在此背景下, 本团队通过“激光直写技术”直接在聚合物表面制备得到三维多孔石墨烯碳材料激光诱导石墨烯(LIG), 基本实现从生物质碳化合物到生物基苯并噁嗪, 再到功能性碳材料转变的路径探索(图 8(a, b))[84]。目前, 已有大量关于利用苯并噁嗪树脂制备 LIG 的研究报道, 这些研究主要集中在光热材料、超疏水材料和电磁屏蔽材料等领域的应用[88,89]。本团队首次探讨了此类 LIG 在摩擦材料中的潜在应用[90], 所得的 LIG 具有独特的三维多孔结构和疏水表面(图 8(c)), 与未经改性的其他碳基润滑剂添加剂(如氧化石墨烯、单壁碳纳米管、炭黑和还原氧化石墨烯)相比展现出更优的分散性能, 将 w=0.1% 的 LIG 添加到聚 α 烯烃基础油

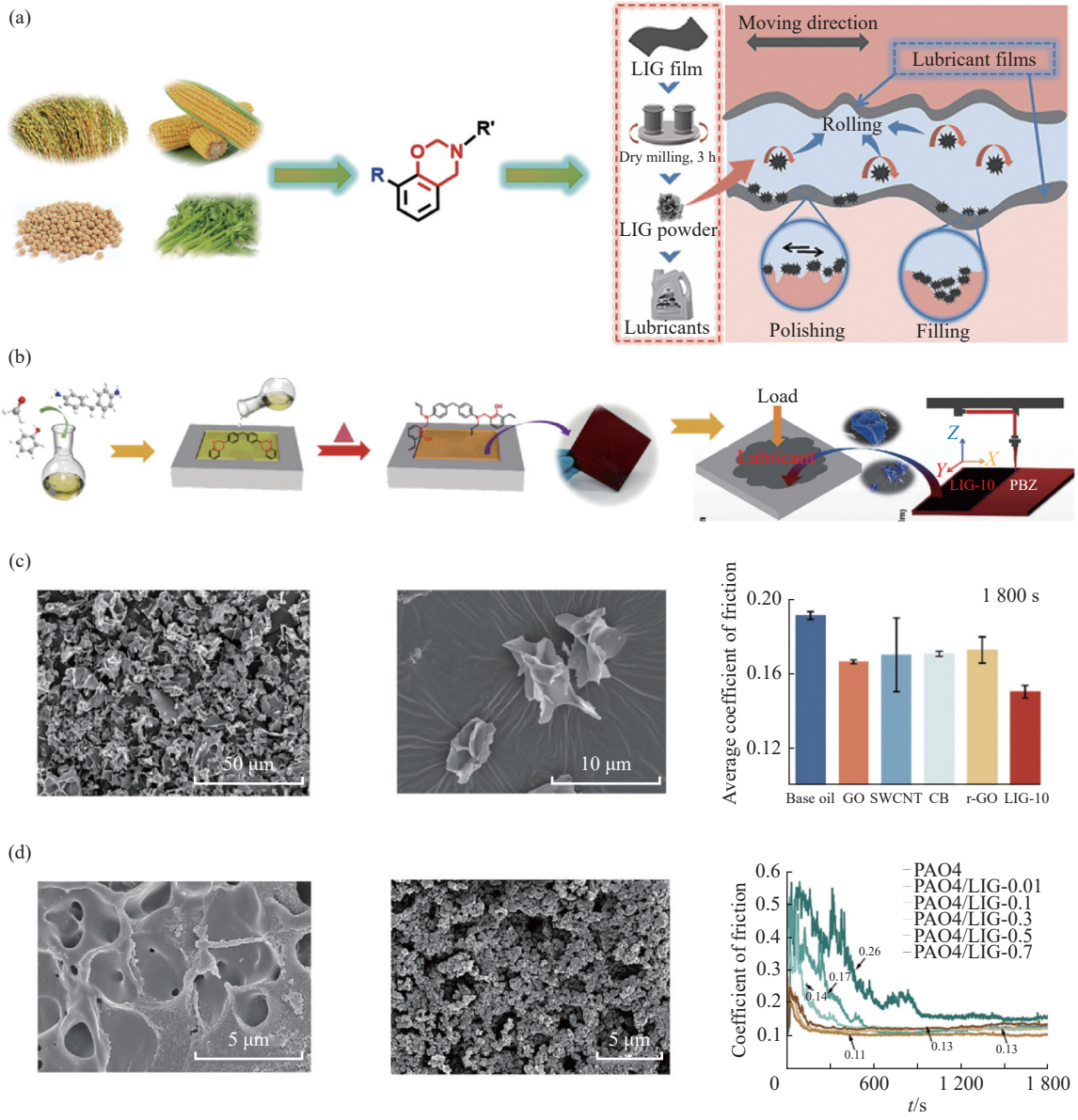

图 8　基于苯并噁嗪激光诱导的石墨烯: (a) 从生物碳资源向功能碳材料的转化[84]; (b) LIG 的制备; (c) 基于聚苯并噁嗪的 LIG; (d) 基于液体生物基苯并噁嗪单体的 LIG[90]

Fig. 8　Laser-induced graphene based on benzoxazine: (a) Transformation from biological carbon resources to functional carbon materials[84]; (b) Preparation of LIG; (c) LIG based on polybenzoxazine; (d) LIG based on liquid bio-based benzoxazine monomer[90]

(PAO4)中时, PAO4 的摩擦系数降低了约 22%, 磨损率系数降低了约 95%, 同时实现了优异的减摩和抗磨效果。然而, 在聚合物基底前驱体上形成 LIG, 将会极大地限制其在实际应用中几何形状和尺寸的可控性。因此, 本团队还基于液体生物基苯并噁嗪单体通过高能激光的光热效应有效促进苯并噁嗪表面 C—O 和 C—N 键的断裂, 实现碳原子重新排列进而生成一种 3D 多孔 LIG 润滑添加剂[90]。