

改性树脂基体玻璃纤维筋-混凝土界面粘结性能演化及提升机制

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摘 要: 纤维增强复合材料(FRP)筋与混凝土粘结性能直接影响 FRP 筋增强混凝土结构承载力与耐久性。通过自合成有机硅与纳米填料表面疏水修饰实现玻璃纤维筋(GFRP 筋)树脂基体改性, 并实现高耐蚀 GFRP 筋制备。探究 60 °C 海水海砂混凝土模拟孔溶液作用下高耐蚀 GFRP 筋与海水海砂混凝土界面粘结性能的退化规律, 并通过界面微结构分析揭示 GFRP 筋-混凝土粘结性能提升机制。结果表明: 相比未改性 GFRP 筋, 高耐蚀 GFRP 筋与混凝土初始界面粘结力提升了 7.87%, 腐蚀 120 d 后界面粘结力提高了 15%左右, 界面处最大应变增加了约 25.87%。GFRP 筋与混凝土界面脱粘主要与 GFRP 筋基体降解有关。基体耐蚀性能的提升有效缓解了筋材的降解速率, 进而改善 GFRP 筋-混凝土界面的粘结性能。

关键词: 基体改性; 界面粘结性能; 数字图像相关技术; 分子模拟; 微结构演变

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海洋环境高浓度氯离子是导致混凝土中钢筋锈蚀的主要原因, 抗氯盐腐蚀的纤维增强复合材料(FRP)在海水海砂混凝土或海洋工程中受到关注和示范性应用。但在高碱、高湿、高温等恶劣环境中, FRP 筋与混凝土界面仍会发生粘结性能大幅度退化, 从而影响到结构的承载力与耐久性^[1-4]。

研究者普遍采用传统拉拔试验获得恶劣环境下玻璃纤维筋(GFRP 筋)与混凝土界面粘结性能的退化规律, 并发现界面粘结强度在腐蚀初期随环境温度升高而增加, 但后期会下降^[3-7]。Porter 和 Barnes 研究发现^[8], 将粘结试件置于 60 °C 溶液中进行暴露试验, GFRP 筋的拉拔粘结强度并没有降低, 但存在材料降解现象。Robert 等^[9]指出, 即使在 50 °C 暴露 6 个月后, GFRP 筋与混凝土界面粘结强度下降百分率非常低(<8%)。但有研究者发现随着腐蚀龄期的延长, FRP 筋-混凝土界面粘结力退化主要原因为 FRP 筋树脂基体在混凝土碱性环境中性能的劣化^[4]。界面处的腐蚀离子最先侵蚀环氧基体, 使其表面发生溶胀及吸湿水解现象, 从而削弱环氧基体与混凝土的界面结合力。此外, 高温环境

下, 热膨胀会在环氧树脂中产生额外的体积, 增大基体吸湿率, 由吸湿引起的膨胀内应力会影响界面的结合。高温下 GFRP 筋与混凝土热膨胀系数的差异, 同样会影响 FRP 与混凝土界面的长期粘结性能。针对此, 研究者探讨了通过添加纳米颗粒、形成互穿网络的基体改性^[10-11]、纤维表面涂附界面改性剂^[12]及混杂纤维^[13-14]等方式提升 FRP 筋的耐久性能; 但对于改性筋材与海水海砂混凝土之间粘结性能演化, 以及改性树脂基体的作用机制研究较少。此外, 传统拉拔试验有一定的局限性, 仅能够获取单向变形数据, 并具有一定的离散性。而采用数字图像相关(DIC)技术可获得粘结区域任意位置与纵横向的应变数据, 并具有较高的准确性^[15-16]。

因此, 基于疏水链段引入与纳米材料表面疏水修饰的方法对 FRP 筋的环氧树脂进行混合改性, 并实现改性树脂基体 GFRP 筋的连续生产。利用 DIC 无损监测技术, 获得腐蚀环境下改性 GFRP 筋与海水海砂混凝土界面粘结性能的退化规律。基于界面微结构劣化分析, 揭示改性 GFRP 筋-混凝土粘结性

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能提升机制, 为 GFRP 筋-混凝土粘结性能提升提供新的方法。

1 实验

1.1 改性环氧树脂基体制备

1.1.1 有机硅合成 将含氢硅油(PMHS)与 γ -(2,3-环氧丙氧)丙基三甲氧基硅烷(KH560)按照 1:1 的质量比例混合, 乙醇作为溶剂, 在 NaOH 的催化作用下, 采用磁力搅拌器(200 r/min)常温反应 8 h 后, 保存备用。

1.1.2 纳米填料表面改性 碳纳米管(CNT)和可膨胀石墨(EG)具有优异的高比强度和高比表面积, 可实现裂缝桥接, 提升聚合物基体的韧性及开裂应力。并通过抑制聚合物链的分子间运动起到防水的作用。此外, EG 可形成稳定膨胀碳层, 延缓或抑制聚合物的热降解。采用的纳米材料性能参数见表 1。通过表面改性, 可增大纳米材料表面的粗糙度, 改善其团聚效应。将 2 种纳米材料分别进行表面改性, 步骤如下所示:

1) CNT: 将 0.03% (质量分数)的 CNTs 搅拌分散至乙醇与 KOH 有机溶剂中, 随后加入含氢硅油(PMHS)与硅酸乙酯(TEOS)超声分散后获得 CNT 改性剂。

2) EG: 将 EG 置于真空环境下, 按照 TEOS/PMHS 的质量比例 3:1 滴至膨胀石墨表面; 随后, 将样品置于 800 W 微波炉中快速膨胀 10 s, 将制得的膨胀石墨置于 KOH 与无水乙醇有机溶剂中加温

搅拌直至混合均匀。

1.1.3 改性环氧树脂混合液 将双酚 A 型环氧树脂(EGEBA)、甲基四氢邻苯二甲酸酐固化剂(MeTHPA)以及促进剂(DMP-30)按照 100:85:5 的质量比例混合。随后, 取 5% 的自合成有机硅与固体含量总量为 0.03% 的 CNT、EG 表面改性纳米填料混合至环氧乳液中, 采用超声结合三辊轴剪切分散的方式将混合溶液搅拌均匀。

