医用材料聚醚醚酮等离子喷涂表面改性研究进展

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摘要：聚醚醚酮材料（PEEK）具有良好的生物相容性、化学稳定性、X 射线可穿透性及优异的力学性能，广泛用于创伤、脊柱和关节等生物医疗领域。然而，PEEK 属于生物惰性材料，其骨整合性不足，这在一定程度上限制了该材料在骨修复与替换等领域的发展和应用。等离子喷涂技术由于工艺简单、经济，喷涂涂层的黏结强度高等特点，是解决聚醚醚酮材料骨整合能力不足的重要表面涂层改性技术。首先，简述了等离子喷涂工艺的涂层沉积机理，并分别对等离子喷涂钛以及羟基磷灰石两种常用涂层进行了介绍；其次，从不同喷涂工艺以及喷涂参数对涂层的影响出发，详细介绍了近几年对 PEEK 基等离子喷涂涂层的结合强度等机械性能的最新研究进展，并对等离子喷涂过程对 PEEK 基体的机械强度、疲劳强度、热性能和化学降解等初始性能影响进行了总结与评价，详细介绍了 PEEK 基等离子喷涂涂层体内外生物性能的最新研究进展；最后，展望了等离子喷涂改性 PEEK 基材料的临床应用前景，以期为未来设计新型 PEEK 基生物材料提供理论指导。

关键词：聚醚醚酮；等离子喷涂；机械性能；生物性能；

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Research Advance in Medical Material Polyether-ether-ketone of Surface Modification by Plasma Spraying

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ABSTRACT: Polyether ether ketone (PEEK) has the advantages of high mechanical strength, excellent chemical stability, and transparency to diagnostic X-rays, and its density and elasticity is closer to bones compared to metals. PEEK is widely used in biomedical fields such as trauma, spine, and joints. However, PEEK is a bioinert material with insufficient osteointegration, which limits the development and application in bone repair and replacement to a certain extent. Plasma spraying (PS) technology is an important surface coating modification technology to solve the problem of bone integration of PEEK materials due to its simple process, economy, and high adhesive strength of the coatings. Firstly, this paper briefly describes the coating deposition mechanism of PS process, then titanium (Ti) and hydroxyapatite (HA) coatings manufactured by PS are introduced respectively; Secondly, based on the different spraying processes and spraying parameters, the latest research progress of plasma sprayed PEEK-based coatings on mechanical properties such as bonding strength in recent years is introduced in detail. The effects of PS process on the initial properties of PEEK substrate, such as mechanical strength, fatigue strength, thermal properties and chemical degradation are summarized and evaluated; The latest research progress of plasma sprayed PEEK-based coatings on biological properties in vitro and in vivo is also introduced in detail; Finally, the clinical application of plasma sprayed PEEK is prospected to provide theoretical guidance for the design of new PEEK-based biomaterials in the future.

KEY WORDS: PEEK; plasma spraying; mechanical property, biological property

金属基生物材料如钛合金由于其优异的耐腐蚀性和较高的机械强度在临床骨科生物医用材料领域得到了广泛的应用[1]。然而，长期使用中金属离子的释放以及应力屏蔽等问题引起了人们广泛的担忧。术后并发症如骨溶解、致敏性以及由植入体松动导致的植入体失败都有可能发生。传统金属基植入材料已不能满足临床应用安全无毒且长寿命等需求[2-3]。因此，新型医用材料的开发与研究显得尤为重要。

聚醚醚酮（PEEK）作为一种热塑性聚合物，具有与人皮质骨相当的弹性模量（3~4 GPa）和密度（1.3 g/cm^3），这在一定程度上减弱或消除了传统金属基植入体的应力屏蔽效应[4-5]。PEEK 具有良好的化学稳定性，极大地方便了其作为植入物在临床上进行多种灭菌处理[6]。此外，PEEK 还具有良好的射线可通过性，存在于人体中进行计算机断层扫描（CT）和磁共振检查（MRI）时不会产生伪影，且在临床检查和诊断时不需要拆除[7]。然而，PEEK 属于惰性材料，其表面生物活性较低，骨整合性不足，不利于细胞的黏附、增殖和分化，易引起植入体与人体骨组织之间纤维组织的生成[8-9]，最终造成许多并发症如种植体移位、笼陷或假性关节等问题发生，这限制了 PEEK 在临床中的进一步应用[10-11]。

虽然 PEEK 在物理和化学性质上都是稳定的，但它可以通过物理或者化学方法如离子喷涂[12]、气溶胶沉积[13]、电子束沉积[14]等在基体表面制备具有生物活性涂层以达到改善表面性能的目的[15]。表面涂层改性能够在不影响基体机械强度和延展性下增加表面生物活性。骨科植入体涂覆涂层能够在不使用额外骨水泥或螺钉的情况下固定植入体，减少术后住院时间，防止过敏反应，从而延长植入体的寿命[16]。因此，近几年表面涂层技术改性植入体生物活性的研究得到了广泛的关注。等离子喷涂技术作为表面涂层改性重要的技术之一，是唯一一种被美国食品与药品管理局（FDA）批准的制备生物涂层的方法，并且已广泛用于临床金属基生物材料表面改性[17-18]。对于新型医用聚合物 PEEK 材料，等离子喷涂改性其表面骨整合性研究是目前该领域研究的热点。本文主要对等离子喷涂改性 PEEK 基植入物材料的相关研究进行了介绍。