与聚合物基底类似, 由液体单体制备的 LIG 表面展现出丰富的多孔结构和褶皱特征(图 8(d))。LIG 参与了边界润滑膜的形成, 显著缩短了磨痕的宽度和深度。当 w(LIG)=0.5% 时, PAO4 润滑剂的平均摩擦系数和磨损率比未添加 LIG 时分别降低了 52% 和 97%。即使摩擦时间延长一倍, PAO4/LIG 润滑剂仍表现出稳定的减摩抗磨性能, 充分体现了三维多孔 LIG 作为润滑添加剂的长寿命特性。

4 总结与展望

本文全面综述了团队近十年来在高性能苯并噁嗪树脂领域的探索与部分研究成果。通过灵活设计的分子结构构筑分子内氢键, 成功制备出兼具低温固化、高热稳定性、阻燃性及介电性能优良的苯并噁嗪热固性树脂。基于黄酮类和香豆素类生物质合成生物基苯并噁嗪树脂新体系, 更是推动苯并噁嗪树脂朝着高性能、可持续发展方向迈进了关键一步。此外, 苯并噁嗪与石墨烯形成的复合材料在热传导、电子屏蔽和润滑剂等多功能领域也取得显著进展, 而采用激光烧蚀的方法, 成功实现了从树脂到功能性碳材料的转变。

尽管高性能苯并噁嗪树脂已取得一些重要突破, 但其大规模商业化仍面临诸多挑战, 需在分子设计、原料来源、功能化应用、工业化生产及树脂回收再利用等方面进行持续探索与优化。具体可优化方面如下: (1)分子设计优化, 深入研究树脂构效关系, 精准调控分子结构与氢键, 进一步优化固化温度、热稳定性等关键特性, 满足航空航天、电工电子等高端领域的严苛要求; (2)绿色可持续发展, 拓展生物质原料的来源, 提升苯并噁嗪树脂中生物基含量, 突破性能瓶颈, 实现对石油基产品的有效替代, 推动行业可持续发展; (3)功能化应用, 持续优化与功能性纳米材料的复合技术, 探索功能材料制备新工艺, 拓展其在诸如新能源、生物医学等前沿领域的应用; (4)工业化推进, 着力攻克量产技术难题, 提高生产效率, 降低成本, 加速科研成果转化, 让高性能苯并噁嗪树脂在各领域发挥更大价值, 为材料科学发展注入新活力; (5)回收再利用, 在苯并噁嗪结构中引入特定可逆键实现可控降解, 在保持高性能的同时, 实现特定条件下的降解和再生利用。