1.2 改性树脂基体 GFRP 筋制备

将混合均匀的改性环氧树脂倒至浸胶槽中, 经过送纱、浸渍、拉挤、绕肋成型、固化等阶段加工成型。其中固化过程中需设置多烘道。依据基体混合溶液的玻璃化转变温度设置烘道的温度以及固化过程中纤维拉挤速率。筋材制备过程中拉挤速率为 0.8 m/min。玻璃纤维为 E 型玻璃纤维(E-glass), 其占比约 80%。树脂含量为 20%。改性 GFRP 筋的生产线为郑州大学纤维复合建筑材料与结构教育部工程研究中心。生产所得 GFRP 筋的肋高为 1.2 mm, 肋间隔距离为 12 mm, 见图 1。

1.3 FRP-混凝土粘结力试验

1.3.1 原材料及混凝土配比

1) 混凝土

海水海砂混凝土原材料包括 P·II 52.5 型硅酸盐水泥、花岗岩(连续级配粒径 5~20 mm)、海砂(细度模数 2.2)、聚羧酸高性能减水剂(减水率 27%), 拌合水采用青岛金沙滩天然海水。海水海砂混凝土设计强度等级为 C50, 其配合比见表 2。

表 1 纳米材料技术参数

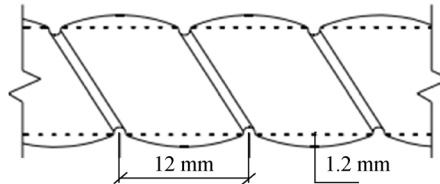
Table 1 Technical parameters of nanomaterials

Nanomaterials	Average diameter	Average length/ μm	Purity	Surface area/ $(\text{m}^2 \cdot \text{g}^{-1})$	Expansion coefficient
CNT	9.5 nm	3~12	>90%	250~300	
EG	75 μm		>95%		50 times

CNT is carbon nanotubes. EG is expanded graphite.



(a) Apparent morphology



(b) Detailed dimensions

图 1 GFRP 筋外观形态和尺寸

Fig. 1 Apparent morphology and dimensions of GFRP bar

表 2 配合比设计及立方体抗压强度

Table 2 Mix ratio design and cubic compressive strength

Mix proportion/ $(\text{kg} \cdot \text{m}^{-3})$					Cubic compressive strength/MPa
Cement	Sea sand	Gravel	Seawater	Water reducing agent	
462	645	1 096	176	1.11	57

2) FRP 筋

采用的 GFRP 筋分为 2 种: 1) 前述生产的改性树脂基体 GFRP 筋, 直径为 10 mm, 其拉伸强度为 1 256 MPa, 命名为 M-GFRP; 2) 传统 GFRP 筋, 直径同样为 10 mm, 其拉伸强度为 1 072 MPa, 命名为 N-GFRP。

1.3.2 试件制作及加载装置

为了便于 DIC 观察 FRP 筋与混凝土界面脱粘过程中的应变演变规律, 将直径为 10 mm 的 GFRP 筋嵌入混凝土上表面, 深度为 5 mm。试验中混凝土的尺寸参考 De Lorenzis^[17] 设置为 100 mm×100 mm×300 mm, 该尺寸的设置可防止横向尺寸影响混凝土的破坏模式, 如图 2a 所示。为确保 GFRP 筋在混凝土表面嵌入深度的精确性, 采用数控机床激光切割将模具上端留孔半径为 5 mm, 见图 2b。为探究 GFRP 筋-混凝土粘结性能演化规律, 将制备好的试件浸泡于 60 °C 的海水海砂混凝土模拟孔溶液中用于模拟混凝土高碱性环境, 其配比基于传统混凝土碱性孔溶液的基础上, 考虑氯离子的影响, 设定为 2.4 g/L 的 NaOH、19.6 g/L 的 KOH、2 g/L 的 Ca(OH)₂、35 g/L 的 NaCl^[18]。将腐蚀 0、30、60、90、120 d

的试样取出晾干、在表面喷射散斑, 待散斑晾干后将其置于防震台上, 拉拔端采用定制锚具固定至千斤顶内部, 全程采用液压手动泵加载。为防止试样两端翘起, 在自由端及千斤顶处采用喉箍固定, 保证筋材始终处于轴心受拉状态。拉拔全程采用 75 mm 微距 CCD 数码相机捕获脱粘全程界面处的位移与变形, 为保证拍摄清晰度, 两侧架设 LED 灯, 如图 2d 所示。图像采集区域为图 2a 中的矩形区域, 尺寸标定为 0.175 mm/pixel, 最后通过 VIC-2D 计算获得所选区域的位移场^[19]。试验过程中为避免数据的离散, 每组均制备 3 个试件, 试验结果取平均值。

1.4 界面微结构表征

为了更为清晰地追踪粘结界面劣化过程中的微结构演变, 制备缩尺样品同步腐蚀并用于扫描电镜 (SEM) 及 X 射线计算机断层扫描技术 (X-ray CT) 观测。缩尺试样的制备流程: 首先准备直径为 30 mm、高度为 10 mm 的 PVC 模具, 将高度 10 mm 的 GFRP 筋固定至底面的塑料薄片, 随后将拌合砂浆灌注至模具内, 标准条件下成型养护 28 d 拆模后, 将其置于模拟混凝土孔溶液中与拉拔试件同步腐蚀。观测前, 使用高速抛光机将试样表面抛至镜面状态。