1 等离子喷涂工艺

等离子喷涂技术是指以等离子体为热源，将粉末喷涂材料加热到熔融或半熔融状态，并经加速沉积到经过预处理的工件表面而形成涂层，如图 1 所示[19]。目前常用的工艺方法有大气等离子喷涂（APS）、真空等离子喷涂（VPS）以及低压等离子喷涂（LPPS）。此外还有超低压等离子喷涂和悬浮液等离子喷涂（SPS）等新型工艺技术[20]。从涂层结构上来看，等离子喷涂涂层组织细密，氧化物含量较低，涂层与基体间的结合以及涂层粒子间的结合形式除以机械结合为主外，还可产生微区冶金结合和物理结合，具有较高的结合强度。从工艺技术上，喷涂材料范围广泛，设备精度高，并且调控喷涂参数可以实现不同厚度、孔隙率等要求的涂层制备[21-22]。

聚醚醚酮作为一种耐高温的工程热塑性材料，具有相对较高的玻璃化转变温度（约 140 ℃）和熔点（约 340 ℃），能在 200 ℃以上的温度短时间暴露[23]。这些特征使得等离子喷涂工艺能够应用于聚醚醚酮基材料改性，前提是准确地调节对基底冷却影响较大的参数，例如：冷却系统、等离子枪与基底的位置和距离、涂覆过程中的相对运动等。

2 PEKK基等离子喷涂生物涂层研究

采用等离子喷涂技术制备生物涂层的研究中，金属材料 Ti 和陶瓷材料羟基磷灰石粉末是两种常用

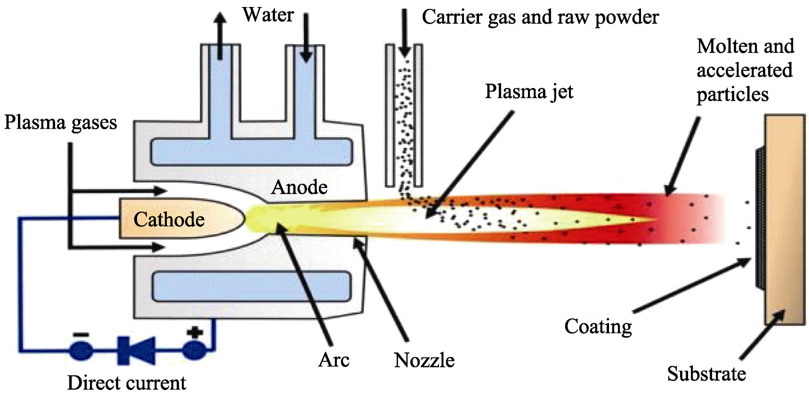


图 1　等离子喷涂工艺过程示意图[19]
Fig.1 Schematic diagram of atmospheric plasma spray process[19]

的喷涂材料。钛涂层不仅具备金属材料较好的机械强度、高粗糙度和多孔性特征，还可增加植入体与骨组织的接触面积，有利于骨长入，提高涂层与骨界面的结合强度；而且，在一定程度上可改变在负载状态下骨植入体与骨之间界面的力学传递方式[24-26]。HA 作为一种生物活性材料，其成分和天然骨相同，具有十分优良的生物相容性和生物活性，可被人体组织降解吸收[27-28]。植入人体后，能够很快地与骨结合，从而获得更稳定的固定强度，同时减少愈合时间和减轻患者疼痛[29]。粗糙多孔 Ti 涂层和生物活性羟基磷灰石涂层在等离子喷涂临床金属基骨科植入物上已经得到了广泛的应用。而等离子喷涂改性新型生物材料 PEEK 基生物涂层的研究仍是该领域研究的热点。