绿色与可持续发展是苯并噁嗪树脂未来发展的主旋律, 而高性能和多功能是苯并噁嗪发展的基石。不断总结苯并噁嗪化合物的结构特征并与性能关联, 针对应用目标设计合成功能性的高性能苯并噁嗪树脂, 并实现特定条件下的降解与再利用, 将助力推动苯并噁嗪树脂的快速发展。

参考文献:

[1] GOTO M, MIYAGI Y, MINAMI M, MINAMI M, SANDA F. Synthesis and crosslinking reaction of polyacetylenes substituted with benzoxazine rings: Thermally highly stable benzoxazine resins [J]. Journal of Polymer Science Part A: Polymer Chemistry, 2018, 56(16): 1884-1893.

[2] LIU Y Q, YUAN L, LIANG G Z, GU A J. Preparation of thermally resistant and mechanically strong biomass benzoxazine resins via green strategy [J]. ACS Sustainable Chemistry and Engineering, 2024, 12(3): 1247-1254.

[3] YANG Y, LU Y, ZHANG K. A highly thermally stable benzoxazine resin derived from norbornene and natural renewable tyramine and furfurylamine [J]. European Polymer Journal, 2023, 187: 111895.

[4] ZHANG K, YU X. Catalyst-free and low-temperature terpolymerization in a single-component benzoxazine resin containing both norbornene and acetylene functionalities [J]. Macromolecules, 2018, 51(16): 6524-6533.

[5] CAO J F, DUAN H J, ZOU J H, ZHANG J J, WAN C, ZHANG C H, MA H R. Bio-based phosphorus-containing benzoxazine towards high fire safety, heat resistance and mechanical properties of anhydride-cured epoxy resin [J]. Polymer Degradation and Stability, 2022, 198: 109878.

[6] ZEGAOUI A, DERRADJI M, MA R K, CAI W A, LIU W B, WANG J, DAYO A Q, SONG S, ZHANG L L. High-performance polymeric materials with greatly improved mechanical and thermal properties from cyanate ester/benzoxazine resin reinforced by silane-treated basalt fibers [J]. Journal of Applied Polymer Science, 2018, 135(21): 46283.

[7] AMARNATH N, APPAVOO D, LOCHAB B. Eco-friendly halogen-free flame retardant cardanol polyphosphazene polybenzoxazine networks [J]. ACS Sustainable Chemistry and Engineering, 2018, 6(1): 389-402.

[8] LIU J, SAFRONAVA N, LYON R E, MAIA J, ISHIDA H. Enhanced thermal property and flame retardancy via intramolecular 5-membered ring hydrogen bond-forming amide functional benzoxazine resins [J]. Macromolecules, 2018, 51(23): 9982-9991.

[9] CHEN K C, LI H T, HUANG S C, CHEN W B, SUN K W, CHANG F C. Synthesis and performance enhancement of novel polybenzoxazines with low surface free energy [J]. Polymer international, 2011, 60(7): 1089-1096.

[10] WANG C F, SU Y C, KUO S W, HUANG C F, SHEEN Y C, CHANG F C. Low-surface-free-energy materials based on polybenzoxazines [J]. Angewandte Chemie: International Edition, 2006, 45(14): 2248-2251.

[11] CHEN J, ZENG M, FENG Z, PANG T, HUANG Y, XU Q. Design and preparation of benzoxazine resin with high-frequency low dielectric constants and ultralow dielectric losses [J]. ACS Applied Polymer Materials, 2019, 1(4): 625-630.

[12] WU J B, XI Y, MCCANDLESS G T, XIE Y H, MENON R, PATEL Y, YANG D J, IACONO S T, NOVAK B M. Synthesis and characterization of partially fluorinated polybenzoxazine resins utilizing octafluorocyclopentene as a versatile building block [J]. Macromolecules, 2015, 48(17): 6087-6095.

[13] ZHANG K, YU X, KUO S W. Outstanding dielectric and thermal properties of main chain-type poly (benzoxazine-*co*-imide-*co*-siloxane)-based cross-linked networks [J]. Polymer Chemistry, 2019, 10(19): 2387-2396.