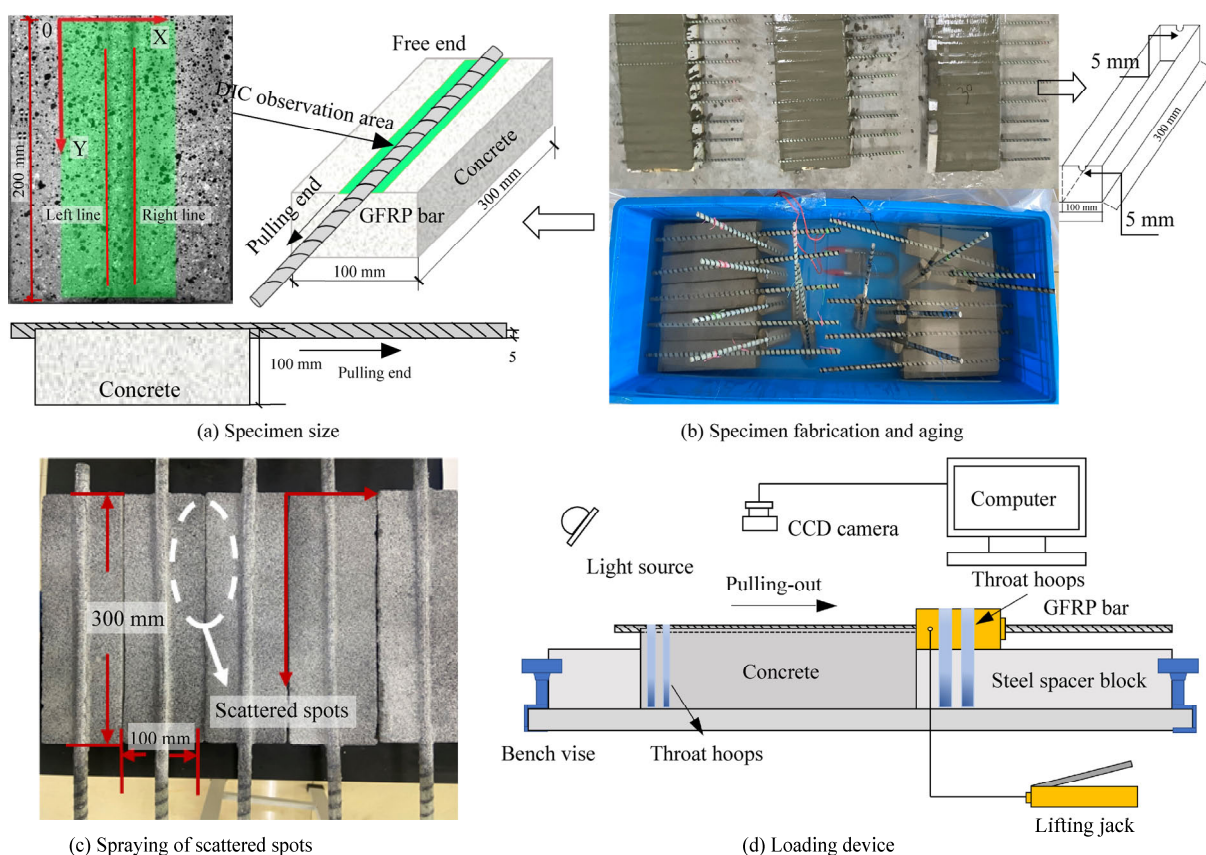


图 2 粘结力试验

Fig. 2 Test of bonding force

2 结果与讨论

2.1 界面破坏模式

GFRP-海水海砂混凝土脱粘破坏模式分为 2 种, 即 GFRP 筋拔出破坏和混凝土劈裂破坏。图 3 中展示了不同腐蚀龄期对应的 GFRP 筋-混凝土界面脱粘模式。未腐蚀时, 筋材与混凝土界面的粘结性能较强, 混凝土内部受到的劈裂应力超过自身的抗剪强度, 混凝土发生劈裂破坏。腐蚀 30 d 后, N-GFRP 筋-混凝土界面破坏形式转变为筋材拔出破坏,

M-GFRP 筋-混凝土界面仅在肋深处形成混凝土拉裂纹。随着老化龄期增至 60 d, N-GFRP 筋表面局部黄化, 为环氧基体降解的标志性现象^[20], 并伴随着少量碳纤维肋的脱落。而 M-GFRP 筋表面仅有少量碳纤维肋起毛现象。此时, 筋材的降解使得界面粘结性能有所下降, 致使筋材直接拔出。腐蚀 120 d 后, N-GFRP 筋表面大面积的树脂降解, 导致纤维暴露及碳纤维肋脱落。而 M-GFRP 筋相比于传统筋材, 腐蚀程度较轻, 其表面仅有斑点状局部黄化和表面粗糙现象。

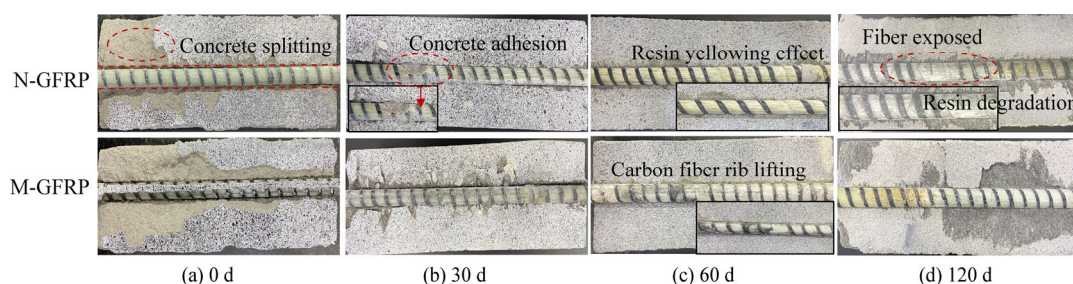


图 3 GFRP 筋与混凝土界面拔出破坏形态
Fig. 3 Damage pattern of GFRP reinforced concrete interface

