

# 功能高分子材料的研究进展

## Research progress in functional polymer materials

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**摘要:** 功能高分子材料是一类具有催化性、导电性、光敏性、生物活性等特殊功能的高分子材料, 对物质、能量、信息具有传输、转换或贮存的作用。功能高分子材料具有质量轻、种类多样、专用性强等特点, 广泛应用于机械、信息技术、生物医学等多个领域。功能高分子材料的发展非常迅速, 为满足各领域对新技术发展的需要, 功能高分子材料逐渐往多功能化方向发展, 比如电磁材料、光热材料等相继出现。而随着智能高分子的出现, 功能高分子材料也逐渐向着智能化发展, 比如自修复功能高分子材料、形状记忆材料等。本文综述了近年来功能高分子材料的研究进展, 重点介绍了反应型功能高分子材料、光功能高分子材料、电功能高分子材料、生物医用功能高分子材料、环境降解高分子材料、形状记忆高分子材料及智能高分子水凝胶这几类功能高分子材料, 并对其应用做了简要阐述。目前功能高分子材料更多的是仅有光电等传统功能或形状记忆等特殊功能, 相信兼有传统功能和特殊功能的功能高分子材料将是未来材料的发展方向。

**关键词:** 功能高分子材料; 生物医用; 环境降解; 形状记忆; 智能水凝胶

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**Abstract:** Functional polymer material is a type of polymer materials with special functions such as catalysis, conductivity, photosensitivity, and biological activity. They have the function of transmitting, converting, or storing substances, energy, and information. Functional polymer materials have the characteristics of light weight, numerous varieties and strong specialty, which make them widely used in machinery, information technology, biomedicine and other fields. The development of functional polymer materials is very rapid. In order to meet the needs of new technologies in various fields, functional polymer materials are gradually developing towards multi-function such as electromagnetic materials and photothermal materials. With the emergence of smart polymers, functional polymer materials are gradually being developed towards intelligence, such as self-healing functional polymer materials and shape memory materials. The research progress of functional polymer materials in recent years was summarized in this article and their applications were briefly described, with emphasis on reactive functional polymer materials, optical functional polymer materials, electrical functional polymer materials, biomedical functional polymer materials, environmentally degradable polymer materials, shape memory polymer materials and smart polymer hydrogel. At present, most functional polymer materials only have traditional functions such as photoelectricity or special functions such as shape memory. It is believed that functional polymer materials with both traditional and special functions will be the development direction of future materials.

**Key words:** functional polymer materials; biomedicine; environmental degradation; shape memory; smart hydrogel

功能高分子材料是 20 世纪 60 年代发展起来的一种新材料,通过在天然或合成高分子主链和侧链上接枝反应性功能基团,使其具有新的诸如催化性、导电性、光敏性、导磁性、生物活性等特殊功能的一类新型高分子<sup>[1-3]</sup>。功能高分子材料对物质、能量、信息具有传输、转换或贮存的作用,又被称为特种高分子材料或者精细高分子材料<sup>[4-6]</sup>。如图 1 所示,功能高分子材料分为反应型功能高分子材料、光功能高分子材料、电磁功能高分子材料、生物医用功能高分子材料等几大类<sup>[7-11]</sup>,因其具有催化性、导电性、光敏性、导磁性、生物活性等特殊的功能而备受人们关注。目前对功能高分子材料的研究主要集中在其结构和性能之间的关系上,通过优化功能高分子材料合成方法,开发出新型功能高分子材料,不断扩展其应用领域。