[14] HAN L, SALUM M L, ZHANG K, FROIMOWICZ P, ISHIDA H. Intrinsic self-initiating thermal ring-opening polymerization of 1, 3-benzoxazines without the influence of impurities using very high purity crystals [J]. Journal of Polymer Science Part A: Polymer Chemistry, 2017, 55(20): 3434-3445.

[15] ISHIDA H, LOW H Y. A study on the volumetric expansion of benzoxazine-based phenolic resin [J]. Macromolecules, 1997, 30(4): 1099-1106.

[16] HIGGINSON C J, MALOLLARI K G, XU Y, KELLEGHAN A V, RICAPITO N G, MESSERSMITH P B. Bioinspired design provides high-strength benzoxazine structural adhesives [J]. Angewandte Chemie International Edition, 2019, 58(35): 11925-12304.

[17] ISHIDA H, ALLEN D J. Physical and mechanical characterization of near-zero shrinkage polybenzoxazines [J]. Journal of Polymer Science Part B: Polymer Physics, 1996, 34(6): 1019-1030.

[18] SONG J, LIANG H, CAO Y, WANG M, WANG Z. Advancing coatings with polybenzoxazines: Insights into molecular design, synthesis, and modification [J]. Journal of Materials Chemistry C, 2024, 12(25): 9094-9111.

[19] LOCHAB B, MONISHA M, AMARNATH N, SHARMA P, MUKHERJEE S, ISHIDA H. Review on the accelerated and low-temperature polymerization of benzoxazine resins: Addition polymerizable sustainable polymers [J]. Polymers, 2021, 13(8): 1260.

[20] ISHIDA H, FROIMOWICZ P. Advanced and Emerging Polybenzoxazine Science and Technology [M]. Amsterdam, Netherlands: Elsevier, 2017.

[21] MACHADO I, SHAER C, HURDLE K, CALADO V, ISHIDA H. Towards the development of green flame retardancy by polybenzoxazines [J]. Progress in Polymer Science, 2021, 121: 101435.

[22] NING X, ISHIDA H. Phenolic materials via ring-opening polymerization: Synthesis and characterization of bisphenol-A based benzoxazines and their polymers [J]. Journal of Polymer Science Part A: Polymer Chemistry, 1994, 32(6): 1121-1129.

[23] AMARNATH N, SHUKLA S, LOCHAB B. Harvesting the benefits of inherent reactive functionalities in fully biosourced isomeric benzoxazines [J]. ACS Sustainable Chemistry & Engineering, 2018, 6(11): 15151-15161.

[24] DUMAS L, BONNAUD L, OLIVIER M, POORTEMAN M, DUBOIS P. Eugenol-based benzoxazine: From straight synthesis to taming of the network properties [J]. Journal of Materials Chemistry A, 2015, 3(11): 6012-6018.

[25] THIRUKUMARAN P, SATHIYAMOORTHI R, SHAKILA PARVEEN A, SAROJADEVI M. New benzoxazines from renewable resources for green composite applications [J]. Polymer Composites, 2016, 37(2): 573-582.

[26] CHONG A M, SALAZAR S A, STANZIONE III J F. Multifunctional biobased benzoxazines blended with an epoxy resin for tunable high-performance properties [J]. ACS Sustainable Chemistry & Engineering, 2021, 9(17): 5768-5775.

[27] TREJO-MACHIN A, ADJAOUD A, PUCHOT L, DIEDEN R, VERGE P. Elucidating the thermal and polymerization behaviours of benzoxazines from lignin derivatives [J]. European Polymer Journal, 2020, 124: 109468.

[28] ZHANG K, HAN M C, LIU Y Q, FROIMOWICZ P. Design and synthesis of bio-based high-performance trioxazine benzoxazine resin via natural renewable resources [J]. ACS Sustainable Chemistry & Engineering, 2019, 7(10): 9399-9407.

[29] LYU Y, ZHANG Y, ISHIDA H. Intrinsically noncombustible polymers without flame retardant additives: Sulfur-containing and bio-based benzoxazines [J]. European Polymer Journal, 2020, 133: 109770.

[30] LIU X Y, ZHANG R H, LI T Q, ZHU P F, ZHUANG Q X. Novel fully biobased benzoxazines from rosin: Synthesis and properties [J]. ACS Sustainable Chemistry & Engineering, 2017, 5(11): 10682-10692.

