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·生物材料专栏 基础研究·

硅烷化改性聚醚醚酮填料对光固化复合树脂理化性能的提升作用

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【摘要】　目的　探讨不同质量分数的硅烷化改性聚醚醚酮（KH-PEEK）填料对光固化复合树脂理化性能的影响，为优化光固化复合树脂的临床应用提供研究基础。**方法**　通过羟基化预处理在聚醚醚酮（PEEK）表面引入活性羟基，采用硅烷偶联剂γ甲基丙烯酰氧基丙基三甲氧基硅烷（KH-570）对其进行表面接枝改性，制备功能化KH-PEEK填料。在本研究体系中，树脂基质由双酚A-双甲基丙烯酸缩水甘油酯（Bis-GMA）与三乙二醇二甲基丙烯酸酯（TEGDMA）组成，树脂基质质量分数固定为40 %，填料总添加量质量分数恒定为60%。在填料中添加不同质量分数占比的KH-PEEK（0%、1%、3%、5%、7%、9%），各组填料的剩余占比由玻璃鳞片补足；将KH-PEEK与玻璃鳞片复配均匀后，再加入树脂基质中进行共混。另设置填料组分质量分数为5% 未改性PEEK与55 % 玻璃鳞片复配组成，树脂基质占比40% 不变的组别。其中1% KH-PEEK组、3% KH-PEEK组、5% KH-PEEK组、7% KH-PEEK组、9% KH-PEEK组为实验组，5% 未改性PEEK组、0% KH-PEEK组为对照组。各组填料与树脂基质共混均匀，按同一流程制备各组光固化复合树脂试件，进行各组理化性能检测。排水法测定体积收缩率；参照ISO 4049：2019标准检测吸水值与溶解值；利用傅里叶变换红外光谱法（FTIR）检测双键转化率；采用三点弯曲试验、维氏硬度测试获取试件老化前后的弯曲强度、弹性模量及表面硬度；通过扫描电镜观察弯曲强度试验后发生断裂的树脂断裂面微观形貌。CCK-8法评价细胞相容性。**结果**　5%KH-PEEK组的综合性能最优。相较于对照组，5个添加KH-PEEK的实验组的体积收缩率均显著降低（$P<0.05$）；相较于对照组，1%KH-PEEK组、3%KH-PEEK组、5%KH-PEEK组、7%KH-PEEK组的吸水值显著降低（$P<0.05$），3%KH-PEEK组、5%KH-PEEK组、7%KH-PEEK组、9%KH-PEEK·组的溶解值显著降低（$P<0.05$）。相较于对照组，5个添加KH-PEEK的实验组的双键转化率显著提高（$P<0.05$）；5%KH-PEEK·组初始弯曲强度、弹性模量及表面硬度较对照组显著提升（$P<0.05$）；且5%KH-PEEK组初始与老化后弯曲强度、弹性模量均显著高于其他实验组（$P<0.05$）。树脂断裂面扫描电镜结果显示，KH-PEEK与树脂基质界面结合紧密，未见明显缝隙；细胞相容性测试表明，各组L929细胞存活率均高于90%，无明显细胞毒性，组间差异无统计学意义（$P>0.05$）。**结论**　KH-PEEK可作为光固化复合树脂的一种良好的有机填料，以5%的质量分数添加时，能够通过构建“PEEK-硅烷-树脂”共价界面网络，协同提升光固化复合树脂的理化性能。

【关键词】　聚醚醚酮；　羟基化；　硅烷偶联剂；　光固化复合树脂；　力学性能；　有机填料；　耐水解性；　耐老化性能
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Enhancing effect of silanized polyetheretherketone fillers on the physicochemical properties of light-cured composite resins

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【Abstract】　Objective　This study aimed to investigate the effects of silanized modified polyetheretherketone (KH-

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PEEK) fillers at different mass fractions on the physicochemical properties of light-cured composite resins and to provide a research foundation for optimizing the clinical application of light-cured composite resins. **Methods** Hydroxylated pretreatment was performed to introduce active hydroxyl groups onto the surface of PEEK. Surface grafting modification was then carried out using the silane coupling agent γ-methacryloxypropyltrimethoxysilane (KH-570) to prepare functionalized KH-PEEK fillers. In this study system, the resin matrix consisted of bisphenol A diglycidyl methacrylate (Bis-GMA) and triethylene glycol dimethacrylate (TEGDMA), with the resin matrix mass fraction fixed at 40% and the total filler addition maintained at 60%. Different mass fractions of KH-PEEK (0%, 1%, 3%, 5%, 7%, and 9%) were added to the filler system, with the remaining filler proportion supplemented by glass flakes. After uniform mixing of KH-PEEK and glass flakes, the resin matrix was added for blending. An additional group was set up using 5% unmodified PEEK and 55% glass flakes as fillers, with the resin matrix proportion unchanged at 40%. The 1%, 3%, 5%, 7%, and 9% KH-PEEK groups were designated as experimental groups, while the 5% unmodified PEEK group and the 0% KH-PEEK group served as control groups. Filler and resin matrix were homogeneously blended in each group, and light-cured composite resin specimens were prepared following the same procedure for physicochemical property testing. The water displacement method was used to determine volumetric shrinkage. Water sorption and solubility were tested according to ISO 4049:2019. Fourier transform infrared spectroscopy (FTIR) was employed to measure the degree of double bond conversion. Three-point bending tests and Vickers hardness tests were conducted to obtain the flexural strength, elastic modulus, and surface hardness of specimens before and after aging. Scanning electron microscopy (SEM) was used to observe the microscopic morphology of resin fracture surfaces after flexural strength testing. Cytocompatibility was evaluated using the cell counting kit-8 assay. **Results** The 5% KH-PEEK group exhibited the optimal overall performance. Compared with the control group, the volume shrinkage of all five experimental groups with KH-PEEK addition was significantly reduced ($P < 0.05$). Additionally, the water sorption values of the 1%, 3%, 5%, and 7% KH-PEEK groups were significantly lower than those of the control group ($P < 0.05$), while the solubility values of the 3%, 5%, 7%, and 9% KH-PEEK groups were also significantly decreased ($P < 0.05$). Furthermore, compared to the control group, the other five experimental groups with KH-PEEK addition demonstrated significantly increased double bond conversion ($P < 0.05$). The 5% KH-PEEK group demonstrated significantly higher initial flexural strength, elastic modulus, and surface hardness than the control group ($P < 0.05$). Notably, both the initial and aged flexural strength and elastic modulus of the 5% KH-PEEK group were significantly higher than those of the other experimental groups ($P < 0.05$). SEM images of the resin fracture surfaces revealed tight interfacial bonding between KH-PEEK and the resin matrix, with no obvious gaps observed. Cytocompatibility tests indicated that the survival rate of L929 cells in all groups was above 90%, showing no obvious cytotoxicity, and the intergroup differences were not statistically significant ($P > 0.05$). **Conclusion** KH-PEEK can serve as an excellent organic filler in the light-cured composite resins. When added at a mass fraction of 5%, it can synergistically enhance the physicochemical properties of light-cured composite resins.