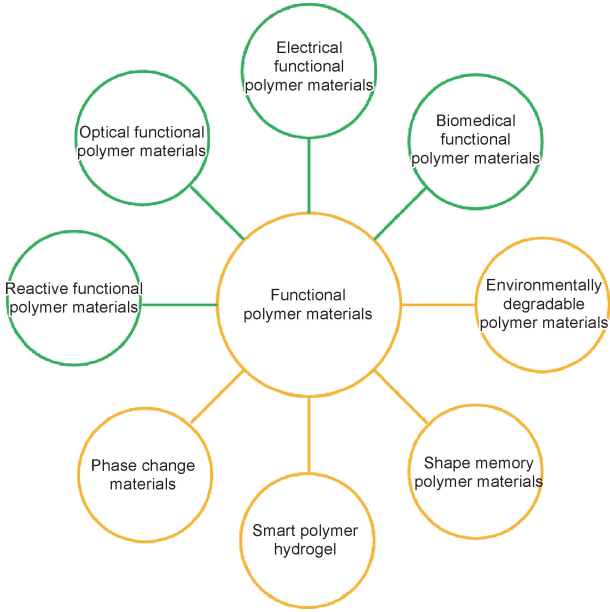


图 1 功能高分子材料种类  
Fig. 1 Types of functional polymer materials

功能高分子材料具有种类多样、产量少、专用性强等特点,此外,与其他功能材料相比,功能高分子材料还具有质量轻、结构配方可设计性强等特点,因此可以广泛满足各个应用领域的要求<sup>[12-14]</sup>。通常合成的功能高分子材料不单单只有一种功能,比如通过高分子改性能够制备具有导热性、导磁性和导电性的多功能高分子材料<sup>[15-18]</sup>。此外,不同功能之间可以相互转换和交叉,比如具有光电效应的材料能够实现光功能和电功能的可逆转换<sup>[19-21]</sup>。随着对功能高分子材料研究的日益成熟,功能高分子材料逐渐形成了光电磁高分子信息材料和医用高分子材料两个主要研究领域,并且正在往高功能化、多功能化和智能化方向发展。因此

许多新型智能高分子材料被陆续开发出来,比如分子自组装材料、形状记忆材料、智能水凝胶和纳米复合材料等<sup>[22-27]</sup>。

功能高分子材料的高性能和专用性的特点使其广泛应用于各个领域。例如,吸附分离功能高分子材料主要包括离子交换树脂和吸附树脂,通过离子交换能够达到分离提纯的目的,在天然产物分离纯化、血液净化治疗等领域有极大的应用<sup>[28-30]</sup>。电磁功能高分子材料具有导电性和导磁性,可以制成导电聚合物膜、电磁制动器、电磁波干扰屏蔽材料和抗静电材料等<sup>[31-33]</sup>。光功能高分子材料具有对光吸收、储存和转化的功能,可以制成光纤、有机玻璃眼镜、光致变色材料等<sup>[34-35]</sup>。生物医用功能高分子材料在当代医学领域具有更广泛的应用,被用作人工器官、药物递送载体等<sup>[36-39]</sup>。本文介绍了几类不同的功能高分子材料的性能及其应用。

1 功能高分子材料发展现状

1.1 反应型功能高分子材料

反应型功能高分子材料包括高分子试剂和高分子催化剂,通过将反应活性中心或催化性中心接枝到高分子链上,实现小分子试剂或催化剂的高分子化<sup>[40]</sup>。常见的高分子试剂根据化学活性可分为氧化试剂、还原试剂、烷基化试剂、酰基化试剂、卤代试剂和固相合成试剂等<sup>[41-43]</sup>。高分子催化剂包括用于酸碱催化的离子交换树脂、过渡金属络合物催化剂、相转移催化剂和固定化酶等<sup>[44-46]</sup>。反应型高分子材料要求具有高反应活性、高选择性和专一性,主要用于化学合成和化学反应。

高分子试剂和催化剂不仅具有小分子的反应性能和催化性能,还具有多孔性、高选择性和化学稳定性等特殊性能,拓展了化学试剂和催化剂的应用范围<sup>[47]</sup>。固相合成试剂是高分子试剂中应用非常广泛的一种试剂,多用于合成多肽、核苷酸、寡糖等生物活性大分子<sup>[48]</sup>。固相合成法是利用连接在载体上的活性官能团与小分子试剂进行连续多步反应,得到最终产物后再通过水解脱除载体的合成方法<sup>[49]</sup>。Li 等<sup>[50]</sup>通过两步固相/溶液法合成了海绵环肽(phakellistatin 15),反应以线性八肽为原料,选用 2-氯三苯甲基氯树脂为固相载体,乙酸/三氟乙醇/二氯甲烷裂解树脂为保护试剂,通过溶液法实现线性八肽的环化。phakellistatin 15 是一种天然的富含脯氨酸的环八肽,具有很好的抗菌性、抗病毒性、酶抑制性和抗肿瘤性,在生物医学中具有很高的应用价值,但 phakellistatin 15 很难从自然界中提取且产率极低,因此需要通过化