2.2 GFRP-混凝土界面粘结力退化

腐蚀环境下 GFRP-混凝土界面粘结性能的退化规律, 如图 4 所示。相比于未改性树脂 GFRP 筋而言, 通过树脂基体改性后, M-GFRP 与混凝土的界面粘结性能有所提升, 粘结力增加了 7.87%左右; 当腐蚀至 120 d 时, N-GFRP 筋、M-GFRP 筋与混凝土界面粘结力分别降至 6.37、7.32 kN, 相比未腐蚀时, 2 类 GFRP 筋-混凝土粘结力分别降低了 7%和 1%。这表明, 树脂基体改性有利于提高 FRP 筋-混凝土界面粘结力, 尤其在腐蚀环境下, FRP 筋树脂基体耐蚀性能的改善使得界面粘结性能损失速率明显减缓。此外, 当腐蚀龄期小于 60 d 时, FRP 筋-混凝土粘结力呈增加的趋势。其原因为: 60 °C 的浸泡腐蚀环境使得混凝土水化持续进行, 其抗劈裂强度有所增加, 进而有利于混凝土与筋材之间的握裹, Hassan 等^[3]在研究中发现了相似的规律。而当腐蚀龄期超过 60 d 时, GFRP 筋的树脂基体降解、老化使得界面粘结性能逐渐下降^[21]。

2.3 GFRP/混凝土脱粘过程应变场演变

通过 DIC 技术获得不同腐蚀龄期 FRP 筋-混凝土界面粘结拉伸过程中应变场演变, 见图 5~图 6。由图中可知: 加载初期, 界面区域有微小应变的产生且分布均匀; 随着荷载的增加, GFRP 筋与混凝土间已有相对滑移, 界面处的位移与变形逐渐增大。

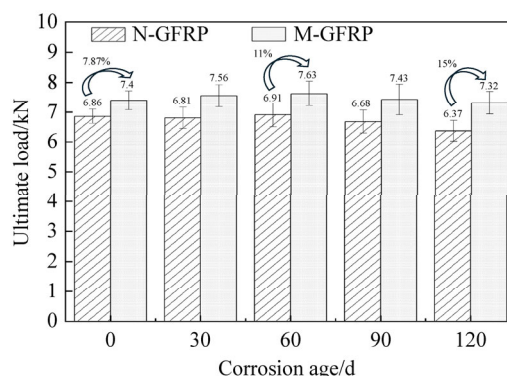


图 4 GFRP-混凝土界面粘结力退化
Fig. 4 Bonding degradation of GFRP-concrete interface

最终在拉拔荷载达到峰值时, 试件发生破坏, 加载端附近区域的应变达到最大。未腐蚀时, 在 5 kN 的拉拔荷载作用下, 2 类 FRP 筋-混凝土界面处的最大应变均为 20×10^{-3} 左右, 无明显差异, 见图 5~图 6a。腐蚀至 60 d 时, FRP 筋-混凝土界面处的应变值有所增大, 拉拔荷载为 5 kN 时, N-GFRP 筋-混凝土、M-GFRP 筋-混凝土界面处的最大应变分别为 26×10^{-3} 、 30.6×10^{-3} 左右, 二者相比, 改性后 FRP 筋-混凝土界面应变值增加了 17%左右, 如图 5~图 6b 所示。当腐蚀至 120 d 时, FRP 筋-混凝土界面处的应变均有减小的趋势, 当拉拔荷载达到 5 kN 时, 二者的界面应变值分别降至 22.8×10^{-3} 、 28.7×10^{-3}

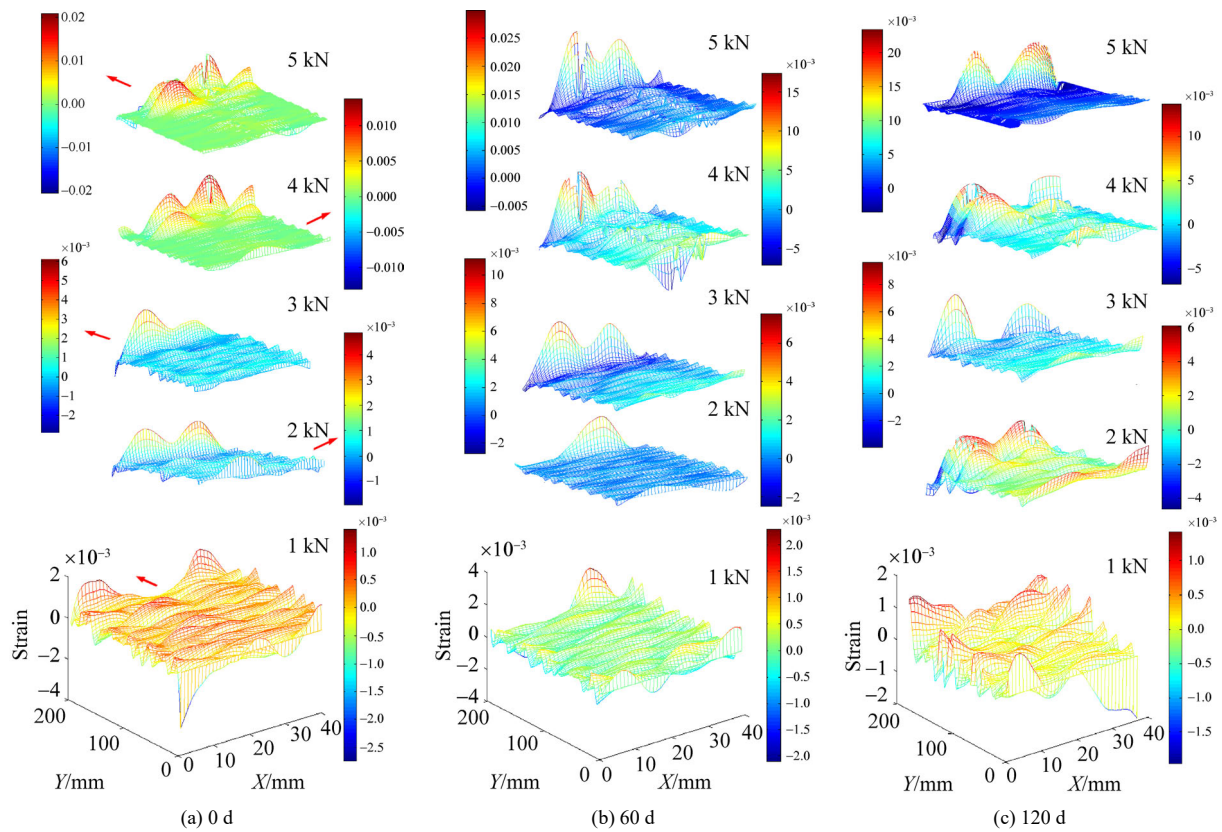


图5 N-GFRP 筋-混凝土粘结界面三维应变场演变

Fig. 5 Evolution of three-dimensional strain field at the bonding interface of N-GFRP bar-concrete