2.1　PEEK 基等离子喷涂涂层的机械性能研究

生物材料聚醚醚酮等离子喷涂生物涂层的研究可以追溯到至少几十年前。Ha 等[30]首次采用等离子喷涂方法对聚醚醚酮植入体进行了涂层研究。通过 APS 工艺在高碳纤维增强聚醚醚酮（CFR–PEEK）基板上沉积了厚度达 200 μm 的 HA 涂层。然而，涂层的结合强度很低，仅有 2.8 MPa。研究发现，在 1 650 ℃以上，HA 颗粒部分熔融导致 PEEK 基体蒸发产生蒸汽膜，蒸汽膜阻碍了 PEEK 基体与涂层的紧密接触进而造成结合强度降低。在之后的研究中，Ha 等[31]又通过 VPS 工艺制备了一系列不同厚度的 Ti 涂层、HA 涂层以及 HA/Ti 复合涂层，涂层都与 PEEK 基体具有良好的连锁反应，认为 VPS 是一种适合在 CFR–PEEK 植入物沉积 HA/Ti 涂层的方法。Beauvais 等[32]利用 APS 工艺成功在聚醚醚酮试样上涂覆了厚度为 150 μm 的 HA 涂层。涂层的结合强度提高到 7.5 MPa，涂层的结晶度为 74%。提出可以通过优化基体喷砂工艺或使用 VPS 工艺制备钛结合层来提高涂层的黏合强度，并且使用高性能黏合剂可以更好地评估强度。Bureau 等[33-34]介绍了两项关于聚醚醚酮上 APS–HAp 涂层的不同研究。第一项研究是关于 APS 参数对 Ca–P 基涂层（HA、α–TCP 和 β–TCP）结晶度和相含量的影响。结果表明不同喷涂工艺参数对羟基磷灰石涂层的晶相与非晶相之间有显著的调节作用。第二项研究介绍一种新的 HA 涂层制备方法，首先在 PEEK 基体上制备了 HA（质量分数 30%）/PEEK 复合层，然后采用 APS 技术在复合层上制备了厚度为 85 μm 的 HA 涂层，力学性能测试表明，该涂层的结合强度为 (20.9±2.1) MPa，远远高于以往的研究。

涂层的制备工艺影响涂层的力学性能，通过改善等离子喷涂工艺参数以适应聚醚醚酮基材，涂层的机械性能逐渐得到改善。Wu 等[35]研究了等离子体功率、喷涂距离、气体流量和送粉速率等 APS 喷涂参数对 HA 粉末表面温度和飞行速率的影响，研究表明，随着载气中氩气含量的增加以及喷涂电流的增加，HA 粒子的飞行速率增大。随着送粉速率和喷涂距离的增加，HA 粒子的飞行速率减小。Zappini 等[36]以 CFR–PEEK 为基体，分别通过 APS 和 VPS 技术研制了从低厚度/低孔隙率到高厚度/高孔隙率的 3 种钛涂层，如图 2 所示。并对 3 种涂层的力学性能进行了评估，结果表明，3 种涂层的结合强度均高于 30 MPa。Suska 等[37]通过使用更小的粉末颗粒尺寸（黏结层为 15~45 μm Ti 粉末，顶层为 15~50 μm 的 HA 粉末）和更长的等离子喷涂距离，对应用于钛合金基底的商业 VPS 工艺进行了改进。测量双层 200 μm 涂层的结合强度为（28.5±2.3）MPa。Ca/P 和结晶度分别为 1.67 和 58.7%。Vogel 等[38]分别采用平均粒度为 90 μm 和 180 μm 的 Ti 粉末制备了两种不同的 VPS–Ti 涂层。较小的粒度导致较低的表面粗糙度和较低的结合强度（细 Ti：*Ra* = 30.2 μm，结合强度为 30.3 MPa；粗 Ti：*Ra* = 64.1 μm，结合强度为 37.8 MPa），但涂层分布更均匀，孔隙率更高（细 Ti 33.3%，粗 Ti 30%）。

钛作为一种高活泼性金属，在等离子喷涂过程中，气体吸附到颗粒上会发生氧化、氮化以及相变，其化学成分会发生变化。因此，通过对喷涂参数的精心优化和喷涂粒子的适当选择，可以获得多种不同特性的等离子喷涂 Ti 涂层，图 3 显示了成功用于钛合