学反应合成。这种两步固相/溶液法相比其他合成方法提高了合成产率(35.46%),缩短了反应时间(1 h)。

酶是一种能加速生化反应和化学反应的大分子生物催化剂,在温和的反应条件下具有较高的催化效率和底物特异性,被广泛应用于各个领域,但其稳定性较差,很容易变性失活,基于这点通常在不影响酶的活性的前提下对酶进行固定化。Cirillo 等<sup>[51]</sup>以聚(乙二醇)二甲基丙烯酸酯为交联剂,N-异丙基丙烯酰胺为单体制备了具有温敏性的水凝胶,并通过自由基聚合将胃蛋白酶共价固定在水凝胶上,合成了具有酶催化活性的温敏水凝胶。通过控制温度能够调节胃蛋白酶的活性,当温度高于水凝胶的临界溶液温度(45℃)时,水凝胶未表现出催化活性,当温度降低到室温时水凝胶恢复酶催化活性。此外,通过热稳定性实验发现,高温下水凝胶仍保留酶的催化活性,即高温不会使酶失活,因此,能够通过改变温度来可逆地获得酶催化作用。Feng 等<sup>[52]</sup>基于碳二亚胺偶联技术实现了脂肪酶与多壁碳纳米管(MWCNT)的共价结合。首先用HNO<sub>3</sub>纯化MWCNT,并用H<sub>2</sub>SO<sub>4</sub>和HNO<sub>3</sub>氧化以引入羧基。经1-乙基-(3-二甲基氨基丙基)碳二亚胺盐酸盐(EDC)和N-羟基琥珀酰亚胺(NHS)活化后,脂肪酶通过酰基酰胺键被固定在羧基化的MWCNT上。固定后的脂肪酶显示出较低的温度依赖性和较高的分离效率。研究表明固定化脂肪酶的二级结构发生了变化,这可能导致酶活性的降低,但其在有机溶剂中的催化活性却得到了显著提高。

1.2 光功能高分子材料

光功能高分子材料是指能够对光能进行吸收存储、传输、转换的一类高分子材料<sup>[53]</sup>。光功能高分子材料主要包括光稳定剂、光敏涂料、荧光剂、光转化材料、光致变色材料和光导材料等<sup>[54-55]</sup>。光功能高分子材料在生产生活中的应用非常广泛,比如光导纤维、太阳能、集成电路和光电池等<sup>[56-57]</sup>。

Lee 等<sup>[58]</sup>通过偶联缩合反应合成了两种基于二苯甲酮的荧光聚合物 pCzBP 和 pAcBP,并将 2-乙基己基侧链接枝在 pCzBP 和 pAcBP 聚合物链段上,从而使 pCzBP 和 pAcBP 具有较好的溶解度,易于溶于常见的有机溶剂,例如甲苯、氯仿和氯苯等。pCzBP 和 pAcBP 能够发射 TADF,其外部量子效率( $\eta_{\text{ext}} = (9.3 \pm 0.9)\%$ )比常规荧光聚合物的理论极限外部量子效率( $\eta_{\text{ext}} < 5\%$ )要高。此外,pCzBP 和 pAcBP 还表现出良好的热稳定性和固态下的非晶态结构,能够用作有机发光二极管。Yu 等<sup>[59]</sup>通过将光敏涂料重氮聚乙醇/苯乙烯涂覆在毛细管的内表面上,制备了一种能用于蛋白质分离的毛细管。如图 2 所示,涂有光敏涂料的毛细管经紫外线照射后,重氮基团发生光化学反应将离子键转变为共价键,共价连接的涂层会抑制蛋白质在毛细管内表面的吸附,实现了核糖核酸酶 A、溶菌酶和牛血清白蛋白的基线蛋白质分离。与非共价涂覆或裸露的毛细管相比,共价连接的毛细管涂层具有更高的电泳分离性能以及出色的可重复性和稳定性,是一种环保、安全的蛋白质分离技术。