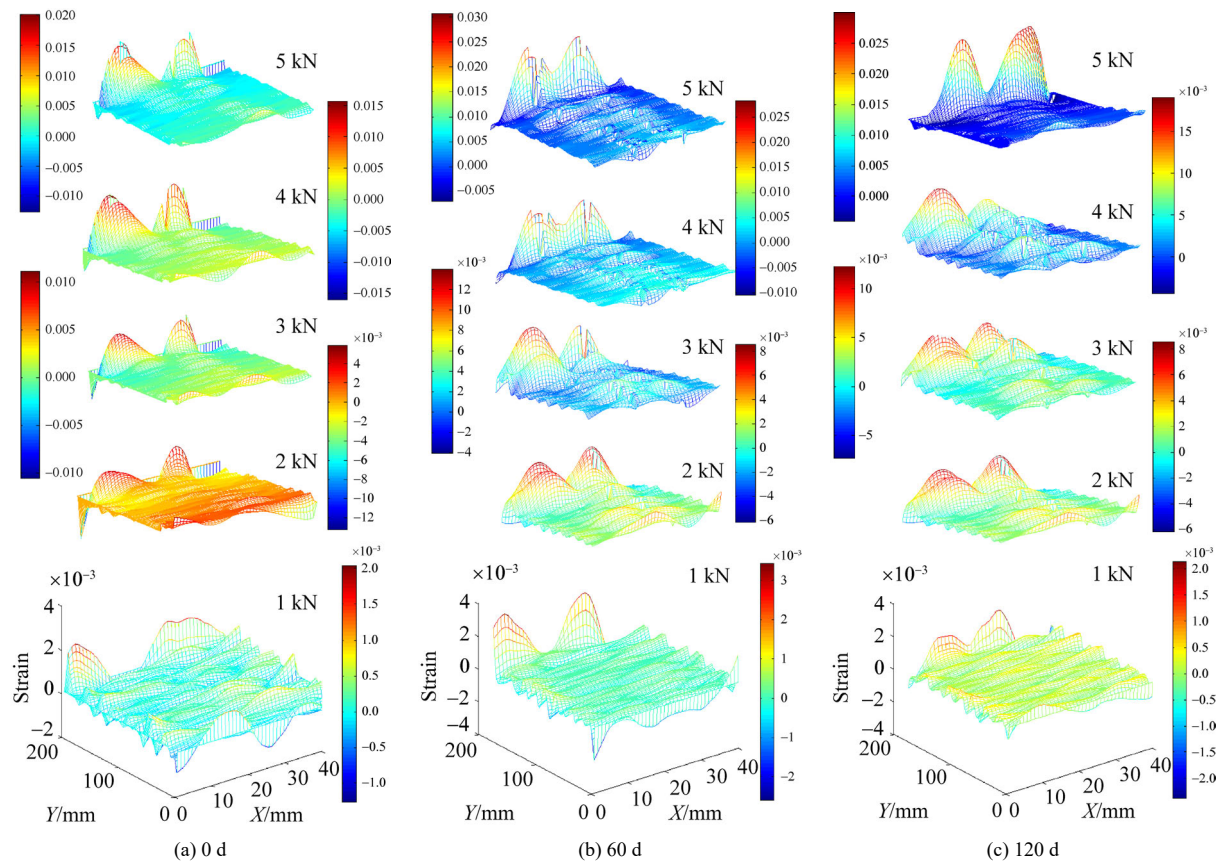


图6 M-GFRP 筋-混凝土粘结界面三维应变场演变

Fig. 6 Evolution of three-dimensional strain field at the bonding interface of M-GFRP bar-concrete

左右, 相比 60 d 同荷载作用, 二者的界面应变分别降低了 12%、7% 左右。因此, FRP 筋树脂基体改性后, 筋材耐蚀性能提升, 能够更好地吸收和分散外部荷载带来的应力, 使得 FRP 筋-混凝土界面处的应力分布更为均匀, 变形量增大, 从而减缓粘结力的损失速率。

2.4 微结构演变

采用 SEM 对缩尺试样不同腐蚀龄期界面区原位观测, 如图 7 所示。未腐蚀时, 2 种 GFRP 筋与混凝土界面处平整光滑, 其界面间距分别为 $78.6\ \mu\text{m}$ 和 $41.58\ \mu\text{m}$; 改性剂与纳米增强材料的加入提高了树脂基体与混凝土间的亲合力, 降低了界面间距。腐蚀 30 d 后, 二者界面处的间距几乎没有增加, 界面处的基体无明显老化现象。而腐蚀 60 d 后,

N-GFRP 筋-混凝土界面间距不断增大, 约 $118.78\ \mu\text{m}$, 相比于未腐蚀时, 界面间距增加了 51% 左右。而 M-GFRP 筋-混凝土界面间距仅增加了 40% 左右, 基体表面仅有轻微龟裂。随着腐蚀龄期增至 120 d, 2 种筋材与混凝土界面间距分别达到 158.11、 $67.91\ \mu\text{m}$, 相比未腐蚀时, 增加了 100% 和 60% 左右。此时, N-GFRP 筋-混凝土界面处的表层基体均已脱落, 并暴露出新的一层。而 M-GFRP 筋-混凝土界面处局部基体剥落, 其腐蚀程度低于 N-GFRP 筋。因此, GFRP 筋与混凝土的脱粘主要取决于界面处基体的劣化程度, 通过基体改性提高了树脂基体与混凝土的亲合力, 疏水网络的引入使得筋材的防水性能有所提升, 有效缓解了筋材树脂基体降解, 进而改善其粘结性能。