【Key words】 polyetheretherketone; hydroxylation; silane coupling agent; light-cured composite resin; mechanical properties; organic fillers; hydrolytic resistance; aging resistance
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光固化复合树脂因具有良好的机械性能和临床操作性，目前是龋病充填治疗的主要材料。然而临床调查显示，光固化复合树脂充填体断裂仍是导致充填失败的主要原因之一。当前常用的商品化复合树脂在光引发剂作用下，单体通过碳碳双键聚合形成高度交联的聚合物网络结构[1]，无机填料包埋于其中，赋予材料良好的机械性能。但无机填料易发生填料-树脂界面脱粘等问题，而各类功能性填料则普遍存在分散性不佳[2-3]、亲水性较强或长期生物安全性不确定[4]等短板。同时，口腔复杂环境下，修复体持续承受咀嚼载荷，还会受到酸碱刺激、温度循环等因素的共同作用，树脂基体易发生水解降解，进而造成材料力学性能逐步衰减[5-7]。因此，开发兼具良好力学性能与长期稳定性等性能的新型复合填料，是目前牙科复合树脂领域研究的重点。

笔者所在课题组前期将二维片状玻璃鳞片引入牙科光固化复合树脂体系，通过氢氟酸蚀刻在

玻璃鳞片表面构建微粗糙结构，再经硅烷偶联剂KH-570接枝，引入可参与聚合的碳碳双键，使玻璃鳞片与树脂基体形成共价键合界面；玻璃鳞片可借助“迷宫效应”延长水分子扩散路径，有效提升牙科复合树脂的耐水解性能，同时改善材料力学性能与抗老化能力；但该填料存在硅烷接枝不完全，易造成无机填料与有机树脂基体界面结合力不足，进而引发界面脱粘，削弱材料的整体耐久性能[8-9]。

聚醚醚酮（polyetheretherketone，PEEK）是一种半结晶性的高性能热塑性特种工程塑料，属于有机高分子材料。在生物医学领域，PEEK展现出独特的应用优势[10-11]。其力学强度高、耐疲劳性好，能够承受长期的循环载荷[12-14]，具有优异的生物相容性与辐射透过性[15]，尤为重要的是，其弹性模量约3~4 GPa，与人体皮质骨相近，能够促进骨整合[16]。基于这些特性，PEEK已成功应用于骨科植入物、颅颌面修复体[17]及可摘局部义齿的框架制作[18]。然而，当PEEK作为增强相被引入牙科复合树脂体系时，其固有的低表面能和高化学惰性成为了不利因素[19-21]。光滑且非极性的PEEK表面与极性树脂单体之间的润湿性差，相容性不佳[22]，导致两者界面主要依靠微弱的范德华力或机械嵌合作用结合。因此，对PEEK填料进行有效的表面改性，以构建牢固的化学结合界面，是发挥其增强能力、制备高性能复合树脂材料的关键前提。但现有PEEK表面改性手段仍存在诸多局限，相关界面调控难题尚未得到妥善解决。

本研究在前期对玻璃鳞片硅烷化改性的基础上，进一步在填料中复配硅烷化改性聚醚醚酮，探讨其对光固化复合树脂理化性能的提升作用。针对PEEK的改性，本研究采用两步法策略：先通过羟基化处理在表面引入活性羟基[23]，再通过硅烷偶联剂KH-570实现PEEK填料与树脂基质的化学共价结合。

本研究旨在验证该两步改性策略的可行性，探究不同质量分数的硅烷化改性聚醚醚酮填料对光固化复合树脂理化性能的影响，筛选最优填料配比，通过强化填料-基质界面结合，改善树脂力学强度与长期稳定性，为高性能牙科光固化复合树脂的开发提供实验依据与理论参考。

1　材料和方法

1.1　主要材料

双酚A-双甲基丙烯酸缩水甘油酯（bisphenol-A-glycidyl methacrylate，Bis-GMA）（纯度99%），三乙二醇二甲基丙烯酸酯（triethylene glycol dimethacrylate，TEGDMA）（纯度95%），樟脑醌（camphorquinone，CQ）（纯度97%）（Sigma-Aldrich，美国），4-二甲氨基苯甲酸乙酯（Ethyl 4-（dimethylamino）benzoate，EDMAB），细胞计数试剂盒8（cell counting kit-8，CCK8）（Beyotime，中国），PEEK（30~50 um，威格斯，英国），二甲基亚砜（dimethyl sulfoxide，DMSO）（阿拉丁，中国），玻璃鳞片（50~80 μm，金川玻璃制品有限公司），KH570（阿拉丁，中国），胎牛血清（Gibco，美国），胰蛋白酶（Hyclone，美国），DMEM培养基（Gibco，美国）。

1.2　主要仪器

万能试验机（AG-Xplus10KN，Shimadzu，日本）；电子数显天平；维氏硬度仪（HMV-G20，Shimadzu，日本）；LED可见光固化灯（SLC-Ⅷ A，中国）；数显千分尺（桂林测量刀具有限公司，中国）；鼓风干燥箱（上海姚氏仪器设备厂，中国）；傅里叶变换红外光谱仪（fourier transform infrared spectroscopy，FTIR）（VERTEX-80V，Bruker，德国）；96孔细胞培养板和6孔细胞培养板（Corning，美国）；恒温培养箱（Thermo Fisher Scientific，美国）。冷场发射扫描电子显微镜（scanning electron microscope，SEM）（Hitachi S-4800，Hitachi，日本）；口腔热循环仪（PTC2c，Proto-Tech，USA）。

1.3　PEEK表面改性

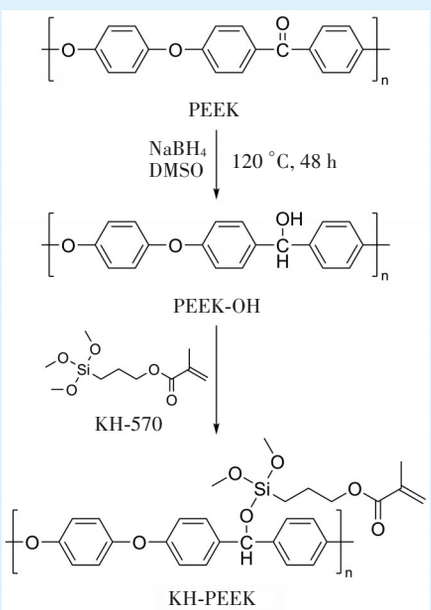
PEEK羟基化改性：将10 g PEEK置于真空干燥箱中，120 ℃干燥4 h以彻底去除水分。随后，将干燥后的PEEK分批次缓慢加入到装有120 mL无水二甲基亚砜（DMSO）和1.5 g无水硼氢化钠（$NaBH_4$）的三颈烧瓶中。反应体系在120 ℃油浴、机械搅拌、氮气保护及冷凝回流条件下持续反应24 h。反应结束后，待体系冷却至室温，对产物进行抽滤，并依次用甲醇、乙醇和去离子水交替洗涤，以除去未反应的原料及副产物。所得固体在80 ℃下干燥24 h，得到羟基化PEEK（hydroxylated polyetheretherketone，PEEK-OH）。

PEEK-OH硅烷化：将PEEK-OH分散于100 mL环己烷中，依次加入1.1 mL KH-570与0.51 mL正丙胺。混合体系经超声处理10 min使其充分分散，随后在室温下高速搅拌30 min。将反应瓶转移至60 ℃油浴中，继续在搅拌下反应30 min，使KH-570的硅氧烷基与PEEK-OH表面的羟基发生偶联反应。反应结束后，将混合物在60 ℃下旋转蒸发，除

去环己烷及低沸点副产物。随后将温度升至95 ℃,继续旋蒸45 min,以彻底去除残余的硅烷低聚物及挥发性组分。所得固体产物置于80 ℃烘箱中干燥24 h,最终得到表面接枝有可聚合双键(C=C)的PEEK,记为硅烷化改性聚醚醚酮(KH-570 silane-modified polyetheretherketone,KH-PEEK)。采用FTIR对PEEK、PEEK-OH、KH-PEEK样品表面官能团进行表征。其合成路线如图1所示。

1.4　玻璃鳞片表面改性

为了提升玻璃鳞片与有机树脂基体之间的界面相容性,采用硅烷偶联剂KH-570对其进行表面改性。通过在其表面接枝可聚合双键,旨在增强填料与树脂的化学结合,从而提高复合材料的综合性能。



$NaBH_4$: sodium borohydride. DMSO: dimethyl sulfoxide. PEEK: polyetheretherketone. PEEK-OH: hydroxylated polyetheretherketone. KH-PEEK: KH-570 silane-modified polyetheretherketone

Figure 1　Synthesis route of KH-PEEK

图1　KH-PEEK的合成路线图

将研磨后的玻璃鳞片置于氢氟酸溶液中搅拌处理8 h,随后以5 000 r/min离心,弃去上清液,收集下层白色沉淀。用适量饱和碳酸氢钠溶液对沉淀进行碱洗,以中和残余氢氟酸。再经去离子水反复洗涤、离心3次,直至水相呈中性。所得固体在100 ℃下干燥48 h,得到活化的玻璃鳞片,备用。