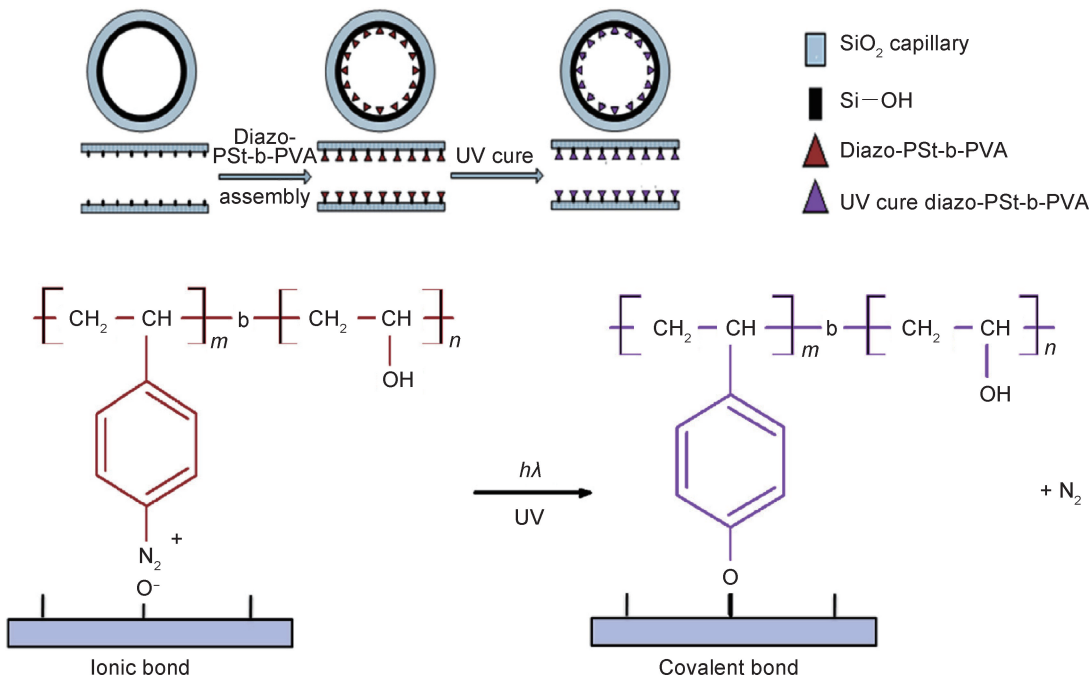


图 2 紫外线照射毛细管表面制备光敏重氮聚乙醇/苯乙烯共价涂层<sup>[59]</sup>

Fig. 2 Preparation of photosensitive diazo-PVA-b-PSt covalent coating on the capillary surface upon UV irradiation<sup>[59]</sup>



光致变色材料是一种应用很广泛的光功能高分子材料,光致变色材料在光学数据存储和光学交换方面具有潜在的应用价值。Tanino 等<sup>[60]</sup>合成了一种基于偶氮苯的新型光致变色非晶态材料,能够应用在防伪、装饰、显示、摄影、信息存储等领域。该新型光致变色非晶态材料自身能够形成均匀的非晶态膜而无需聚合物黏合剂,并表现出玻璃化转变现象。研究发现,合成的光致变色材料在非晶态膜和溶液中均容易表现出光致变色特性,其作为非晶薄膜的反式-顺式光异构化的量子产率要低于溶液中的量子产率。此外,基于材料结构的不同,光致变色非晶态膜的顺式-反式热异构化的表观速率常数也与溶液中的稍有不同。Mutoh 等<sup>[61]</sup>以聚(甲基丙烯酸甲酯)和聚(丙烯酸丁酯)组成的三嵌段聚合物(PMMA-b-PBA)为基体,3H-蔡并吡喃为光致变色分子合成了一种能够快速光致变色的聚合物膜。3H-蔡并吡喃通过光致变色反应能够改变其分子结构和偶极矩,而 3H-蔡并吡喃 2 和 10 取代位上的溴、苯基和苄基等大取代基会引起空间和静电排斥,从而提高其褪色速度,极大地提高了 3H-蔡并吡喃光致变色反应的效率。此外,PMMA-b-PBA 同时具有刚性链和柔性链,刚性链提高了聚合物膜的力学性能,柔性链则为光致变色反应中的结构变化提供了足够的自由体积。

### 1.3 电功能高分子材料

导电功能高分子材料按组成可分为结构型导电高分子和复合型导电高分子两类<sup>[62]</sup>。结构型导电高分子依靠自身提供的导电载流子导电,这类高分子经掺杂后导电率能够大幅度提升,而复合型导电高分子需要通过添加炭黑、金属粉、箔等来实现导电<sup>[63-64]</sup>。结构型导电高分子材料主要有聚乙炔、线型聚苯、氮硫高聚物、聚酮酞菁等,但单一的结构型导电高分子材料电导率不高,在实际应用中,需要掺杂电子受体或电子给体<sup>[65-66]</sup>。复合型导电高分子材料包括导电塑料、导电橡胶、导电涂料和导电薄膜等<sup>[67-68]</sup>,在复合型导电高分子中,高分子充当黏合剂的角色,本身不具有导电性。复合型导电高分子材料制备简单,实用性强,其主要应用于发光二极管、电致发光和电磁屏蔽器等领域中<sup>[69-70]</sup>。

Aydin 等<sup>[71]</sup>设计了一种用于检测人血清和唾液中白细胞介素的生物传感器。通过将四臂星形聚甲基丙烯酸缩水甘油酯(SPGMA)、导电剂炭黑和黏合剂聚偏氟乙烯(PVDF)混合制备出均质的导电复合浆料,然后将其涂布在 ITO 电极表面上,白细胞介素抗体与星形聚合物的环氧基团共价连接,制备了具有电化学性能的生物传感器。导电复合材料提高了该生物