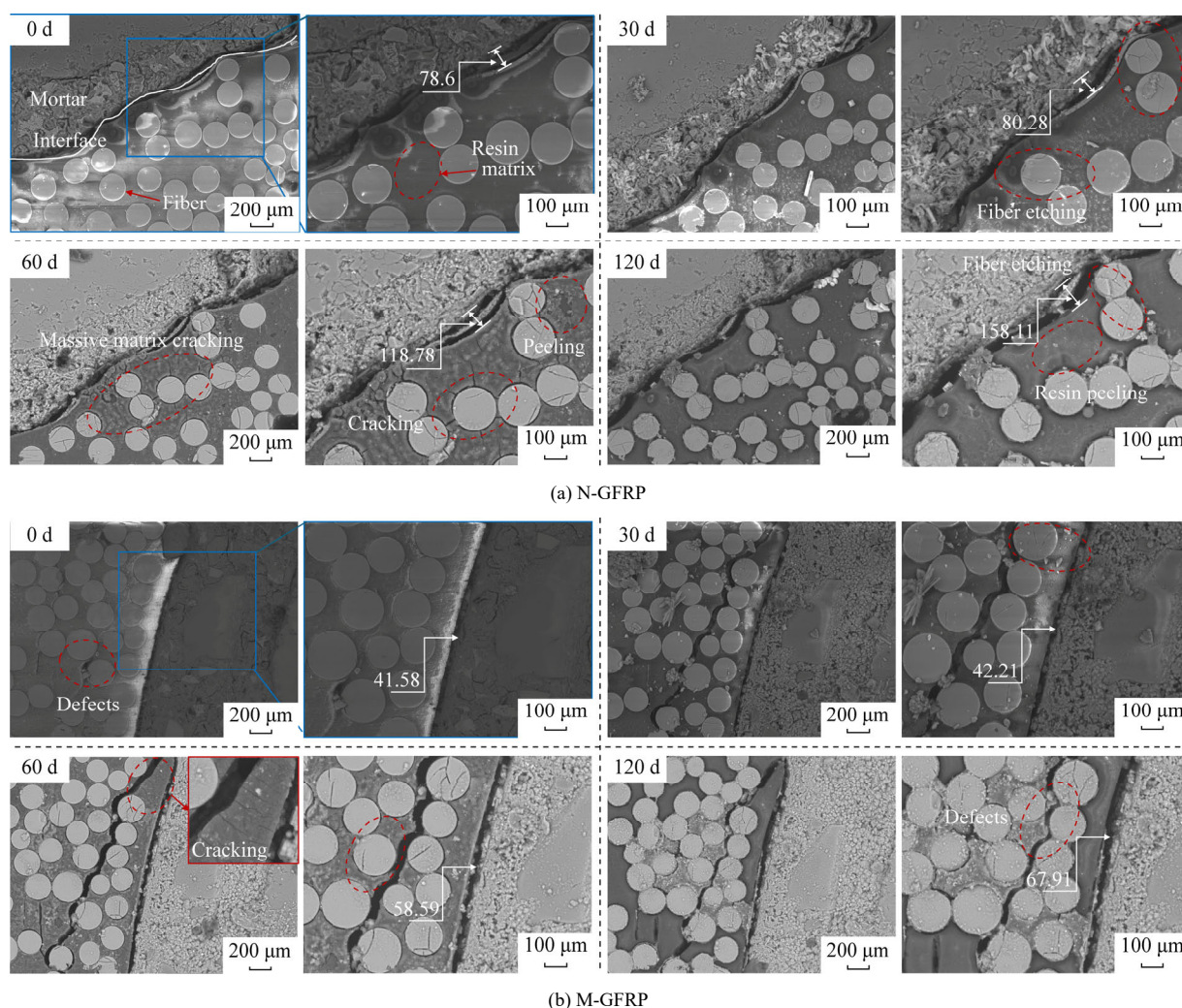


图 7 GFRP 筋-混凝土界面微结构演变
Fig. 7 Microstructural evolution of GFRP-concrete interface

图 8 为缩尺样品的 X-ray CT 扫描结果。在重建的三维 CT 图像基础上, 分割感兴趣区域, 基于 X

射线吸收度与灰度值的关系, 定量分析混凝土/GFRP 筋界面处各组分的体积含量, 分别为纤维(V_f)、树脂

(V_f)和空隙(V_v)。

未腐蚀时, 界面处的空隙率较低, 树脂较为充盈, V_v 、 V_f 为 1.02%和 30.02%。随着腐蚀龄期的增加, 可明显观察到界面处的空隙增大, 逐渐占据树脂区域, 腐蚀 120 d 后, N/M-GFRP 与混凝土粘结界面处的 V_f 分别降至 18.52%和 23.35%, V_v 分别增加至 19.38%和 11.45%。显然, 腐蚀后 M-GFRP 的 V_f 含量高于 N-GFRP, 该现象表明环氧基体改性后,

有效缓解了基体的腐蚀速率。而 N/M-GFRP 筋界面处 V_f 的下降幅度相较于树脂基体较低, 腐蚀 120 d 后, 二者分别下降了 6.86%和 3.76%, 说明基体降解为 GFRP 筋与混凝土界面粘结性能劣化的主要影响因素。

基于 X-ray-CT 扫描获得 N/M-GFRP-混凝土界面的基体体积分数含量, 拟合其与 GFRP 筋/混凝土粘结界面最大应变值的关系, 见图 9。由图 9 可见,