取13.6 g上述干燥玻璃鳞片与250 mL甲苯加入500 mL反应瓶中,于90 ℃油浴中机械搅拌。另将54.4 g KH-570与11.8 g水(物质的量比约1∶3)置于100 mL锥形瓶中,滴加冰醋酸调节pH至约4,室温搅拌30 min,制得KH-570水解液。将该水解液缓慢滴加至上述甲苯悬浮液中,继续反应24 h。反应结束后抽滤,依次用甲苯和乙醇交替洗涤产物,以除去未反应的硅烷及其副产物。最终产物在80 ℃下干燥48 h,得到KH-570表面修饰的玻璃鳞片,备用。采用FTIR对玻璃鳞片和改性后的玻璃鳞片样品表面官能团进行表征。

1.5　KH-PEEK填料光固化复合树脂的制备

CQ和EDMAB为光引发体系,Bis-GMA和TEGDMA单体的质量比为6∶4,在避光条件下搅拌4 h,得到均匀的光固化树脂基质,避光保存备用。本实验共设置2个对照组:5%未改性PEEK组、0%KH-PEEK组和5个实验组(1%KH-PEEK组、3%KH-PEEK组、5%KH-PEEK组、7%KH-PEEK组、9%KH-PEEK组),具体填料组成成分详见表1。使用真空搅拌机在1 500 r下搅拌120 s后,使用三辊研磨机将填料与基质充分混合,得到光固化复合树脂于避光环境中静置保存。

表1　各组KH-PEEK填料光固化复合树脂组成

Table 1　Compositions of light-cured resin composites filled with KH-PEEK particles in various groups　wt%

Group	KH-PEEK	Glass flakes	Unmodified PEEK	Bis-GMA/TEGDMA (6:4)	CQ/EDMAB (1:1)
0%KH-PEEK	0%	60%	0%	38%	2%
1%KH-PEEK	1%	59%	0%	38%	2%
3%KH-PEEK	3%	57%	0%	38%	2%
5%KH-PEEK	5%	55%	0%	38%	2%
7%KH-PEEK	7%	53%	0%	38%	2%
9%KH-PEEK	9%	51%	0%	38%	2%
5%Unmodified PEEK	0%	55%	5%	38%	2%

PEEK: polyetheretherketone. KH-PEEK: KH-570 silane-modified polyetheretherketone. Bis-GMA: bisphenol-A-glycidyl methacrylate.TEGDMA: triethylene glycol dimethacrylate. CQ: camphorquinone. EDMAB: Ethyl-4-(dimethylamino) benzoate

1.6　KH-PEEK填料光固化复合树脂的理化性能检测

1.6.1　KH-PEEK填料光固化复合树脂体积收缩率检测　于恒定温度环境下，设置共计7组树脂进行检测，根据预实验结果设置每组5个平行样本。通过检测光固化复合树脂固化前后的密度差异，计算得到各组试样的体积收缩率（volumetric shrinkage，VS）。采用比重法测定树脂固化前密度：选用5 mL规格比重瓶，先通过电子分析天平称量空瓶质量，记为m_1；再向瓶中注满蒸馏水后称量，记为m_2；向瓶中紧密注满未固化树脂并称量，记作m_3。计算公式：固化前密度$\rho_{uncured}=[(m_3-m_1)/(m_2-m_1)]\times\rho_{水}$，其中$\rho_{水}$为测量温度下水的密度。将树脂注入不锈钢模具（d=15 mm，h=1 mm）中进行固化。固化结束后，用酒精棉球清理表面。根据阿基米德原理，利用密度天平测定树脂固化后密度ρ_{cured}，计算VS。$VS=[(\rho_{cured}-\rho_{uncured})/\rho_{cured}]\times100\%$。

1.6.2　KH-PEEK填料光固化复合树脂吸水值与溶解值检测　制备直径15 mm、厚度1.0 mm的圆片状试件，设置共计7组树脂进行检测，根据预实验结果设置每组5个平行样本；按照ISO 4049：2019标准[24]采用可见光固化灯进行照射，圆形试件中心取1个点，周边8个点进行重叠照射以保证充分固化，照射距离为1 mm，单次光照固化时间设定为20 s，光照强度为1 000 mW/cm^2，对试件正反两面均按相同参数完成全区域固化。将试件置于37 ℃避光真空干燥器中干燥至质量恒定（变化≤0.01 mg），记录质量为m_1，并测量其体积V；随后将试件完全浸入37 ℃蒸馏水中7 d，取出吸干表面水分后立即称重得m_2；接着再次将试件放入37 ℃真空干燥器中干燥至质量恒定，记录最终质量为m_3。计算各树脂的吸水值和溶解值。吸水值/(μg·mm^3)=$(m_2-m_3)/V$，溶解值/(μg·mm^3)=$(m_1-m_3)/V$。

1.6.3　KH-PEEK填料光固化复合树脂双键转化率测试　采用配备衰减全反射附件的傅里叶变换红外光谱仪，对各组复合树脂的双键转化率（degree of conversion，DC）进行定量分析，设置共计7组树脂进行检测。实验中，所有试样的红外光谱均于光固化处理前后分别采集，测试参数设置为：分辨率4 cm^{-1}，扫描次数32次，波数范围4 000~400 cm^{-1}。测试流程如下：首先，利用压片机将溴化钾粉末制成透明圆片，作为光谱采集的背景基线；随后，将未固化的树脂试样均匀涂布于溴化钾片表面，立即采集固化前的红外光谱；接着，使用光固化灯对试样照射40 s，完成固化后再次采集光谱。根据固化前后树脂中C=C双键（特征吸收峰位于1 637 cm^{-1}）的吸收峰强度变化计算DC，以苯环大π键（特征吸收峰位于1 608 cm^{-1}）作为内标进行校正。DC值按规定公式计算，每组设置5个平行样品，取平均值作为最终结果。

$$DC(\%)=\left[1-\frac{(A_{1637}/A_{1608})_{cured}}{(A_{1637}/A_{1608})_{uncured}}\right]\times100\%$$

其中，A_{1637}和A_{1608}分别是C=C双键在1 637 cm^{-1}苯环大π键在1 608 cm^{-1}的吸光度峰面积；$(A_{1637}/A_{1608})_{uncured}$和$(A_{1637}/A_{1608})_{cured}$分别是光固化前后官能团的归一化吸光度。

1.6.4　KH-PEEK填料光固化复合树脂弯曲强度和弹性模量检测（老化前后）　根据ISO 4049：2019标准，为挠曲强度（flexural strength，FS）与弹性模量（elastic modulus，EM）测试准备试件（l = 25.0 mm，b = 2.0 mm，h = 2.0 mm），根据预实验结果设置共计7组树脂进行检测，每组5个平行样本。

将树脂混合料注入定制模具内，于模具上下表面分别覆盖聚乙烯薄膜，隔绝空气以避免氧气抑制光固化复合树脂的聚合反应。采用LED光固化灯自模具一端逐步进行光照固化，从左到右照射5个点，照射距离为1 mm，单次光照固化时间设定为20 s，光照强度为1 000 mW/cm^2，对试件正反两面均按相同参数完成全区域固化。结束后取出试件，打磨除去表面不规则的地方。将试件置于37 ℃蒸馏水中浸泡24 h后，采用万能试验机以恒定加载速度1 mm/min进行三点弯曲测试，直到试件断裂时计算出弯曲强度FS（单位：MPa）与弹性模量EM（单位：GPa）：$FS=3FL/2bh^2$，$EM=F_1L^3/4fbh^3$。F为试件断裂时记录的最大载荷（单位：N）；L为支座跨距，设定为20 mm；b和h分别为试件截面的宽度与高度。F_1表示某一特定载荷值（单位：N），f则为在该载荷F_1作用下试件所产生的挠度（单位：mm）。

将样本在口腔热循环仪（PTC2c，Proto-Tech，USA）中进行10 000次冷热循环处理，设定温度区间5 ℃~55 ℃，高低温停留时间各30 s，单次循环总时长60 s。冷热循环后，再次采用万能试验机对样本的弯曲强度和弹性模量进行检测。