[31] ZHAO J Q, LIU Y, ZHANG S M, QIU J J, LIU C M. Bio-based, main-chain type polybenzoxazine precursor derived from sustainable furfurylamine and salicylaldehyde: Synthesis, characterization and properties [J]. Reactive and Functional Polymers, 2020, 149: 104516.

[32] AGAG T, LIU J, GRAF R, SPIESS H W, ISHIDA H. Benzoxazole resin: A novel class of thermoset polymer via smart benzoxazine resin [J]. Macromolecules, 2012, 45(22): 8991-8997.

[33] FROIMOWICZ P, ZHANG K, ISHIDA H. Intramolecular hydrogen bonding in benzoxazines: When structural design becomes functional [J]. Chemistry: A European Journal, 2016, 22(8): 2691-2707.

[34] ZHAO W Q, YANG R, YANG S F, ZHANG K. Experimental and computational investigations on ring-opening polymerization mechanisms of amide-functional benzoxazines [J]. Macromolecular Research, 2023, 31(1): 45-52.

[35] LI N, YANG S F, ZHANG K. Thiophene-rich benzoxazines with an amide moiety: Integration of structural and hydrogen bonding influence on the polymerization mechanism by experimental and computational studies [J]. Macromolecules, 2023, 56(17): 6667-6678.

[36] ZHANG K, HAN L, FROIMOWICZ P, ISHIDA H. A smart latent catalyst containing *o*-trifluoroacetamide functional benzoxazine: Precursor for low temperature formation of very high performance polybenzoxazole with low dielectric constant and high thermal stability [J]. Macromolecules, 2017, 50(17): 6552-6560.

[37] SUN L, ZHANG K, MIN C Y, LIU Y Q, WANG Y T, ZHANG J X, LI S J. Synthesis, characterization and structural thermally rearrangement of *ortho*-amide functional benzoxazine containing acetylene group [J]. Thermochimica Acta, 2018, 668: 1-8.

[38] YANG R, HAO B R, SUN L, ZHANG K. Cross-linked poly (benzoxazole-*co*-siloxane) networks with high thermal stability and low dielectric constant based on a new *ortho*-amide functional benzoxazine [J]. Journal of Applied Polymer Science, 2021, 138(6): 49792.

[39] ZHANG K, SHANG Z K, EVANS C J, HAN L, ISHIDA H, YANG S F. Benzoxazine atropisomers: Intrinsic atropisomerization mechanism and conversion to high performance thermosets [J]. Macromolecules, 2018, 51(19): 7574-7585.

[40] ZHANG K, LIU Y Q, SHANG Z K, EVANS C J, YANG S F. Effects of end-caps on the atropisomerization, polymerization, and the thermal properties of *ortho*-imide functional benzoxazines [J]. Polymers, 2019, 11(3): 399.

[41] ZHANG K, LIU J, ISHIDA H. An ultrahigh performance cross-linked polybenzoxazole via thermal conversion from poly (benzoxazine amic acid) based on smart *o*-benzoxazine chemistry [J]. Macromolecules, 2014, 47(24): 8674-8681.

[42] HAO B, LIU Y Q, YU X Y, ZHANG K. Synthesis, polymerization kinetics and thermal properties of benzoxazine resin containing *ortho*-maleimide functionality [J]. Macromolecular Research, 2021, 29: 24-32.

[43] LU Y, PENG Y L, YANG Y, LIU J H, ZHANG K. Low-temperature terpolymerizable benzoxazine monomer bearing norbornene and furan groups: Synthesis, characterization, polymerization, and properties of its polymer [J]. Molecules, 2023, 28(9): 3944.

[44] ZHANG K, HAO B R, ISHIDA H. Synthesis of a smart bisbenzoxazine with combined advantages of bismaleimide and benzoxazine resins and its unexpected formation of very high performance cross-linked polybenzoxazole [J]. Polymer, 2021, 223: 123703.

[45] ZHANG K, LIU Y Q, EVANS C J, YANG S F. Easily processable thermosets with outstanding performance via smart twisted small-molecule benzoxazines [J]. Macromolecular Rapid Communications, 2020, 41(5): 1900625.