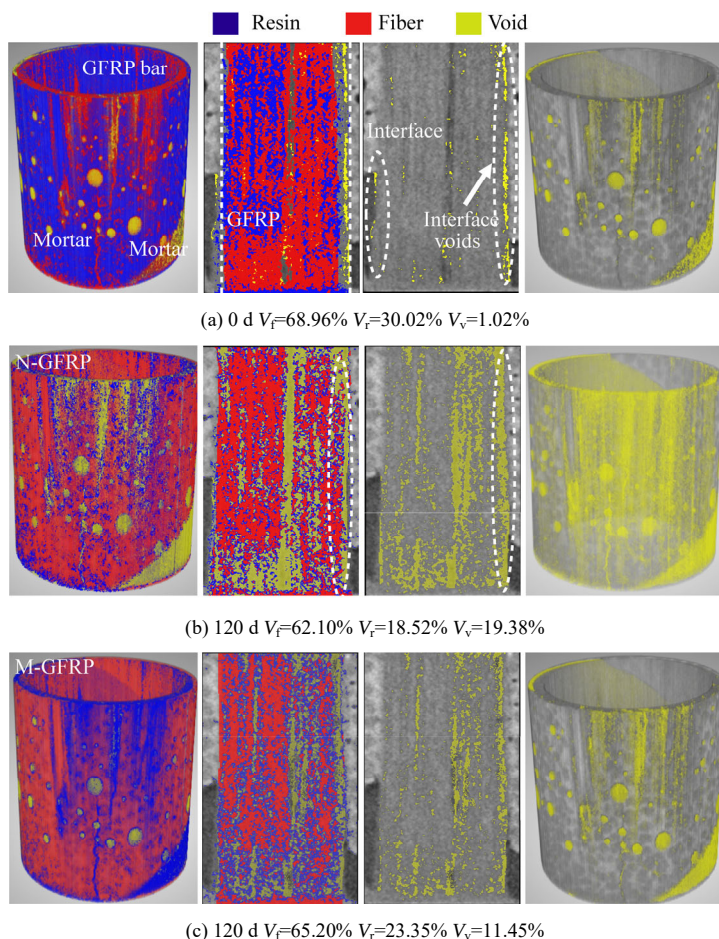


图 8 混凝土/GFRP 筋界面区域的 X-ray CT 图

Fig. 8 X-ray CT images of the concrete/GFRP reinforcement interface region

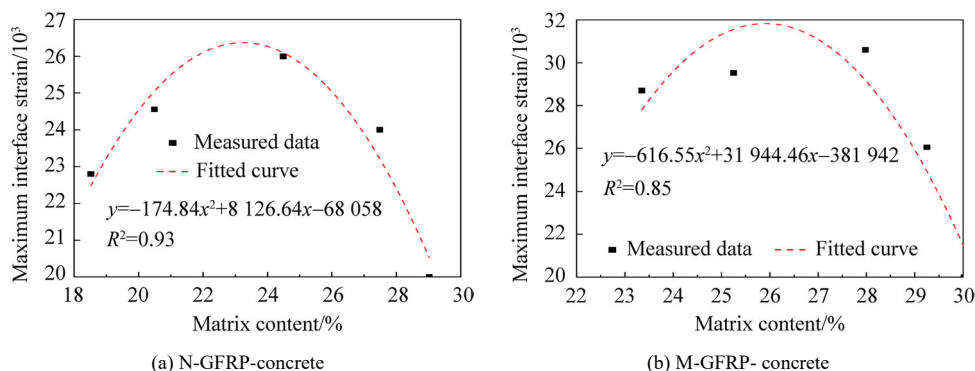


图 9 GFRP/混凝土界面基体体积分数含量与粘结界面最大应变的拟合曲线

Fig. 9 Fitted curves of matrix content at the GFRP/concrete interface versus maximum strain at the bond interface

基体体积分数含量与界面最大应变呈二次函数关系。腐蚀初期 V_r 含量小幅降低, 但粘结界面处应变有所上升。腐蚀初期, 筋材表面虽有一定程度的降解, 但该过程可能导致基体表面粗糙度的增加或吸湿膨胀, 从而增加界面粘结力; 高温下混凝土的持续水化, 使其劈裂强度增加, 有利于筋材与混凝土间的握裹。但随着腐蚀龄期的持续增加, 筋材表面基体的降解程度显著, 使得 GFRP 筋与混凝土间的界面粘结性能劣化, 从而导致粘结界面处的应变下降。

3 结论

1) 采用微波 EG、工业 CNT 表面疏水修饰和新型有机硅混合改性环氧的方法获得耐蚀 GFRP 筋。相比未改性筋材, 耐蚀 GFRP 筋与混凝土初始界面粘结力提升了 7.87%, 腐蚀 120 d 后界面粘结力提高了 15% 左右, 且脱粘过程的破坏模式以混凝土开裂和 GFRP 筋拔出为主。

2) 基于 DIC 获得粘结界面处的应变随着拉拔荷载的增加逐渐增大, 在加载端附近达到最大值。腐蚀 120 d 后, N-GFRP、M-GFRP 与混凝土界面最大应变值分别降至 22.8×10^{-3} 、 28.7×10^{-3} , 二者相比, 改性后界面处的最大应变增加了约 25.87%。

3) 基于界面微结构表征得到 GFRP 筋与混凝土脱粘主要表现为界面处基体的降解。经腐蚀离子侵蚀, 基体表面发生大面积龟裂与降解, 使得界面间距不断扩大, 当腐蚀至 120 d 后, N-GFRP、M-GFRP 与混凝土界面间距比未腐蚀时分别增加了 100% 和 60% 左右。M-GFRP 与混凝土粘结界面处的 V_r 值(23.35%)高于 N-GFRP(18.52%)。基体改性缓解了界面基体的降解速率, 改善了 GFRP 筋与混凝土界面的粘结性能。