1.6.5　KH-PEEK填料光固化复合树脂表面硬度检测（老化前后）　根据预实验，制作6 mm×2 mm的圆形树脂片（n=5），设置共计7组树脂进行检测，采用可见光固化灯进行照射，圆形试件中心取一

个点，周边8个点进行重叠照射以保证充分固化，照射距离为1 mm，单次光照固化时间设定为20 s，光照强度为1 000 mW/cm²，对试件正反两面均按相同参数完成全区域固化。将试件置于在37 ℃蒸馏水中浸泡24 h后采用维氏硬度仪进行测试。加载力设定为980 mN，加载时间设定为10 s，稳定后记录表面硬度值。每个试件随机选取3个不同区域进行测试，取算术平均值作为该试件的硬度值。将样本在口腔热循环仪中进行10 000次冷热循环处理，设定温度区间5～55 ℃，高低温停留时间各30 s，单次循环总时长60 s。冷热循环后，再次对样本的表面强度进行检测。每个样本在不同区域测量5次取平均值。

1.6.6　KH-PEEK填料光固化复合树脂试件断裂面电镜分析　采用Hitachi S-4800型冷场发射扫描电子显微镜，加速电压为3 kV。根据预实验，选取实验中具有代表性的待测样本分为3组：0%KH-PEEK组、5%KH-PEEK组和5%未改性PEEK组。每组5个平行样本。试样取自1.6.4弯曲强度试验后发生断裂的树脂试件。

将尺寸为2 mm × 2 mm的断裂面试样置于100 ℃烘箱中干燥24 h，取出后用氮气吹扫表面，随后进行喷金处理以增强导电性。将处理后的试样置于样本台上，通过扫描电子显微镜观察并记录各组的断裂面的形貌特征。

1.7　KH-PEEK填料光固化复合树脂细胞相容性评估

将7组光固化复合树脂制备成直径为15 mm、厚度为1 mm（表面积约为400 mm²）的圆形试件，经紫外线照射24 h后备用。按照试件表面积（cm²）与培养液体积（mL）之比为1.25∶1，在6孔板中加入含10%胎牛血清的DMEM培养液，将试件浸泡其中，置于37 ℃、5% CO_2培养箱中孵育72 h。取出浸提液，经0.22 μm微孔滤膜过滤，收集后于4 ℃冰箱保存备用。L929细胞在37 ℃、5% CO_2培养箱中常规培养，每2~3天传代1次，待细胞生长至对数期、覆盖培养瓶底面积约2/3时，用含10% FBS的DMEM培养液制备浓度为8 000个/mL的细胞悬液。将细胞悬液接种于96孔板，每孔200 μL，于37℃、5% CO_2培养箱中培养24 h，待细胞贴壁后吸弃原培养液。

1%KH-PEEK组、3%KH-PEEK组、5%KH-PEEK组、7%KH-PEEK组、9%KH-PEEK组、5%未改性PEEK组加入上述6组材料浸提液，0%KH-PEEK组加入新鲜DMEM培养液，空白组仅加DMEM培养液（无细胞），每组设5个复孔，每孔200 μL，继续培养24 h。

培养结束后，每孔加入CCK-8试剂，于培养箱中避光孵育2~4 h，使用酶标仪在450 nm波长处测定各孔吸光度值（OD）。按以下公式计算细胞相对增殖率（relative growth rate，RGR）。每组5个平行样品，每个样本检测3次取平均值。

$$RGR = (OD_{实验组} - OD_{空白组}) / (OD_{0\%KH\text{-}PEEK组} - OD_{空白组}) \times 100\%$$

参照细胞毒性分级标准对结果进行评价：RGR≥100%为0级或1级（合格）；75%～99%为1级（合格）；50%～74%为2级（轻度毒性，需结合细胞形态综合判断）；25%～49%为3级（中度毒性）；1%～24%为4级（重度毒性）；< 1%为5级（不合格）。3级及以上视为不合格。

1.8　统计学分析

使用Graphpad prism9统计软件进行统计学分析。n值代表每组样本数。采用Shapiro-Wilk检验进行各组数据正态性检验，满足正态分布后对各组光固化复合树脂吸水值、溶解值、双键转化率、细胞相对增殖率进行单因素方差分析。即刻和老化后弯曲强度、弹性模量、表面硬度进行双因素方差分析。所有组间数据比较进行Tukey′s检验，将显著性水平设置为α=0.05。

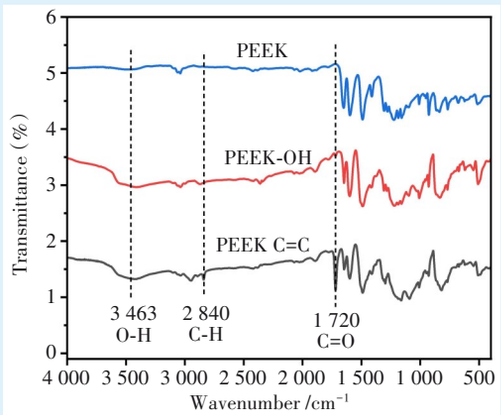
2　结　果

2.1　PEEK表面改性表征

PEEK、PEEK-OH、KH-PEEK样品FITR结果如图2所示，3 463 cm^{-1}处出现明显的羟基特征吸收峰，表明PEEK表面已成功引入羟基官能团。与纯PEEK及羟基化PEEK（PEEK-OH）相比，KH-PEEK在1 720 cm^{-1}附近出现了KH-570中羰基（C=O）的特征吸收峰，该峰对应甲基丙烯酸酯基团的酯羰基振动，直接证明了KH-570已成功接枝至PEEK表面；同时，KH-PEEK在2 840 cm^{-1}处的饱和C-H伸缩振动峰强度较PEEK-OH显著增强，进一步证实了硅烷偶联剂烷基链的引入，辅助验证了硅烷化改性的完成。

2.2　玻璃鳞片表面改性表征

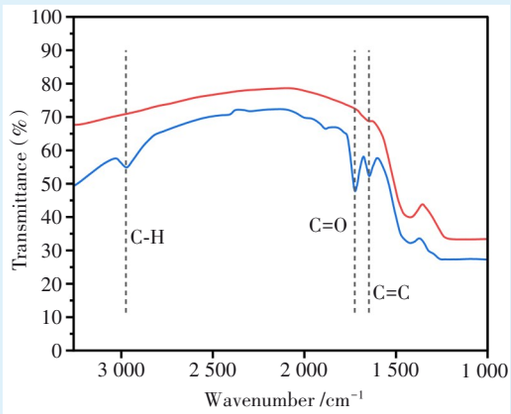
对于玻璃鳞片及KH-570改性玻璃鳞片的FITR结果如图3所示：改性玻璃鳞片在1 637 cm^{-1}、1 714 cm^{-1}和2 958 cm^{-1}处出现明显特征吸收峰，分别对应KH570分子中C=C键、C=O键和C-H键的



The stretching vibration peak of hydroxyl (O-H) is at 3 463 cm^{-1}. The increased peak intensity of PEEK-OH and KH-PEEK at this position indicates the successful introduction of hydroxyl groups by hydroxylation modification. The absorption peak at 2 840 cm^{-1} is assigned to methylene (C-H) stretching vibration, and the enhanced intensity of KH-PEEK further verifies the grafting of the silane coupling agent KH570. The characteristic peak at 1 720 cm^{-1} corresponds to the carbonyl group (C=O) of KH570, confirming the successful grafting of methacrylate groups onto the PEEK surface without damaging the main structure of PEEK. Individual spectra have been vertically offset to prevent overlapping and improve readability. PEEK: polyetheretherketone. PEEK-OH: hydroxylated polyetheretherketone. KH-PEEK: KH-570 silane-modified polyetheretherketone. FTIR: Fourier transform infrared spectroscopy

Figure 2　FTIR of PEEK, PEEK-OH, and KH-PEEK

图2　PEEK、PEEK-OH及KH-PEEK的傅里叶变换红外光谱图



The silanized modified glass flakes (blue curve) show obvious characteristic absorption peaks at 1 714 cm^{-1}, 1 637 cm^{-1} and 2 958 cm^{-1}, corresponding to the stretching vibrations of C=O, C=C, and C-H bonds, respectively. No such peaks are observed in the unmodified glass flakes (red curve), indicating that the silane coupling agent has been successfully grafted onto the surface of the glass flakes. FTIR: Fourier transform infrared spectroscopy