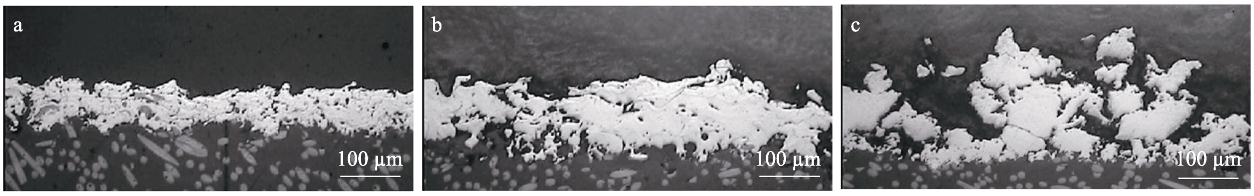
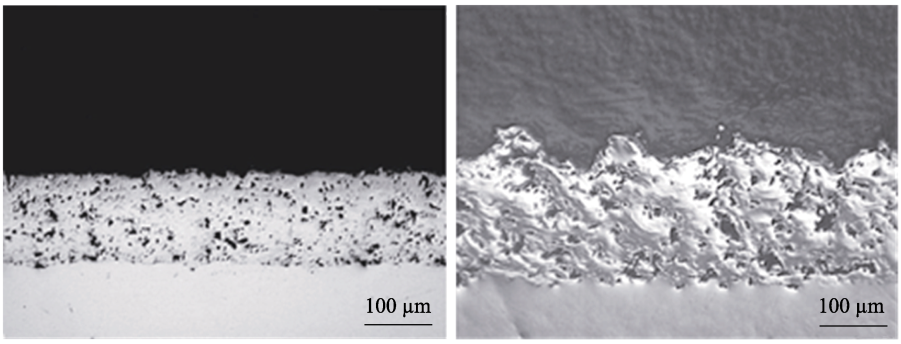
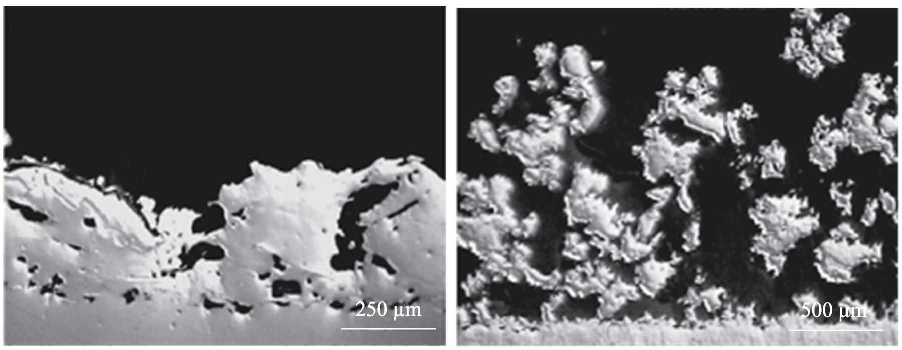


图 2　（a）低厚度/低孔隙率钛涂层，（b）中等厚度/中等孔隙率钛涂层，（c）高厚度/高孔隙率钛涂层[36]
Fig.2 Low thickness/low porosity Ti-coating (a), medium thickness/medium porosity Ti-coating (b), high thickness/high porosity Ti-coating (c)[36]

金或钴铬合金金属植入体的不同钛涂层[21]。一般情况下，与 APS 工艺相比，VPS 工艺等离子体的焰流的直径和长度更大，气体流速更快。这导致涂层具有高密度、低氧化物含量以及高结合强度[39]。此外，表面预处理同样也是影响涂层与基材结合强度的关键因素之一。喷砂作为一种廉价、简单且快速的技术，已经被广泛应用于这一目的。喷砂因素如磨料颗粒的类型、硬度和尺寸、工艺压力和时间等必须考虑在内，且需根据不同的基材仔细调整。而对于 HA 涂层，其较差的力学性能阻碍了HA作为高应力区域的大块材料的使用。将生物活性 HA 涂层和机械强度高的金属结合是成功制造承重外科植入物的关键。在获得 HA 涂层的不同方法中，等离子喷涂仍然被认为是成本/效益最高的工艺技术。HA 涂层的重要属性如相组成、结晶度、微观结构性能和结合强度取决于等离子喷涂过程的各种参数，这些特性显著影响着涂层的机械强度、化学稳定性以及植入后的生物反应。对金属基植入体 HA 涂层的研究表明，电弧功率越大，气体流量越大，粉末尺寸越小，涂层组织越均匀，孔隙率越低。较低的等离子体功率以及气体流量和较大的粉末尺寸会导致涂层微观结构的不均匀性和多孔性。当喷涂距离增大到一定值时，涂层均匀性增大，随着喷涂距离增大，均匀性减小[40]。对于 PEEK 基植入物，与金属基板相比，其熔化和分解温度较低，建议使用较小的粉末颗粒尺寸和较长的喷涂距离。此外，HA 在等离子喷涂过程中同样也会发生化学变化和相变化，羟基磷灰石在高温（超过 1 350 ℃）下是不稳定的、部分 HA 会分解成磷酸三钙（TCP）、磷酸四钙（TTCP）和非晶相等杂质。由于这些杂质比 HA 的溶解度高得多，降解快，使得涂层在载荷和人体体液腐蚀的共同作用下变得不稳定，导致涂层早期溶解，从而降低涂层与基底之间的结合强度。就涂层与骨的结合来看，涂层溶解和降解造成 Ca、P 局部浓度相对较高，却能与骨细胞的蛋白质分子相互作用，并刺激骨生



a 低粗糙度APS钛涂层　　b 高粗糙度APS钛涂层



c 高孔隙率SPS钛涂层　　d 海绵状VPS钛涂层

图 3　不同喷涂工艺下的等离子喷涂钛涂层[21]
Fig.3 Examples of different Ti coatings obtained with plasma spray technologies[21]:
a) low-roughness APS coating; b) high-roughness APS coating;
c) high-porosity SPS coating; d) sponge-like VPS coating