[46] SHENG W C, YIN R, CHEN J F, ZHANG K. High-performance highly cross-linked networks based on *ortho*-imide functional mono-benzoxazines containing benzocyclobutene group [J]. Reactive and Functional Polymers, 2022, 171: 105154.

[47] YU X Y, ZHANG K. Studies on the isomeric effect of nitrile functionality on the polymerization and thermal properties of *ortho*-norbornene-based benzoxazine resins [J]. Journal of Polymer Research, 2020, 27: 1-8.

[48] ZHANG K, ISHIDA H. Thermally stable polybenzoxazines via *ortho*-norbornene functional benzoxazine monomers: Unique advantages in monomer synthesis, processing and polymer properties [J]. Polymer, 2015, 66: 240-248.

[49] ZHANG K, LIU Y Q, WANG Y T, SUN L. A high performance polybenzoxazine via smart *ortho*-norbornene functional benzoxazine monomer based on ring-opening metathesis polymerization [J]. High Performance Polymers, 2019, 31(5): 513-520.

[50] ZHANG K, QIU J M, LI S J, SHANG Z K, WANG J Y. Remarkable improvement of thermal stability of main-chain benzoxazine oligomer by incorporating *o*-norbornene as terminal functionality [J]. Journal of Applied Polymer Science, 2017, 134(41): 45408.

[51] ZHANG K, YU X Y, WANG Y T, LIU Y Q. Thermally activated structural changes of a norbornene-benzoxazine-phthalonitrile thermosetting system: Simple synthesis, self-catalyzed polymerization, and outstanding flame retardancy [J]. ACS Applied Polymer Materials, 2019, 1(10): 2713-2722.

[52] LU Y, YU X Y, EVANS C J, YANG S F, ZHANG K. Elucidating the role of acetylene in *ortho*-phthalimide functional benzoxazines: Design, synthesis, and structure-property investigations [J]. Polymer Chemistry, 2021, 12(35): 5059-5068.

[53] WANG Y T, YOU S J, HU J, ZHANG K. Synthesis and properties of benzoxazine monomers bearing both

3-methyltetrahydrophtalimide and nitrile groups: *para-para vs*. *ortho-ortho* [J]. Macromolecular Research, 2020, 28(1): 74-81.

[54] ZHANG K, LIU Y Q, HAN L, WANG J Y, ISHIDA H. Synthesis and thermally induced structural transformation of phthalimide and nitrile-functionalized benzoxazine: Toward smart *ortho*-benzoxazine chemistry for low flammability thermosets [J]. RSC Advances, 2019, 9(3): 1526-1535.

[55] YANG R, WANG Y T, HAO B R, ZHANG K. Synthesis of *ortho*-methyltetrahydrophthalimide functional benzoxazine containing phthalonitrile group: Thermally activated polymerization behaviors and properties of its polymer [J]. High Performance Polymers, 2021, 33(2): 196-204.

[56] ASHRAF W, REHMAN A, HUSSAIN A, KARIM A, SHARIF H R, SIDDIQUY M, LIANFU Z. Optimization of extraction process and estimation of flavonoids from fenugreek using green extracting deep eutectic solvents coupled with ultrasonication [J]. Food and Bioprocess Technology, 2024, 17(4): 887-903.

[57] LI F N, BOATENG I D, CHEN S M, YANG X M, SOETANTO D A, LIU W M. Pulsed light irradiation improves degradation of ginkgolic acids and retainment of ginkgo flavonoids and terpene trilactones in ginkgo biloba leaves [J]. Industrial Crops and Products, 2023, 204: 117297.

[58] MAHUNU G K, ZHANG H, APALIYA M T, YANG Q Y, ZHANG X Y, ZHAO L N. Bamboo leaf flavonoid enhances the control effect of pichia caribbica against penicillium expansum growth and patulin accumulation in apples [J]. Postharvest Biology and Technology, 2018, 141: 1-7.

[59] ZHANG H, QI S, DAI Z, ZHANG M, SUN J F, DU D L. Allelopathic potential of flavonoids identified from invasive plant conyza canadensis on agrostis stolonifera and lactuca sativa [J]. 2017, 41(2): 223-238.