Figure 3　FTIR of the glass flakes and silanized glass flakes

图3　玻璃鳞片和硅烷化玻璃鳞片的傅里叶变换红外光谱图

伸缩振动;而上述特征峰在未改性玻璃鳞片的红外光谱中未检测到,证实KH-570已成功接枝于玻璃鳞片表面。

2.3　KH-PEEK填料光固化复合树脂的理化性能

2.3.1　KH-PEEK填料光固化复合树脂的体积收缩率　与0%KH-PEEK组相比,1%KH-PEEK组、3%KH-PEEK组、5%KH-PEEK组、7%KH-PEEK组、9%KH-PEEK组材料的体积收缩率均显著降低($P < 0.05$),且整体变化趋势一致。7% KH-PEEK组的体积收缩率最低,与各组差异均具有统计学意义($P < 0.05$)。当KH-PEEK添加量超过7%时,材料的体积收缩性能开始下降。其中0%KH-PEEK组与5%未改性PEEK组的体积收缩率差异无统计学意义($P > 0.05$)(表2)。

2.3.2　KH-PEEK填料光固化复合树脂的吸水值和溶解值　如表3所示,与0% KH-PEEK组相比,1% KH-PEEK、3% KH-PEEK、5% KH-PEEK、7% KH-PEEK组吸水值显著降低($P < 0.05$);3% KH-PEEK、5% KH-PEEK、7% KH-PEEK、9% KH-PEEK组溶解值显著降低($P < 0.05$)。1% KH-PEEK组溶解值、9% KH-PEEK组吸水值分别与0% KH-PEEK组比较,差异均无统计学意义($P > 0.05$)。

表2　各组KH-PEEK填料光固化复合树脂的体积收缩率

Table 2　Volumetric shrinkage of light-cured resin composites filled with KH-PEEK particles in various groups　$\bar{x}\pm s$

Group	Volumetric shrinkage(η/100%)
0%KH-PEEK	2.94±0.02^{d}
1%KH-PEEK	2.85±0.03^{c}
3%KH-PEEK	2.86±0.02^{c}
5%KH-PEEK	2.83±0.03^{b}
7%KH-PEEK	2.75±0.03^{a}
9%KH-PEEK	2.84±0.02^{b}
5%Unmodified PEEK	2.95±0.03^{d}
F	32.08
P	< 0.001

n=5 parallel specimens per group; each specimen was measured 3 repeated times to reduce test error. Statistical analysis used One-way analysis of variance. Different lowercase letters indicate significant differences between groups by Tukey-HSD post-hoc test ($P < 0.05$). PEEK: polyetheretherketone. KH-PEEK: KH-570 silane-modified polyetheretherketone

5% KH-PEEK组吸水值与1% KH-PEEK组、3% KH-PEEK组、7% KH-PEEK组、9% KH-PEEK组、0% KH-PEEK组及5%未改性PEEK组相比，差异均具有统计学意义（$P < 0.05$）；其溶解值与1% KH-PEEK组、3% KH-PEEK组、7% KH-PEEK组、0% KH-PEEK组及5%未改性PEEK组相比差异具有统计学意义（$P < 0.05$）。

当KH-PEEK添加量超过5%时，材料的吸水性能开始下降。其中9%KH-PEEK组的吸水值与0%KH-PEEK组差异无统计学意义（$P > 0.05$）。

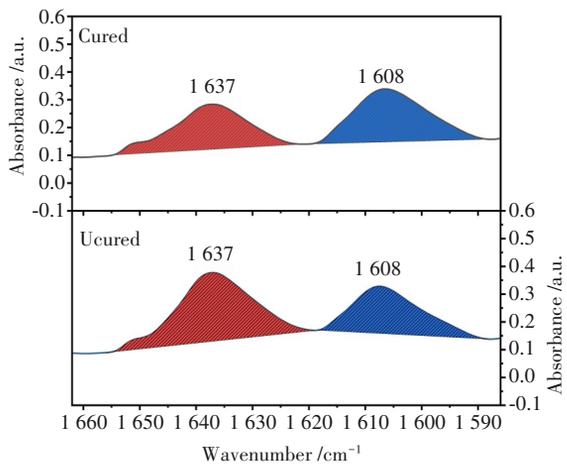
表3　各组KH-PEEK填料光固化复合树脂的吸水值和溶解值

Table 3　Water sorption and solubility of light-cured resin composites filled with KH-PEEK in various groups　$\bar{x}\pm s$

Group	Water sorption /(μg·mm³)	Water solubility /(μg·mm³)
0%KH-PEEK	32.13±1.20[d]	1.65±0.09[d]
1%KH-PEEK	26.19±1.09[c]	1.60±0.09[d]
3%KH-PEEK	23.18±0.48[b]	1.49±0.08[c]
5%KH-PEEK	22.23±0.50[a]	1.38±0.03[b]
7%KH-PEEK	23.47±0.39[b]	1.32±0.02[a]
9%KH-PEEK	31.82±0.35[d]	1.38±0.02[b]
5%Unmodified PEEK	32.49±0.64[d]	1.62±0.02[d]
F	74.32	62.18
P	< 0.001	< 0.001

n=5 specimens per group. Statistical analysis used one-way analysis of variance. In accordance with ISO test standards, each individual specimen could only be subjected to one complete test of water sorption and solubility. Three independent batch experiments were performed, with newly prepared specimens used in each experiment. Different lowercase letters indicate significant differences between groups ($P < 0.05$). PEEK: polyetheretherketone. KH-PEEK: KH-570 silane-modified polyetheretherketone

2.3.3　KH-PEEK填料光固化复合树脂的双键转化率　光固化前后的红外光谱变化代表性结果如图4所示。1 637 cm^{-1}处为C=C双键特征吸收峰，随光聚合反应进行峰强度降低；1 608 cm^{-1}处为芳香环特征峰，在固化过程中保持稳定，作为内标参考峰。图5展示了不同组别光固化复合树脂的双键转化率结果。添加经羟基化及KH-570接枝的PEEK（KH-PEEK）可显著提升树脂的双键转化率。与0%KH-PEEK组（50.92% ± 0.85%）相比，1%KH-PEEK组（57.26% ± 0.96%）、3%KH-PEEK组（58.44% ± 0.26%）、5%KH-PEEK组（57.12% ± 0.96%）、7%KH-PEEK组（55.43% ± 0.13%）、9%KH-PEEK组（53.44% ± 0.17%）的转化率均显著提高（$P < 0.05$），数值集中在57.38%至58.44%之间，其中3% KH-PEEK组的转化率最高。然而，5%未改性PEEK组的转化率（51.75% ± 0.16%）与0%KH-PEEK组差异无统计学意义。在1%至9%的添加范围内，转化率呈现先升高后降低的组间变化。以上结果表明，PEEK表面的化学改性是提高树脂网络交联密度的关键，而非PEEK填料的物理添加。

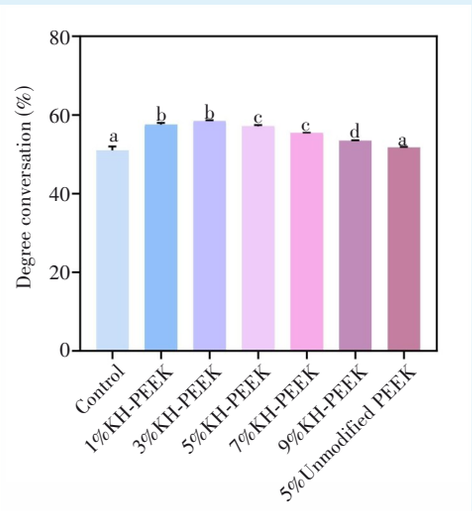


The aromatic ring internal standard peak is 1 608 cm^{-1}, and the C=C double bond characteristic peak is 1 637 cm^{-1}. Peak areas were used for the calculation of double bond conversion. Representative results from the five KH-PEEK groups, with five specimens per group. KH-PEEK: KH-570 silane-modified polyetheretherketone. FTIR: Fourier transform infrared spectroscopy

Figure 4　Representative FTIR spectra of light-cured composite resins filled with KH-PEEK particles before and after curing