长，使植入体与骨形成化学和生物结合。因此，适量的溶解和降解是必须的，重要的是应避免涂层过早的溶解而减弱涂层与基底的牢固结合，即需控制涂层中 HA 的含量。

2.2　等离子喷涂工艺对 PEEK 基体初始性能影响的研究

等离子喷涂工艺涂覆聚醚醚酮植入物时，调整等离子喷涂工艺参数以提高涂层附着力或优化粗糙度以及孔隙率可能会对 PEEK 基底特性产生负面影响。聚醚醚酮基体的机械性能和化学性能在涂覆过程后应保持不变或至少应保持在一定的安全限值内，因此，那些可能受涂层工艺影响的 PEEK 的性能如机械强度、疲劳强度、热性能和化学降解得到了研究者的广泛关注，以期实现保障 PEEK 自身优异性能的前提下，提高其骨整合性能。

Beauvais 等[32]对喷涂前后 PEEK 基体的拉伸强度、冲击强度、拉伸伸长率和弯曲强度进行了测量。结果表明，涂覆 HA 涂层导致 PEEK 拉伸强度、冲击强度、弯曲强度值略有提高。而拉伸伸长率变从 32%降至 15%。等离子体产生大量紫外线等辐射，聚醚醚酮拉伸伸长率的降低可以用紫外线照射来解释。Oliveira 等[41]通过 APS 工艺在聚醚醚酮表面涂覆了 HA 涂层，研究了等离子喷涂过程对 PEEK 疲劳性能和拉伸性能的影响。三点弯曲试验和拉伸试验表明，等离子喷涂过程对 PEEK 材料的拉伸强度没有明显的影响，材料的弯曲强度和疲劳应力衰减率略有提高。Vogel 等[38]采用了 VPS 工艺在聚醚醚酮表面涂覆了 Ti 涂层。试验结果表明，涂层工艺对 PEEK 材料的弯曲模量、5%弯曲应变时的弯曲应力和断裂应变并没有显著影响。试样的拉伸强度、物理化学性能没有发生改变。Sargın 等[42]对聚醚醚酮喷涂前后进行了红外光谱分析（FTIR），如图 4 所示，以评估等离子喷涂工艺对聚醚醚酮化学结构和官能团的变化。结果显示，聚醚醚酮聚合物在涂覆期间或之后没有发生任何化学变化。

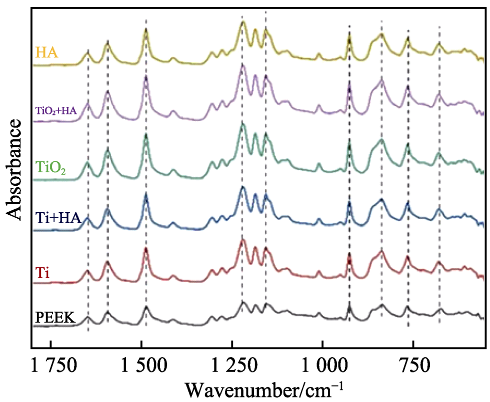


图 4　聚醚醚酮表面涂层和聚醚醚酮样品的红外光谱比较[42]

Fig.4 Comparison of the FTIR spectra of coated and uncoated PEEK samples[42]

在 PEEK 基上涂覆等离子喷涂涂层需要考虑的重要方面是它在紫外线照射下的化学降解。由于紫外线的吸收，芳香族醚键处的聚合物链可能会发生断裂而产生羟基（—OH）和酯基（O—C═O），造成 PEEK 机械性能的损失和变色。因此，还必须规范涂层工艺，最大限度地减少 PEEK 基材暴露的紫外线辐射[43-45]。

2.3　PEEK 基等离子喷涂涂层体外生物性能研究

植入物表面涂层的体外生物性能测试是评估制备涂层生物活性的主要手段，体外生物性能的结果也是表面涂层改性植入物是否有效的主要依据。Yoon 等[46]将人骨髓间充质干细胞（hMSCs）以一定密度接种到不同表面粗糙度的等离子喷涂后的 PEEK–Ti 上。研究表明，表面形貌直接影响细胞黏附和增殖的能力。细胞要在粗糙的表面上生长，必须形成伪足并相互作用。如果细胞深陷在超粗糙表面的深孔中，它们就无法通过伪足形成相互作用，即表面粗糙度不能超过一定的范围。Barillas 等[47]使用二氧化钛（TiO_2）作为黏结层，采用 APS 制备了 HA–TiO_2–PEEK 复合材料，并对涂层的微观结构、物理化学性质以及稳定性进行了评估。将人成骨肉瘤细胞（MG63）种植到制备好的涂层上培养 1 h 后，细胞开始在涂层表面附着生长，体外生物试验表明，该涂层体现了良好的生物相容性与生物活性。Beard 等[48]通过测量不同基体促进骨相关基因表达的能力来评估基体与细胞之间的相互作用。将小鼠骨髓间充质干细胞（BM–MSCs）分别种植在 Ti、PEEK 以及 PEEK–Ti 基体上，采用两步 RT–qPCR 分析碱性磷酸酶（AlP）、骨钙素（OCN）、RUNX2 等骨形成标志物的基因表达。试验结果表明，与 Ti、PEEK 基体相比，PEEK-Ti 在 14 d 内显示出更高的成骨基因表达和细胞存活率。Sargın 等[43]采用大气等离子喷涂在 PEEK 基体上分别喷涂了 Ti、Ti–HA、TiO_2–HA 涂层。在模拟体液（SBF）中进行的体外实验表明，HA、Ti–HA 和 TiO_2–HA 涂层均具有良好的生物活性。