传感器的灵敏性,降低了白细胞介素的检测限,此外,该生物传感器的制备过程简单,并且与酶联免疫吸附测定试剂盒兼容。

Aycan 等<sup>[72]</sup>制备了一种海藻酸钠/明胶/透明质酸/氧化石墨烯导电复合聚合物薄膜(SAlg/Gel/HA/RGO),其中 SAlg/Gel/HA 作为聚合物网络,RGO 通过分子间的范德华相互作用和氢键作用均匀分布在聚合物网络中。RGO 作为电活性材料,为 SAlg/Gel/HA/RGO 聚合物薄膜提供了导电性。RGO 的掺入提高了聚合物薄膜的电导率,但随着 RGO 添加量的增大电导率逐渐降低,RGO 分子也会发生团聚,研究表明 RGO 最佳添加量的体积分数为 10%。此外,SAlg/Gel/HA/RGO 聚合物膜相比纯聚合物膜具有更优异的力学性能,RGO 的加入提高了聚合物薄膜的弹性模量、拉伸强度和断裂伸长率。研究发现,SAlg/Gel/HA/RGO 聚合物膜还具有良好的透气性和药物缓释性能,能够很好地释放布洛芬抗炎药,提高了 SAlg/Gel/HA/RGO 膜对伤口的愈合效果。SAlg/Gel/HA/RGO 膜在伤口敷料方面具有很好的应用前景。

### 1.4 生物医用功能高分子材料

生物医用高分子材料是一种用于生理系统疾病的诊断和治疗,修复或替换生物体组织器官的高分子材料,包括医用高分子和药用高分子两大类<sup>[73-74]</sup>。生物医用高分子材料被广泛应用于人工器官、药物释放、生物组织工程等领域<sup>[75-77]</sup>。由于生物医用高分子材料直接应用于人体,因此要求其要无毒无害,其次要有良好的生物相容性,此外根据使用场合的不同对材料还有其他的特殊要求<sup>[78-79]</sup>。

Meng 等<sup>[80]</sup>通过将果胶(QP)和蒙脱土(MMT)简单共混制备了 QP-MMT 杂化膜,该膜具有良好的药物缓释性能。果胶具有良好的生物相容性,易降解,被广泛用作药物载体,但果胶在体内易被溶解且药物释放速度较快,因此作者通过混入 MMT 来减缓药物的释放速度,达到药物缓释的目的。选用 5-氟尿嘧啶为释放药物,研究了 QP-MMT 杂化膜的体外药物缓释性能,发现最佳膜表现出较高的药物包封率(36.50%)和载药率(80.30%)。此外,MMT 的存在确实改善了果胶的缓释性能,QP10-MMT0.1 杂化膜的药物累积释放率在前 0.5 h 均在 20%左右,药物持续释放时间超过了 8 h。此外,研究人员进行了细胞毒性实验,证明了 QP-MMT 杂化膜具有良好的生物相容性。

Bai 等<sup>[81]</sup>等通过阳离子聚(苄-亚苯基)衍生物(PFP-NMe<sup>3+</sup>)与葫芦[7]尿嘧啶(CB[7])合成了一种超分子络合物(PFP-NMe<sup>3+</sup>/CB[7]),能够用于快速原位检测和鉴别多种病原体。真菌和细菌的细胞壁均