图4　KH-PEEK填料光固化复合树脂固化前后的傅里叶变换红外光谱对比代表图

2.3.4　KH-PEEK填料光固化复合树脂的弯曲强度和弹性模量　与0%KH-PEEK组相比，3%KH-PEEK组、5%KH-PEEK组、7%KH-PEEK组的初始弯曲强度和初始弹性模量显著提升，以5%KH-PEEK组添加量最高，5%未改性PEEK组则显著低于其他组（$P < 0.05$）。经老化处理后，各组力学性能均显著下降（$P < 0.05$），但5%KH-PEEK组仍保持最高水平，1%KH-PEEK组、3%KH-PEEK组与7%KH-PEEK组组间差异无统计学意义（$P > 0.05$），且均显著优于9%KH-PEEK组、0%KH-PEEK及5%未改性PEEK（$P < 0.05$）（表4）。



n=5 parallel specimens per group, with each specimen tested in triplicate. Degree of conversion, F = 146.72; P < 0.001. Different lowercase letters indicate significant differences between groups as determined by a Tukey-HSD post-hoc test (P < 0.05). KH-PEEK: KH-570 silane-modified polyetheretherketone

Figure 5　Degree of conversion of light-cured composite resins filled with KH-PEEK particles in various groups

图5　各组KH-PEEK填料光固化复合树脂的双键转化率

2.3.5　KH-PEEK填料光固化复合树脂的表面硬度　与0%KH-PEEK组相比，添加KH-PEEK可显著提升材料的即刻表面硬度（P < 0.05）。硬度值随添加量的增加呈先升后降趋势，7%KH-PEEK组即刻硬度达到最高，5%KH-PEEK组添加量组次之，两组间差异具有统计学意义（P < 0.05）。经老化处理后，所有组的表面硬度均出现显著下降（P < 0.05）；老化后，5%KH-PEEK组与7% KH-PEEK组的表面硬度在数值上仍为最高，且二者间的差异无统计学意义（P > 0.05），但均显著高于0%KH-PEEK、1% KH-PEEK组、9% KH-PEEK组及5%未改性PEEK组（P < 0.05）（表5）。

2.3.6　KH-PEEK填料光固化复合树脂的断裂面观察　本研究选取0% KH-PEEK组、5% KH-PEEK组、5%未改性PEEK组三组代表性试样，对复合树脂断裂面微观形貌进行系统观察，结果如图6所示。在5 000倍低倍放大视野下：0%KH-PEEK组断裂面仅呈现树脂基质包裹玻璃鳞片的结构特征（图6a）。5%KH-PEEK组在断裂后，图片中间区域可见，部分KH-PEEK发生脱粘，但剩余部分与周围基质仍保持紧密的界面结合（图6b）。5%未改性PEEK组，未改性PEEK填料与树脂基质间已形成肉眼可辨的清晰界面缝隙，填料与基质结合松散（图6c、6d）。

为进一步观察界面微观缺陷，对5%未改性PEEK组的缝隙区域进行10 000高倍放大（图6e、6f分别为图6c、6d对应区域的10倍放大），可清晰观察到未改性PEEK填料与树脂基质间存在大面积界面脱粘、微小孔隙及裂隙结构。箭头清晰指示了两者间的缝隙边界，进一步证实了未改性PEEK与树脂基质界面相容性差的问题。

表4　各组KH-PEEK填料光固化复合树脂的弯曲强度和弹性模量

Table 4　Flexural strength and elastic modulus of light-cured resin composites filled with KH-PEEK particles in various groups $\bar{x}\pm s$

Group	Flexural strength/MPa		Elastic modulus/GPa	
	Immediate	Aged	Immediate	Aged
0%KH-PEEK	128.16 ± 2.27^{Ac}	114.47 ± 3.43^{Bc}	8.46 ± 0.25^{Ac}	6.39 ± 0.16^{Bc}
1%KH-PEEK	134.47 ± 2.25^{Ac}	124.28 ± 5.42^{Bb}	9.61 ± 0.48^{Ab}	8.09 ± 0.17^{Bb}
3%KH-PEEK	142.56 ± 3.49^{Ab}	127.72 ± 4.29^{Bb}	10.23 ± 0.71^{Ab}	9.29 ± 0.11^{Bb}
5%KH-PEEK	159.35 ± 3.64^{Aa}	141.21 ± 3.65^{Ba}	11.70 ± 0.72^{Aa}	10.32 ± 0.36^{Ba}
7%KH-PEEK	144.07 ± 4.05^{Ab}	131.59 ± 4.81^{Bb}	9.86 ± 0.68^{Ab}	8.75 ± 0.30^{Bb}
9%KH-PEEK	129.43 ± 2.97^{Ac}	112.07 ± 2.02^{Bc}	8.59 ± 0.52^{Ac}	7.02 ± 0.21^{Bc}
5%Unmodified PEEK	102.79 ± 3.44^{Ad}	86.60 ± 5.75^{Bd}	7.85 ± 0.36^{Ad}	5.36 ± 0.28^{Bd}
F	209.26	257.04	123.24	237.30
P	< 0.001	< 0.001	< 0.001	< 0.001
Group × condition (interaction, F)	1.37	-	3.93	-
P(interaction)	-	0.243	-	0.003

n=5 specimens per group, Two-way ANOVA revealed significant main effects of group and aging status on both flexural strength and elastic modulus. Different lowercase letters denote significant differences between groups under the same treatment. Different uppercase letters denote significant differences between immediate and aged conditions within the same group (P < 0.05). KH-PEEK: KH-570 silane-modified polyetheretherketone

表5　各组KH-PEEK填料光固化复合树脂的表面硬度

Table 5　Surface hardness of light-cured resin composites filled with KH-PEEK particles in various groups　$\bar{x}\pm s$

Group	Immediate	Aged
0%KH-PEEK	42.10 ± 0.78^{Af}	40.67 ± 0.84^{Bd}
1%KH-PEEK	44.32 ± 0.73^{Ae}	42.28 ± 0.48^{Bc}
3%KH-PEEK	47.21 ± 1.30^{Ac}	44.69 ± 0.24^{Bb}
5%KH-PEEK	48.69 ± 0.76^{Ab}	45.25 ± 1.06^{Ba}
7%KH-PEEK	49.15 ± 1.16^{Aa}	45.31 ± 0.70^{Ba}
9%KH-PEEK	46.71 ± 1.06^{Ad}	44.70 ± 0.97^{Bb}
5% unmodified PEEK	46.36 ± 0.79^{Ad}	42.55 ± 0.58^{Bc}
F	59.55	175.44
P	0.000 1	0.000 1
Group × condition (interaction, *F*)	3.16	-
P(interaction)	-	0.010

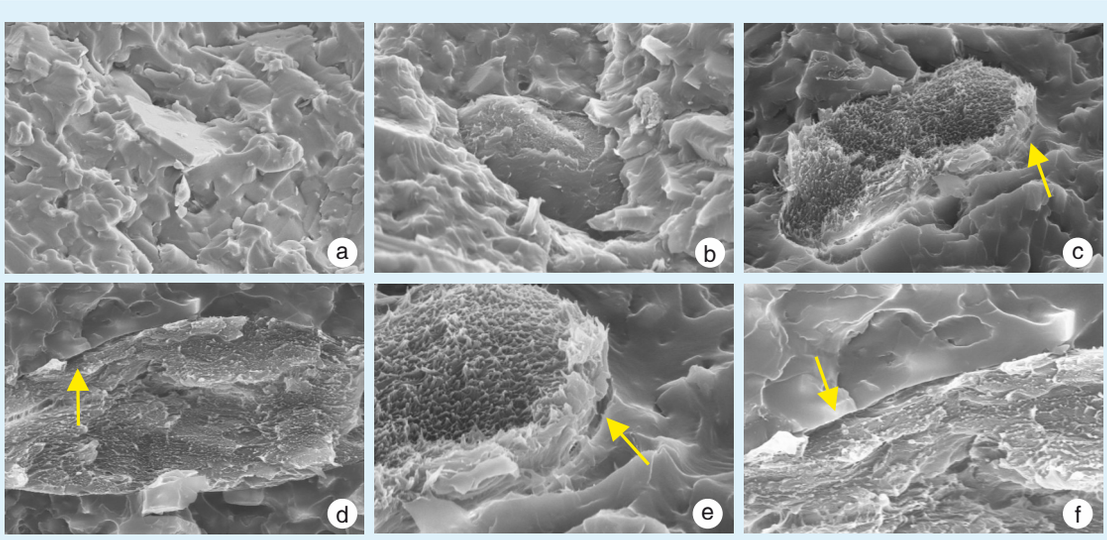
n=5 five specimens per group, each measured in triplicate. Different lowercase letters denote significant differences between groups under the same treatment condition ($P < 0.05$). Different uppercase letters denote significant differences between immediate and aged conditions within the same group ($P < 0.05$). Two-way ANOVA revealed significant main effects of group and aging status. KH-PEEK: KH-570 silane-modified polyetheretherketone