骨植入体植入后会形成促进骨生长的表面，这一过程始于骨祖细胞附着在植入体表面会沉积一层富钙、无胶原的界面层。它为分化后的骨祖细胞生成胶原骨基质提供了基础。Hickey 等[49]为了探究界面层的沉积条件，将人转染成骨细胞（hFOB 1.19）种植在 PEEK–Ti、未改性 PEEK 和 Ti–6Al–4V 基体的表面，比较了不同基体表面界面层的沉积情况。PEEK–Ti 粗糙表面为细胞增殖提供了更大的接触面积，仅细胞培养 24 h 后，PEEK–Ti 表面所测得的钙沉积量分别比未改性 Ti–6Al–4V 和 PEEK 高出 305%和 470%，如图 5 所示。碱性磷酸酶的缺乏则证实了细胞仍未分化。这些试验结果表明 PEEK-Ti 表面可以通过刺激未

分化的骨祖细胞加速富钙界面的形成从而促进骨生长，这与普遍认为只有成熟的成骨细胞沉积钙的观点相反。后续需要更多的研究来阐明其作用机制。表 1 总结了近几年聚醚醚酮植入物上等离子喷涂生物涂层的体外生物性能的研究。

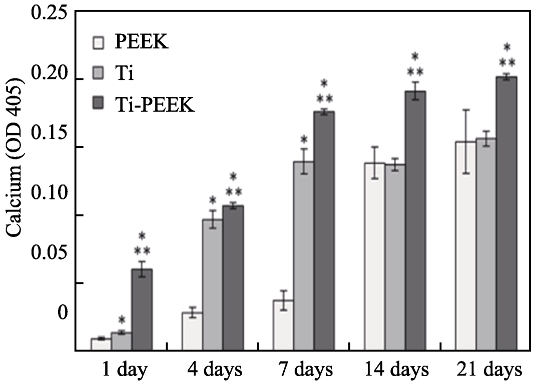


图 5　不同基体表面 hFOB 1.19 细胞钙相对沉积量[49]
Fig.5 The relative amount of calcium deposited from hFOB1.19 cells grown on different substrates[49]

2.4　PEEK 基等离子喷涂涂层体内生物性能研究

在聚醚醚酮基底上成功制备具有足够机械性能的钛和羟基磷灰石涂层后体外细胞实验，研究者倾向于关注这些涂层的体内行为。Devine 等[50]分别采用真空等离子喷涂（VPS）和物理气相沉积（PVD）2 种不同的技术在 CF/PEEK 螺钉上分别涂覆了 Ti 涂层。与 PVD 制备的钛涂层螺钉相比，VPS 制备的钛涂层螺钉具有更高的去除扭矩和直接骨接触。Suska 等[37]采用 VPS 在 CFR-PEEK 基板上涂覆了 HA/Ti 复合涂层，经过清洁与消毒后植入 11 只成年雌性新西兰白兔中。植入 6 周后，对手术部位进行组织学研究，发现 HA/Ti 包覆的 CFR–PEEK 植入物与 HA 涂覆的钛合金植入物具有同等的骨结合性，后者被普遍接受为工业标准。Walsh 等[51]研究了等离子喷涂 Ti 涂层的 PEEK 材料对骨/植入体界面的力学和组织学性能的影响。利用建立好的绵羊模型，成功在 4 只绵羊的股骨远端和胫骨近端移入了涂覆 Ti 涂层的 PEEK 植入体。体内试验表明，植入 4 周后，与未改性的 PEEK 相比，多孔钛涂层提高了骨/植入体界面的剪切强度，并且随着时间的推移剪切强度持续升高，组织学检查显示等离子喷涂的 Ti 涂层可以实现骨与植入体的直接结合。随后 Walsh 等[52]继续对等离子喷涂 HA 涂层的 PEEK 材料进行了绵羊体内研究。试验结果表明，与纯 PEEK 植入体相比，PEEK–HA 植入体在颈椎融合模型试验中能够改善骨生长和融合效果，如图 6 所示。Stübinger 等[53]比较了不同等离子喷涂涂层（APS–Ti、VPS–Ti、VPS–Ti 黏接层+APS–HA 表层）对 PEEK 和 CFR–PEEK 植入体的体内行为。将 108 根聚醚醚酮棒植入 6 只绵羊的骨盆中，分别在 2 周和 12 周后对手术部位进行组织学检查并进行拔出试验测试。与未涂层的植入物相比，等离子喷涂后的植入体在骨结合方面有显著改善，且 12 周后显示出更高的拔出值（$P<0.001$）。其中双层涂层（钛结合层和羟基磷灰石表层）在 2 周和 12 周后显示出最优异的结果。他们得出结论，等离子喷涂钛和羟基磷灰石涂层对骨结合有显著的改善作用。Sclafani 等[54]对 44 名在接受前路腰椎体间融合术（ALIF）中移入 VPS–Ti–PEEK 植入体的患者进行了术后随访。随访入体上的