带有负电荷,具有两亲结构的 PFP-NMe<sup>3+</sup> 可通过静电和疏水相互作用与病原体带负电荷的细胞壁结合。CB[7]能够掩埋 PFP-NMe<sup>3+</sup> 侧链上的烷基从而减弱 PFP-NMe<sup>3+</sup> 与病原体表面的疏水相互作用,当向 PFP-NMe<sup>3+</sup>/CB[7]络合物中添加金刚烷胺(AD)后,由于 AD 会与 CB[7]形成更加稳定的 CB[7]/AD 络合物,从而使 PFP-NMe<sup>3+</sup> 从 PFP-NMe<sup>3+</sup>/CB[7]络合物中释放。因此,PFP-NMe<sup>3+</sup>/CB[7]络合物在添加 AD 前后会与病原体表现出不同的相互作用方式。通过计算添加 AD 前后被 PFP-NMe<sup>3+</sup>/CB[7]染色的病原体荧光强度的变化,实现对病原体简单、快速区分。研究发现,添加 AD 后,革兰氏阳性菌的荧光强度显著增加,而革兰氏阴性菌和真菌的荧光强度则明显减少,表明 PFP-NMe<sup>3+</sup>/CB[7]络合物能够成功检测出一个样品中的多种病原体。而且该检测方法快速、简单,仅需 2 h 即可对各种病原体进行分层,并且不需要特定的生物标记或细胞标记。Ishihara 等<sup>[82]</sup>合成了 2-甲基丙烯酰氧乙基磷酸胆碱聚合物(MPC),具有良好的血液相容性和生物相容性,可用于制造人工器官等。MPC 聚合物相比于传统材料具有很好的血液相容性,在没有使用抗凝剂的情况下与血液接触也可以有效抑制血液的凝固。将人全血分别涂覆在玻璃和 MPC 聚合物上,发现血液在玻璃上的凝结时间为 8.4 min,而在 MPC 聚合物上的凝结时间显著增加为 28 min,这是因为 MPC 聚合物能够有效抑制血浆蛋白的减少和吸附蛋白的变性。此外,MPC 聚合物具有良好的抗蛋白质吸附和细胞黏附性能,因此被广泛应用于临床器官的表面修饰和生物医学设备。

## 2 功能高分子材料发展趋势

### 2.1 环境降解高分子材料

近年来,高分子材料的发展非常迅速,应用也日益广泛,但高分子材料在自然环境中很难分解,造成大量的白色污染,这就使发展可降解高分子材料成为必然趋势<sup>[83]</sup>。降解高分子材料分为光降解高分子材料和生物降解高分子材料两类<sup>[84-86]</sup>。高分子材料通过引入感光基团或添加光敏剂来制备光降解高分子材料,在光的作用下光降解高分子材料的聚合物链断裂,分子量降低<sup>[87]</sup>。光降解高分子材料主要用于包装材料和农膜,但其应用条件苛刻、价格较贵,因此生物降解高分子材料在近几年更受关注<sup>[88-89]</sup>。生物降解高分子材料是指通过生物酶作用或微生物化学作用能够发生降解的高分子。生物降解高分子材料包括淀粉、纤维素、甲壳素、透明质酸等天然高分子材料和乳酸、聚己内酯

等合成高分子材料<sup>[90-92]</sup>。生物降解高分子材料具有质量轻、价格便宜以及易降解等特点而被广泛应用于生物工程和医用降解高分子材料等领域。

Nayanathara 等<sup>[93]</sup>通过苯乙烯(St)与天然肉桂油和合成肉桂醛(Cin)之间的自由基共聚合制备了两种苯乙烯-肉桂醛聚合物薄膜(St-co-Cin),研究了在室外风化条件下和紫外线辐射条件下薄膜的光降解作用。研究发现,紫外线照射下苯乙烯-肉桂醛共聚物的羰基吸收光后诱发 Norrish I 和 Norrish II 降解反应,反应产生的自由基会通过自氧化作用继续降解。在室外风化条件下,苯乙烯-肉桂醛共聚物的失重率远高于聚苯乙烯均聚物的失重率,而且在风化 10 天后共聚物开始变色,而聚苯乙烯均聚物没有发生变色。此外,随着肉桂醛含量的增加,苯乙烯-肉桂醛共聚物薄膜的失重率增高。在各时间间隔内,通过合成肉桂醛制备的共聚物的失重率均高于与天然肉桂油合成的共聚物的失重率。因此,制备的苯乙烯-肉桂醛共聚物薄膜在药用包装以及食品包装工业中具有潜在的应用。

Sevostyanov 等<sup>[94]</sup>合成了一种聚乳酸-乙醇酸薄膜(PLGA),具有生物降解性和药物缓释性能。研究发现,合成的 PLGA 膜具有一定的力学性能,相对伸长率为 25%~165%,拉伸强度为 20~55 MPa。此外,PLGA 膜是可生物降解的,每天的降解率为 0.5%~1.0%。PLGA 薄膜能够持续和定向释放生物大分子,特别是具有高溶栓活性的链激酶分子,经 PLGA 膜释放的链激酶分子约 90%,保持其活性,链激酶的释放速率为每天 0.01~0.07 mg/cm<sup>2</sup>。当将 PLGA 薄膜样品植入动物体内两个月后,仅在组织中检测到了微量的 PLGA,并且在术后没有并发症,表明合成的 PLGA 膜对细胞没有任何毒性作用。因此,合成的新型可生物降解的 PLGA 聚合物膜具有一定的力学性能,并且能够持续定向地释放药物,在生物医药领域具有巨大的应用潜能。