2.4　光固化复合树脂的细胞相容性评估

细胞相容性测试结果表明，各组L929细胞的存活率均高于90%，组间差异无统计学意义（$P > 0.05$）（图7）。所有实验组材料的细胞毒性分级均符合合格标准。

3　讨　论

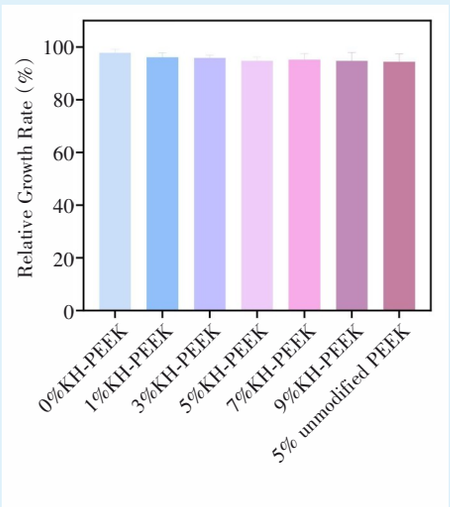
光固化复合树脂的长期临床性能，在很大程度上取决于其有机基质与无机填料间的界面结合强度[25]。该界面是复合材料中的薄弱环节，易成为应力集中区域，导致修复体断裂[4]。同时，该界面也是水分子及口腔内生物酶等物质渗透扩散的主要路径，可引发树脂基质的塑化、增韧剂溶出、聚合物网络水解，并最终造成界面脱粘接[26-27]。这些理化过程综合作用，表现为材料力学性能的显著衰减及修复体边缘的微渗漏[28-29]。因此，如何构建稳定的界面结合，是提升复合树脂长期耐久性的关键问题。本研究通过羟基化联合硅烷偶联改性策略，解决了原始PEEK填料表面化学惰性、树脂界面结合弱的难题。经硅烷化改性的PEEK可作为一种良好的有机填料，以5%的质量分数添加时，能够通过构建“PEEK - 硅烷 - 树脂”共价界面网络，协同提升光固化复合树脂的弯曲强度、弹性模量和表面硬度等力学性能、耐水解性与抗老化能力，同时维持良好的双键转化率和细胞相容性，



a: control group (0% KH-PEEK): fracture surface showing typical glass flakes embedded in the resin matrix. b: 5% KH-PEEK group: fracture surface with KH-PEEK fillers tightly bound to the resin matrix, with no obvious interfacial gaps. c&d: 5% unmodified PEEK group (×5 000): distinct interfacial gaps exist between unmodified PEEK fillers and resin matrix (arrows). e&f: 5% unmodified PEEK group (×10 000, magnified regions corresponding to Figures c and d): severe interfacial debonding between fillers and matrix is clearly observed at high magnification (arrows). Representative images from five specimens per group (a, b, c, d, e, f). Magnification: a-d: ×5 000; e-f: ×10 000

Figure 6　Representative scanning electron microscopy images of fracture surfaces of light-cured composite resins filled with KH-PEEK particles in various groups

图6　各组KH-PEEK填料光固化复合树脂断裂面扫描电镜代表图



n=5 batches of material extracts prepared per group; each extract was tested in triplicate, and the average value was used for statistical analysis. One-way ANOVA (F = 1.463, P = 0.2084) followed by Tukey's multiple comparisons test revealed no significant difference among all groups (all adjusted P > 0.05). FTIR: Fourier transform infrared spectroscopy

Figure 7　Relative growth rate of cells cultured with light-cured composite resins filled with KH-PEEK particles in various groups

图7　各组KH-PEEK填料光固化复合树脂细胞相对增殖率

证实硅烷化改性PEEK填料可有效调控复合树脂理化性能，为该改性树脂的临床应用提供实验支撑。

3.1　KH-PEEK填料光固化复合树脂的体积收缩率

体积收缩率是评价牙科复合树脂临床应用潜力的重要指标。光固化过程中树脂单体发生交联聚合，分子间距离减小引发体积收缩，易产生聚合应力、边缘微渗漏，进而诱发继发龋、充填体脱落等临床问题，直接影响修复体长期使用寿命。PEEK为疏水型高分子填料，KH-570接枝的有机长链同样具备疏水性，经羟基化-硅烷偶联两步改性后，KH-PEEK可与树脂基质形成Si-O-C共价键，将惰性填料转化为可参与聚合反应的活性增强相。该结构可有效限制树脂单体聚合过程中的分子链运动，同时填料均匀分散形成物理阻隔网络，约束树脂基体的聚合收缩行为。

本研究中发现，与0%KH-PEEK组相比，1%KH-PEEK组、3%KH-PEEK组、5%KH-PEEK组、7%KH-PEEK组、9%KH-PEEK组均可显著降低树脂的体积收缩率，收缩抑制效果随添加量提升先增强后减弱，并在7%添加量时达到最优。当KH-PEEK添加量超过7%时，填料易发生团聚，界面缺陷增多，应力分布不均，反而导致聚合收缩性能下降。其中0%KH-PEEK组与5%未改性PEEK组的体积收缩率差异无统计学意义，进一步证实未改性PEEK因界面结合薄弱，无法参与树脂交联网络构建，难以改善复合树脂的聚合收缩问题。

3.2　KH-PEEK填料光固化复合树脂的吸水值与溶解值

吸水值与溶解值是评价牙科复合树脂长期耐久性的关键指标。吸水值反映了水分向材料内部渗透的能力，水分渗透会导致树脂基质膨胀、成分溶出及聚合物网络水解，从而引发力学性能衰减、尺寸不稳定乃至修复体失效[21]。溶解值则与残余单体、低聚物等小分子物质的溶出相关，直接影响材料的生物安全性与结构完整性[30-31]。PEEK本身是疏水聚合物，KH-570的有机长链也具有疏水性。PEEK经羟基化后，其表面-OH与KH-570水解产生的硅羟基（-SiOH）发生缩合反应，形成共价键（Si-O-C）[32]。同时，KH-570另一端的甲基丙烯酸酯基团在光固化时与树脂聚合。将惰性的PEEK填料转化为能与树脂网络形成化学键合的"活性增强相"，显著减少了填料与树脂基质间的微间隙，从而降低了可溶性成分（如残余单体）的析出[33-34]。本研究中发现，与0%KH-PEEK组相比，1%KH-PEEK组、3%KH-PEEK组、5%KH-PEEK组、7%KH-PEEK组、9%KH-PEEK组均显著改善了耐水性，并在5%添加量时达到最优。

3.3　KH-PEEK填料光固化复合树脂的双键转化率

双键转化率是衡量树脂单体在光固化过程中向聚合物转变效率的核心指标，直接决定了聚合物网络的交联密度与结构完整性，进而影响复合树脂的机械性能、耐水解性及长期稳定性。理论上转化率可达100%，但在实际固化中，体系快速凝胶化与玻璃化会限制分子链运动，使部分残余单体被包裹；同时，空气中的氧阻聚效应也进一步制约了转化率的提升，导致实际值难以达到理论值。

本研究中，1%KH-PEEK组、3%KH-PEEK组、5%KH-PEEK组、7%KH-PEEK组、9%KH-PEEK组其双键转化率均显著高于0%KH-PEEK组（P < 0.05）。KH-570末端甲基丙烯酸酯基团直接参与树脂基体的光固化交联反应，在玻璃鳞片与树脂之间形成化学键合的同时，更在刚性PEEK颗粒表