表 1　等离子喷涂 PEEK 植入体的体外生物活性研究总结
Tab.1 A summary of bioactivity on plasma-sprayed PEEK implants in vitro

Composites	Method	Results	Bioactive evaluation	Ref.
PEEK-Ti	hMSCs cells were seeded onto PEEK-Ti at an initial density of 2.5×10^4 cells/cm^2	hMSCs tended to form stronger adhesion and greater pseudopodia extensions on finer rougher roughness surfaces	The morphology of rough titanium surface directly affects cell adhesion and bone growth	[46]
PEEK-TiO_2-HA	MG63 cells were cultivated for 1 h on coating	Cells adhered and started to grow on the TiO_2-HA surfaces, maintaining good cellular morphology	Show the clinical potential of the presented bioactive coatings and polymers	[47]
PEEK-Ti	Coatings were seeded with BM-MSCs at a density of 5.6×10^3 cells/cm^2	PEEK-Ti exhibited higher cell count and markers of osteogenesis (ALP, OCN,VEGF, and RUNX2)	Future research is needed in animal models to evaluate the osteointegration potential of PEEK-Ti in vivo	[48]
PEEK-Ti、PEEK-HA、PEEK-TiO_2-HA	all samples were immersed in SBF for 21 days	bone-like apatite formation in the samples which have HA layer on the surface	Ca and P elements in the HA coated samples first dissolved in SBF environment and then precipitated back to the surface by forming bone-like apatite.	[42]
PEEK-Ti	hFOB cells were seeded onto coating at a density of 2.5×10^4 cells/cm^2	undifferentiated osteoprogenitor cells deposited calcium before they differentiate into mature osteoblasts	Contrary to popular view that only mature osteoblasts deposit calcium. More investigation is needed to elucidate the mechanism of action.	[49]

VPS–Ti 涂层为骨-植入体界面提供了快速而稳定的固定，显著改善了术后患者的临床结果。

通过动物体内试验，Ti 涂层以及 HA 涂层脊柱植入物的临床试验也取得了良好的结果，但需要进一步的临床试验来证明涂层的长期稳定性。聚醚醚酮植入物上等离子喷涂生物涂层的体内生物性能的研究总结见表 2。

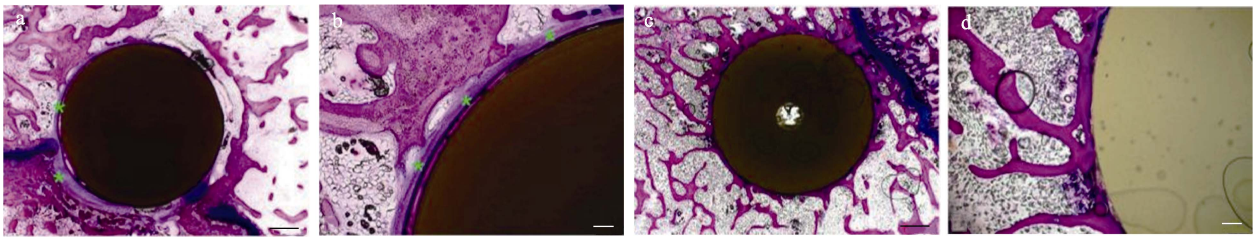


图 6　植入 12 周后 PEEK(a,c)和 PEEK–HA(b,d)分别在松质骨部位骨生长[52]

Fig.6 12 weeks after implantation，PEEK(a,c) and PEEK-HA(b,d) showed bone growth at the cancellous bone site, respectively, indicating that PEEK presented a fibrous tissue interface, while PEEK-HA could observe a bone-implant interface in direct contact[52]

表 2　聚醚醚酮植入物上等离子喷涂生物涂层的体内生物性能研究总结

Tab.2 A summary of bioactivity on plasma-sprayed biological coating PEEK implants in vivo