### 2.2 形状记忆高分子材料

形状记忆材料是在改变并固定其形状后,通过改变外界条件(温度、pH、电场力等)能够使其恢复初始形状的材料<sup>[95]</sup>。形状记忆高分子材料根据引起形状记忆效应条件的不同分为热致感应型、电致感应型、光致感应型和化学感应型,其中热致感应型形状记忆高分子材料应用最为广泛<sup>[96-98]</sup>。形状记忆高分子材料具有质量轻、形变量大、成型容易等优点,被用于医疗、包装、建筑等领域<sup>[99]</sup>。

Gopinath 等<sup>[100]</sup>通过熔融共混法制备了具有热响应形状记忆功能的高分子纳米复合材料,该材料由聚己内酯(PCL)、聚苯乙烯-丁二烯-苯乙烯嵌段共聚物

(SBS)和碳纳米纤维(CNF)共混合成(如图 3 所示)。其中,PCL 因为熔点较低(60 ℃)充当开关聚合物,提供热响应形状记忆性能。此外,PCL 和 SBS 的混合能够提供材料更好的弹性和柔韧性,而 CNF 会增强材料的导热性和导电性。研究表明,PCL 含量会影响纳米复合材料的形状记忆性能,当 PCL 含量低于 12.5%时,材料不具有形状记忆功能。SBS 弹性体有助于材料形状的恢复,此外合成的纳米复合材料还具有较好的热稳定性。Capiel 等<sup>[101]</sup>通过自由基聚合反应由月

桂酸、油酸、甲基丙烯酸缩水甘油酯和苯乙烯制备了一种形状记忆材料。该材料高度半透明且不溶于常见的有机溶剂和水,此外还具有适度的交联密度。研究还发现,高的交联密度有利于材料的形状恢复。Ma 等<sup>[102]</sup>选用星形聚乳酸和低聚苯胺合成了一种兼有形状记忆功能和导电功能的共聚物(ESMP)。低聚苯胺的加入增强了 ESMP 共聚物的拉伸应力,使所得的形状记忆共聚物具有很高的机械强度。另外,ESMP 共聚物还具有优异的形状记忆能力和生物降解性。

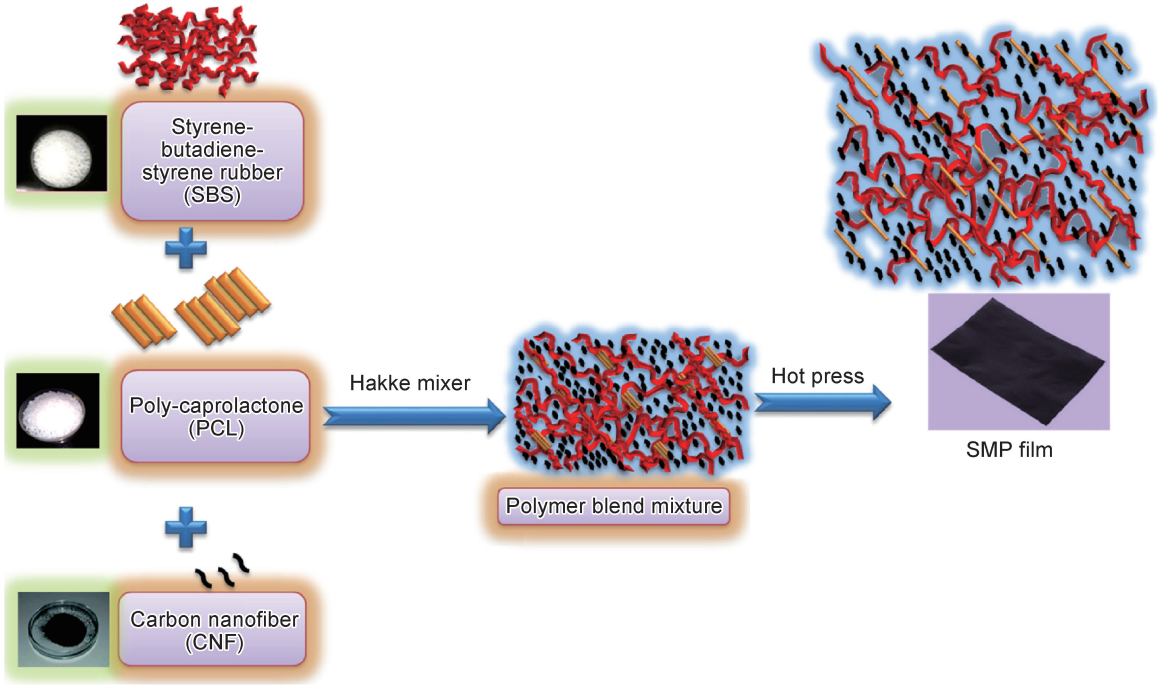


图 3 SBS,PCL 和 CNF 合成的形状记忆聚合物纳米复合材料示意图<sup>[100]</sup>

Fig. 3 Schematic view of the synthesis of the shape memory polymer nanocomposite built from SBS, PCL and CNF<sup>[100]</sup>