面为自由基聚合提供了更多反应位点，从而促进整体交联网络的构建，提高双键转化效率。相比之下，未改性PEEK组因缺乏可聚合基团，无法提供额外反应位点，其转化率与0%KH-PEEK组无显著差异。此外，不同KH-PEEK添加量组间的转化率未呈现显著差异，均保持在相近的高水平，在研究的添加比例范围内，KH-570引入的可聚合位点已足以引发充分交联。

3.4　KH-PEEK填料光固化复合树脂的的弯曲强度和弹性模量（老化前后）

在口腔修复领域，复合树脂的机械性能是其承受咀嚼应力、实现长期功能的基础[35]。弯曲强度反映材料抵抗断裂的能力，直接决定修复体在循环负载下的服役寿命；弹性模量表征刚性，理想值应与牙体组织相匹配，以均匀传递应力，避免应力屏蔽或应力集中导致的修复失效。修复体的机械完整性能，其优劣取决于树脂基质交联网络、无机填料增强效应及界面结合效果的综合作用。羟基改性并通过KH-570接枝的PEEK对复合树脂机械性能的增强，其原因在于界面结合从物理吸附到化学偶联的转变[36]，从而提升了应力传递效率。未改性的PEEK与树脂基质界面结合薄弱，在外力作用下易成为裂纹萌生与扩展的起点，因此5%未改性PEEK组的弯曲强度与弹性模量甚至低于不含KH-PEEK的0%KH-PEEK组。而KH-PEEK表面的KH-570可同时与PEEK的羟基及树脂基质中的双键发生化学反应，形成“有机填料-硅烷-树脂”的共价键桥联[37-38]。这种强界面结合能确保载荷从相对柔韧的树脂相高效地传递给刚性更高的PEEK相，使填料的增强潜力得以充分发挥，从而在宏观上表现为弯曲强度与弹性模量的显著提升。实验数据表明，在5%添加量时达到峰值。这对应着填料在基质中实现理想分散，并形成有效应力传递网络的最佳状态。过量填料可能引发团聚，引入新的应力缺陷，同时可能影响树脂基质的连续性，导致性能下降[39]。此外，经过老化处理后，5% KH-PEEK组仍保持最高的力学性能与保持率，这进一步证实了共价键界面优异的抗水解稳定性，能够有效抵抗口腔湿、热环境对界面的侵蚀，保障了增强效果的长期性。

3.5　KH-PEEK填料光固化复合树脂的的表面硬度（老化前后）

表面硬度反映材料抵抗局部压痕塑性变形的能力，受树脂基质网络结构、填料分散以及界面结合质量共同影响，体现抗刮擦和塑性变形的能力，对维持表面光洁度、防止菌斑附着及抵抗磨耗具有重要意义[40]。本研究中，5%未改性PEEK组的PEEK与树脂基质相容性有限，界面结合较弱，受压易发生界面滑移或局部脱粘，导致压痕变形更易在基质相内扩展，硬度提升不明显。相比之下，羟基化并接枝KH-570的PEEK可与树脂基质形成更稳定的界面连接，增强填料对基质的约束作用，使载荷在填料与基质间更有效传递，从而提高维氏硬度。硬度在5%~7%时较优，含量过高可能引入分散不均或缺陷，导致硬度下降。

3.6　KH-PEEK填料光固化复合树脂的断裂面观察

在断裂面微观形貌中，0%KH-PEEK组仅见树脂基质包裹玻璃鳞片，界面结合较为松散；未改性PEEK组断裂后，PEEK与基质间出现明显缝隙，两者仅依靠物理嵌合，界面结合薄弱，易成为裂纹萌生与扩展的起点。而KH-PEEK组断裂后，剩余部分与周围基质仍保持紧密贴合，未见明显界面分离。这一微观结构与宏观性能高度吻合。表面硬度测试结果显示，5%KH-PEEK组在24 h和老化后均保持较高的硬度值，显著优于0%KH-PEEK组及5%未改性PEEK组，良好的界面结合使填料能够有效约束基质变形，在受到压痕载荷时更有效地抵抗塑性变形，从而表现出更高的表面硬度。

3.7　KH-PEEK填料光固化复合树脂的生物相容性

良好的生物安全性是光固化复合树脂临床应用的核心前提，直接决定了材料与人体组织的生物相容性。本研究通过L929小鼠成纤维细胞体外毒性实验对所制备的复合树脂浸提液进行生物安全性评估，结果显示，各组的细胞存活率均处于较高水平，与0%KH-PEEK组差异不具有统计学意义，材料未表现出细胞毒性，符合临床应用的安全性要求。

3.8　KH-PEEK填料界面结构与现有改性体系的对比分析

因此，尽管KH-570同样被用于无机填料的表面改性，但两者所构建的界面结构存在本质差异。对于玻璃鳞片而言，KH-570通过形成Si－O－Si键连接其表面，而另一端再与树脂基质发生聚合，构建的是“无机–硅烷–有机”的异质界面结构[41]。由于无机相与有机基质在极性、表面能及弹性模量等方面存在显著差异，该界面在本质上仍属于物理性质不连续的过渡层，界面相容性有限[42]。

而对于KH-PEEK体系，PEEK本身为有机高分

子材料，其经改性后所引入的反应性基团可直接参与树脂基质的聚合反应，从而在固化过程中形成“有机-有机”的界面结构。该界面在共价键连接与化学组成上与树脂基质具有更高的一致性，使界面由传统的相分离界面转变为具有更高连续性和相容性的界面过渡区[20]。这种结构不仅降低了界面能、提高了相容性，同时显著增强了应力在填料与基质之间的传递效率，减少了界面处的应力集中与裂纹萌生，为力学性能与耐老化性能的提升提供了结构基础。

近年来，关于PEEK表面改性以增强其与复合树脂界面结合的研究已有较多报道。Ma等[20]对比了硫酸酸蚀、喷砂、激光处理、等离子体处理等多种物理化学改性方法，发现所有改性方式均可显著提升PEEK与复合树脂的粘接强度，其中硫酸酸蚀组的粘接强度最高（13.28±1.69）MPa，但表面粗糙度与粘接强度之间并无显著相关性。这一结果提示，单纯依靠物理粗糙化构建的机械嵌锁界面不足以形成稳定结合，化学键合作用可能才是决定界面粘接性能的关键因素。

Ge等[43]采用硼氢化钠（$NaBH_4$）还原法在PEEK表面引入羟基，并结合浓硫酸磺化处理构建了兼具化学键合与物理嵌锁效应的复合界面；XPS与ATR-FTIR表征证实，硅烷偶联剂成功接枝于PEEK表面并形成了Si-O-C共价键。该研究的表面化学改性策略，与本文采用的羟基化和KH-570接枝思路具有一致性。不同之处在于，Ge等将改性后的PEEK作为基体材料与复合树脂进行粘接，而本文则进一步将KH-PEEK作为增强填料直接掺入复合树脂内部，在树脂基质与填料之间构建了更广泛、更均匀的共价界面网络，为提升材料整体性能提供了新路径。

Schmeiser等[36]系统研究了填料类型、含量及硅烷化处理对PAEK复合材料力学性能的影响，证实硅烷化改性能够显著提升材料的弯曲强度、弹性模量及表面硬度。这一发现与本实验结果高度吻合，进一步验证了硅烷偶联剂在构建稳定填料-基质界面、改善树脂力学性能中的关键作用。

值得注意的是，上述研究多聚焦于改性方法对粘接强度的即刻影响，而对湿热老化后界面稳定性的系统评估相对有限。本文通过冷热循环老化实验进一步证实，KH-PEEK构建的共价界面在湿热环境下仍能保持较高的力学性能保持率，这为PEEK改性复合树脂的长期临床应用提供了更具参考价值的实验依据。

羟基化改性并经KH-570接枝的PEEK（KH-PEEK）作为有机填料，可有效提升光固化复合树脂的综合性能；在5%质量分数添加量下，材料在弯曲强度、弹性模量、表面硬度等力学性能、耐水解性及双键转化率上达到良好的平衡。此外，KH-PEEK构建的共价键界面能良好提升复合树脂的耐老化性能，使其在湿热循环老化后仍保持良好的力学性能保留率，展现出良好的长期应用潜力。

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