[60] 延玺, 刘会青, 邹永青, 任占华. 黄酮类化合物生理活性及合成研究进展 [J]. 有机化学, 2008, 28(9): 1534-1544.
YAN X, LIU H Q, ZOU Y Q, REN Z H. Progress in the physiological activity and synthesis of flavonoids [J]. Organic Chemistry, 2008, 28(9): 1534-1544.

[61] ZHANG K, TAN X X, WANG Y T, ISHIDA H. Unique self-catalyzed cationic ring-opening polymerization of a high performance deoxybenzoin-based 1, 3-benzoxazine monomer [J]. Polymer, 2019, 168: 8-15.

[62] GOLEIJ P, KHANDAN M, KHAZEEI TABARI M A, SANAYE P M, ALIJANZADEH D, SOLTANI A, HOSSEINI Z, LARSEN D, KHAN H, KUMAR A P, DAGLIA M. Unlocking the potential: How flavonoids affect angiogenesis, oxidative stress, inflammation, proliferation, invasion, and alter receptor interactions in endometriosis [J]. Food Science & Nutrition, 2025, 13(1): e4607.

[63] GÓRNIAK I, BARTOSZEWSKI R, KRÓLICZEWSKI J. Comprehensive review of antimicrobial activities of plant flavonoids [J]. Phytochemistry Reviews, 2019, 18: 241-272.

[64] TENG H, ZHENG Y M, CAO H, HUANG Q, XIAO J B, CHEN L. Enhancement of bioavailability and bioactivity of diet-derived flavonoids by application of nanotechnology: A review [J]. Critical Reviews in Food Science and Nutrition, 2023, 63(3): 378-393.

[65] ZHOU Q, CHENG K W, XIAO J B, WANG M F. The multifunctional roles of flavonoids against the formation of advanced glycation end products (AGEs) and AGEs-induced harmful effects [J]. Trends in Food Science & Technology, 2020, 103: 333-347.

[66] ZHANG K, LIU Y Q, HAN M C, FROIMOWICZ P. Smart and sustainable design of latent catalyst-containing benzoxazine-bio-resins and application studies [J]. Green Chemistry, 2020, 22(4): 1209-1219.

[67] HAO B, HAN L, LIU Y Q, ZHANG K. An apigenin-based bio-benzoxazine with three polymerizable functionalities: Sustainable synthesis, thermal latent polymerization, and excellent thermal properties of its thermosets [J]. Polymer Chemistry, 2020, 11(36): 5800-5809.

[68] ZHAO W Q, HAO B R, LU Y, ZHANG K. Thermal latent and low-temperature polymerization of a bio-benzoxazine resin from natural renewable chrysin and furfurylamine [J]. European Polymer Journal, 2022, 166: 111041.

[69] DAI J Y, TENG N, SHEN X B, LIU Y, CAO L J, ZHU J, LIU X Q. Synthesis of biobased benzoxazines suitable for vacuum-assisted resin transfer molding process via introduction of soft silicon segment [J]. Industrial & Engineering Chemistry Research, 2018, 57(8): 3091-3102.

[70] QU L, XIN Z. Preparation and surface properties of novel low surface free energy fluorinated silane-functional polybenzoxazine films [J]. Langmuir, 2011, 27(13): 8365-8370.

[71] HAO B R, WANG J Q, ZHANG Y, SHENG W C, ZHANG K. Chrysin-based bio-benzoxazine: A copolymerizable green additive for lowering curing temperatures and improving thermal properties of various thermosetting resins [J]. ACS Applied Polymer Materials, 2022, 4(2): 1286-1297.

[72] YANG R, YANG R, YANG S F, ZHANG K. Hydrogen bonding-rich bio-benzoxazine resin provides high-performance thermosets and ultrahigh-performance composites [J]. ACS Sustainable Chemistry & Engineering, 2024, 12(4): 1728-1739.

[73] YANG R, ZHANG K. Design and synthesis of flavonoid-based mono-, bis-, and tri-benzoxazines: Toward elucidating roles of

oxazine ring number and hydrogen bonding on their polymerization mechanisms and thermal properties [J]. Macromolecules, 2025, 58: 616-626.

[74] CAO D X, LIU Z Q, VERWILST P, KOO S, JANGJILI P, KIM J S, LIN W. Coumarin-based small-molecule fluorescent chemosensors [J]. Chemical Reviews, 2019, 119(18): 10403-10519.