2.3 智能高分子水凝胶

高分子水凝胶是一种由亲水性高分子通过化学或物理交联而形成的具有三维网络结构的聚合物,能够吸收并保持大量的水<sup>[103]</sup>。高分子水凝胶具有与天然组织相似的微环境,都有很高的含水量(最高达 99%),在生物医药领域有广泛的应用,如伤口敷料、隐形眼镜、组织工程和药物递送领域<sup>[104-106]</sup>。当高分子水凝胶所处的环境(温度、pH、离子浓度、光、磁场、电场和化学物质等)发生变化时,高分子凝胶的结构或体积相变也会产生相应的改变,这种水凝胶被称为智能水凝胶。基于智能高分子水凝胶的刺激响应性,其被广泛应用于传感器、驱动器、药物载体和生物催化等领域<sup>[107-109]</sup>。

Zheng 等<sup>[110]</sup>合成了一种基于壳聚糖的温敏性可注射水凝胶,通过将壳聚糖溶液(CS)与 β-甘油磷酸盐(β-GP)物理混合制得,此外凝胶中还封装了光热材料

(MoS<sub>2</sub>/Bi<sub>2</sub>S<sub>3</sub>-PEG,MBP 纳米片)和抗肿瘤药物(阿霉素,DOX),从而实现了结肠癌的光热和化学疗法的结合。当温度高于 37 ℃时,由于 CS 和 β-GP 之间的氢键、静电相互作用和疏水相互作用增强,水凝胶会发生溶胶-凝胶转变。当 CS/MBP/DOX 溶液注入人体后会发生凝胶化,实现 DOX 和 MBP 纳米片的封装从而阻止其进入血液循环,提高药物治疗的安全性。此外,CS 基水凝胶还具有很好的抗菌能力,进一步增强了载药凝胶的安全性。研究表明,CS/MBP/DOX 水凝胶的凝胶温度可以通过近红外激光辐照来控制,因此 DOX 的释放是可控的,该水凝胶能够有效地用于肿瘤治疗。Solomevich 等<sup>[111]</sup>研究了基于葡聚糖磷酸酯(DP)水凝胶的脯氨酸药物递送系统,以及其用于局部癌症治疗的可能性。研究表明,制得的 DP 水凝胶对 pH 敏感,并且具有生物降解性。此外,还研究了水凝胶的药物释放性能,发现药物的释放量取决于外部介



质的 pH 值,并且随着 DP 水凝胶中磷基含量的增加而减少。研究还发现,DP 水凝胶具有体外细胞毒性和体内抗肿瘤活性。这证明 DP 水凝胶可以用作药物控释的载体,在治疗胃肠道恶性肿瘤方面具有巨大的潜力。

### 3 结束语

本文介绍了反应型功能高分子材料、光功能高分子材料、电功能高分子材料和生物医用功能高分子材料等几类常用的功能高分子,对其分类、作用机理以及应用等方面进行了简要阐述。随着功能高分子材料的蓬勃发展和实际应用的需求,功能高分子材料向着环境友好型和智能化发展,因此本文还着重介绍了环境降解高分子材料、形状记忆高分子材料和智能高分子水凝胶。

多功能高分子材料由于其功能的多样化,在生产生活中具有更加广泛的应用。因此,功能高分子材料近年来逐渐向着多功能化方向发展,电磁材料、导电材料、光热材料等相继出现。此外,随着科学技术的不断进步,研究人员对高分子结构与性能之间关系的研究也逐渐深入,制备出越来越多的具有特殊功能的新型功能高分子材料,比如生物高分子材料、隐身高分子材料等,进一步扩大了功能高分子材料的范围。基于对高分子材料应用方面的更高要求,为克服高分子材料强度低、易老化、使用寿命短等缺点,兼有传统功能(电功能、光功能等)和特殊功能(自修复、形状记忆功能等)的功能高分子材料将是未来材料的研究方向。相信随着对高分子材料结构的深入研究,兼有两种或以上功能的高分子材料将进一步被扩展,有望应用于航空航天、医疗、食品、工业等各个领域。

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