Composites	Method	Results	Bioactive evaluation	Ref.
PEEK-Ti	VPS-coated and PVD-coated CFR-PEEK screws were placed in a sheep tibia.	The removal torque of the VPS-coated screws was significantly higher than that of uncoated screws and PVD-coated screws	VPS-coated coating successfully modified the bone-implant interface and significantly improved the quantity and quality of bone growth	[50]
PEEK-Ti-HA	The study was conducted in a rabbit model, both in femur trabecular bone as well as in tibia cortical bone.	HA-coated PEEK implants stimulated higher bone formation and a better direct bone contact than uncoated PEEK	HA-Ti coated PEEK implants can be equally ossoeintegrated as the industrial standard HA-coated titanium alloy implants.	[37]
PEEK-Ti	Ti-coated PEEK implants were placed in cortical bone and cancellous bone of adult sheep	Ti-coated PEEK significantly improved the shear strength at the bone-implant interface at 4 weeks and continued to improve with time compared with PEEK	The Ti-coated coating improved mechanical properties in the cortical parts and the histology in cortical and cancellous parts.	[51]
PEEK-HA	HA-coated PEEK implants were placed in cortical bone and cancellous bone of adult sheep at 4 and 12 weeks as well as interbody cervical fusion at 6, 12, and 26 weeks.	A better direct bone contact was reported for HA-coated PEEK compared to uncoated samples in histological examination.	HA-Ti coated PEEK provides a more favorable environment than PEEK alone for bone ongrowth. HA-coated PEEK improved Cervical fusion compared with PEEK alone as well as allograft bone interbody devices.	[52]
PEEK-Ti PEEK-Ti-HA	In six sheep, 108 implants were placed in the pelvis.	After 12 weeks, coated implants demonstrated higher pull-out values in comparison to uncoated implants. The double coating showed the most favorable results after 2 and 12 weeks.	Plasma-sprayed titanium and hydroxyapatite coatings on PEEK or CFR-PEEK demonstrated a significant improvement of osseointegration.	[53]
PEEK-Ti	Post-surgical follow-up of 44 patients that received a VPS-Ti coated PEEK ALIF implant.	Coated implants exhibited a clinically significant improvement in post-operative pain. Successful arthrodesis with a solid fusion rate of 96 % at an average of (7.3 ± 2.3) months was observed.	VPS-Ti coated PEEK implant provides rapid and stable fixation at the bone-implant interface, significantly improving pain outcomes, low implant subsidence and a high definitive rate of arthrodesis.	[54]

3 结论与展望

PEEK 作为一种有机热塑性聚合物，有着十分优异的生物相容性、化学稳定性、X 射线可穿透性以及与人体自然骨相匹配的力学性能。然而，PEEK 属于惰性材料，其表面生物活性较低，骨整合能力欠佳。等离子喷涂作为重要的表面涂层改性技术，应用在 PEEK 材料上的力学和生物学研究已经有 30 年历史。研究者们分别对等离子喷涂 PEEK 基涂层机械性能以及体内外生物性能进行了研究，并对等离子喷涂工艺对 PEEK 基体的初始性能影响进行了探索。

在制备 PEEK 基生物涂层的等离子喷涂工艺中，APS 是最具成本效益的方法，有会议论文报道，符合国际标准的生物相容性 Ti 和 HA 涂层都可以用 APS 在 PEEK 基材上生产，目前，国际期刊上没有同行评议的文章报告其结合强度超过标准中规定的下限。另一方面，与 APS 相比，VPS 具有更高的纯度和结合强度，且调控喷涂参数可以实现不同厚度、孔隙率、粗糙度等要求的涂层制备。但工艺成本较高，耗时较长。为了提高 APS 涂层在 PEEK 植入体上的性能，未来可采用悬浮液等离子喷涂或遮蔽式等离子喷涂等方法代替。在悬浮液等离子喷涂法中，通过液体载体将细粉末注入等离子体中，较低的喷涂温度以及较高的粒子飞行速度提供了较高的结晶度以及结合强度。此外，用这种方法能够用细粉末生产非常薄的涂层。在遮蔽式等离子喷涂方法中，使用气体或固体屏蔽来防止喷涂的粒子与周围空气中的氧气接触。因此，在不使用真空室的情况下，依旧可以得到较低氧化物含量和较高纯度的涂层，从而获得较好的机械性能。

从目前仅有的文献来看，等离子喷涂工艺应用在 PEEK 基涂层主要是 HA 以及 Ti 涂层为主，其他类型的生物涂层文献鲜有报道。研究主要集中在涂层的机械性能以及涂层生物活性方面。而对涂层的机械性能研究主要体现在结合强度等方面，对于涂层的综合性能还缺乏系统的研究。如何调控喷涂工艺参数在保证基体初始性能的条件下制备具有优异综合性能的 PEEK 基生物涂层还需要进一步探索。此外，涂层的抗菌性能亦是植入体植入成功的关键因素之一，Ti 涂层属于生物惰性材料，自身不具备生物活性以及抗菌性能。而 HA 作为一种生物活性材料，其抗菌作用差、骨诱导能力弱等体内生物性能等问题限制了其在临床上的应用。采用等离子喷涂工艺制备 PEEK 基生物涂层的研究方兴未艾，随着研究的深入，未来应有更多的生物活性涂层被开发出来。制备兼具生物活性、抗菌性能以及优异机械性能的 PEEK 基等离子喷涂涂层是目前攻克的重要难题。

PEEK 植入体目前主要还处于研究阶段，尚未投入大规模临床生产，关于 PEEK 植入体生物学性能研究还仅局限于动物模型试验，PEEK 植入体能否替代传统观金属基植入体还需更长久的研究。

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（上接第 26 页）

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