[75] FROIMOWICZ P, RODRIGUEZ ARZA C, OHASHI S, ISHIDA H. Tailor-made and chemically designed synthesis of coumarin-containing benzoxazines and their reactivity study toward their thermosets [J]. Journal of Polymer Science Part A: Polymer Chemistry, 2016, 54(10): 1428-1435.

[76] KISKAN B, YAGCI Y. Thermally curable benzoxazine monomer with a photodimerizable coumarin group [J]. Journal of Polymer Science Part A: Polymer Chemistry, 2007, 45(9): 1670-1676.

[77] ARZA C R, FROIMOWICZ P, ISHIDA H. Smart chemical design incorporating umbelliferone as natural renewable resource toward the preparation of thermally stable thermosets materials based on benzoxazine chemistry [J]. RSC Advances, 2015, 5(118): 97855-97861.

[78] SINI N K, ENDO T. Toward elucidating the role of number of oxazine rings and intermediates in the benzoxazine backbone on their thermal characteristics [J]. Macromolecules, 2016, 49(22): 8466-8478.

[79] LU Y, ZHANG Y, ZHANG K. Renewable biomass resources to access halogen-and phosphorus-free flame retardant thermosets with ultra-low heat release capacity [J]. Chemical Engineering Journal, 2022, 448: 137670.

[80] LU Y, LI N, PENG Y, MOHAMED M G, KUO S W, ZHANG K. Facile and eco-friendly synthesis of hydrogen bonding-rich bio-based bisbenzoxazine resins with low surface free energy, strong adhesion strength and high thermal stability [J]. Molecular Systems Design & Engineering, 2024, 9(1): 86-98.

[81] LU Y, YANG Y, WANG J Q, ZHANG K. Development of intrinsically flame-retardant bio-thermosets with further enhanced thermal stability through a photo-thermal dual polymerization strategy [J]. Polymer Degradation and Stability, 2024, 229: 110948.

[82] ZHAO J, CHEN J P, ZHENG X X, LIN Q, ZHENG G C, XU Y L. Urushiol-based benzoxazine containing sulfobetaine groups for sustainable marine antifouling applications [J]. Polymers, 2023, 15(10): 2383-2399.

[83] YAO Z H, LU Y, SONG J N, ZHANG K. Synthesis of daidzein and thiophene containing benzoxazine resin and its thermoset and carbon material [J]. Molecules, 2023, 28(13): 5077-5089.

[84] LIU J M, GUO P L, YU W J, ZHAO W W, ZHANG K, LIU X Q. Direct conversion of liquid bio-benzoxazine precursor into porous graphene-based lubricant additive by laser irradiation [J]. ACS Applied Nano Materials, 2024, 7(4): 4355-4363.

[85] LIU J K, ZHANG L Y, ZHU X B, CHEN Q, ZHANG K, LIU X Q. Design of a low-temperature ring-opening benzoxazine system using a supramolecular hydrogen-bond structure [J]. ACS Applied Polymer Materials, 2023, 5(8): 6595-6606.

[86] LU Y, YU X Y, HAN L, ZHANG K. Recent progress of high performance thermosets based on norbornene functional benzoxazine resins [J]. Polymers, 2021, 13(9): 1417-1426.

[87] ZHANG K, ISHIDA H. An anomalous trade-off effect on the properties of smart *ortho*-functional benzoxazines [J]. Polymer Chemistry, 2015, 6(13): 2541-2550.

[88] CHEN G M, ZHAO W W, WEN S F, LIU X Q. Three dimensional graphene/copper dual networks as composite conductors with enhanced current carrying capacity [J]. ACS Applied Nano Materials, 2024, 7(7): 8164-8174.

[89] YU W J, PENG Y Y, CAO L J, ZHAO W W, LIU X Q. Free-standing laser-induced graphene films for high-performance electromagnetic interference shielding [J]. Carbon, 2021, 183: 600-611.

[90] LIU J M, CHEN B B, GUO P L, YU Z Q, SHENG W C, ZHANG K, LIU X Q. Fabrication of 3D porous graphene materials for oil-based lubrication: Tribological and wear performance [J]. Carbon, 2024, 221: 118892.

（责任编辑：王吉晶）