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Evolution of Bonding Performance and Improvement Mechanism of Glass Fiber Reinforced Plastics-Concrete Based on Resin Matrix Modification

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Extended Abstract

Introduction The bonding properties of Fiber Reinforced Plastics (FRP) -concrete composites is directly related to the load carrying capacity and durability of FRP reinforced concrete structures. In addition, the study of bond properties can help us better understand how FRP bars behave in concrete and how they react under specific environmental conditions (*e.g.*, high temperature, humidity, corrosion, *etc.*). This is valuable for predicting and improving the long-term performance of concrete structures. However, in offshore engineering, structures are exposed to strong corrosive environments all year round. Under the erosion of internal FRP bars by corrosive ions and the highly alkaline environment of the concrete pore solution, the matrix on the surface of FRP bars firstly suffers from deterioration phenomena such as dissolution, plasticization, and microcrack formation. Consequently, the bonding properties of the FRP-concrete interface are seriously affected, leading to the deterioration or failure of the concrete structure. Therefore, improving the corrosion resistance of FRP reinforcement is an important measure to ensure the long-term service of FRP-reinforced concrete structures. In this paper, the resin matrix modification of GFRP bars was realized by self-synthesized organosilicones and surface hydrophobic modification of nanofillers to obtain highly corrosion-resistant GFRP bars. To investigate the degradation of the interfacial adhesion between highly corrosion-resistant GFRP reinforcement and seawater-seasand concrete (SSC) in simulated pore solution of SSC at 60 °C, and to reveal the mechanism of GFRP reinforcement-concrete adhesion enhancement through interfacial microstructure analysis.

Methods Organosilicon synthesis: Hydrogen-containing silicone oil (PMHS) was mixed with γ -(2,3-epoxypropyloxy) propyltrimethoxysilane (KH560) in a mass ratio of 1:1, with ethanol as the solvent, and reacted under the catalytic effect of NaOH for 8 h at ambient temperature using a magnetic stirrer (200 r/min), and then kept for spare.

CNT surface modification: 0.03% (mass fraction) of CNTs was stirred and dispersed into an ethanol and KOH organic solvent, and the CNT modifier was subsequently obtained by adding hydrogen-containing silicone oil (PMHS) and ethyl silicate (TEOS) after ultrasonic dispersion.

Surface modification of EG: EG was dripped onto the surface of expanded graphite in the mass ratio of TEOS:PMHS=3:1 in a vacuum environment; subsequently, the samples were placed in a microwave oven at 800 W for a rapid expansion for 10 s. The modified expanded graphite was placed in the organic solvents of KOH and anhydrous ethanol with heating and stirring until the mixture was homogeneous.

Preparation of modified epoxy resin hybrids: A bisphenol A-type epoxy resin (EGEBA), methyl tetrahydrophthalic anhydride curing agent (MeTHPA), and an accelerator (DMP-30) were mixed in a mass ratio of 100:85:5. Subsequently, 5% of the self-synthesized organosilicon was mixed with CNT and EG surface-modified nanofillers with a total solid content of 0.03% into the epoxy emulsion, and the mixed solution was stirred homogeneously using ultrasonication combined with triple-roller shear dispersion to obtain the modified epoxy resin mixture.

Preparation and testing of pull-out specimens: modified GFRP bars were embedded in the upper surface of concrete to a depth of 5 mm, and the size of the concrete was set to 100 mm × 100 mm × 300 mm. Hydraulic jacks were used to carry out single-end pull-out tests on the bonded specimens, and a digital CCD camera was used to capture the displacement and deformation of the interface throughout the entire process of de-bonding.

Microstructural characterization: the scaled-down specimens were prepared, and the microstructural changes at the FRP-concrete interface of the scaled-down specimens after corrosion were observed using scanning electron microscopy and X-ray computed tomography.

Results and discussion From the pull-out damage pattern of the GFRP-concrete interface, it can be seen that after 120 d of corrosion, large areas of resin degradation on the surface of the N-GFRP reinforcement resulted in fiber exposure and carbon fiber rib detachment. Compared with N-GFRP, the corrosion degree of M-GFRP bar is less severe, and its surface only has speckled local yellowing and surface roughness phenomenon. Compared with the unmodified bars, the initial interfacial adhesion between corrosion-resistant GFRP bars and concrete was improved by 7.87%, and the interfacial adhesion was improved by about 15% in the 120 d-corrosion experiment. In addition, the maximum strain values at the interfaces of N-GFRP and M-GFRP with concrete decreased to 22.8×10^{-3} 、 28.7×10^{-3} , respectively in the 120 d-corrosion experiment. After the modification of the resin matrix of the FRP bars, the corrosion resistance of the bars is improved, which can better absorb and disperse the stress brought by the external load, making the stress distribution at the FRP-concrete interface more uniform and the deformation increased, thus slowing down the rate of loss of adhesive force.

Corrosion to 120 d, the interfacial spacing between N/M-GFRP and concrete reached 158.11 μm and 67.91 μm , respectively, which increased by about 100% and 60% compared to the uncorroded condition. The V_f value at the M-GFRP-concrete bonded interface (23.35%) was higher than that of N-GFRP (18.52%). The surface substrates at the N-GFRP reinforcement-concrete interface all were detached and a new layer was exposed. In contrast, the localized matrix spalling at the M-GFRP-concrete interface was less corrosive than that of the N-GFRP bars. Therefore, the debonding of GFRP-concrete mainly depends on the degradation degree of the matrix at the interface. The affinity between the resin matrix and the concrete was improved by matrix modification, and the introduction of hydrophobic network led to the improvement of the waterproofing performance of the bars, which effectively mitigated the degradation of the resin matrix of the bars, and then improved their bonding performance.

Conclusions The main conclusions of this paper are summarized as following. Compared with the unmodified bars, the initial interfacial adhesion between corrosion-resistant GFRP bars and concrete was improved by 7.87%, and the interfacial adhesion was improved by about 15% in the 120 d-corrosion experiment. In addition, the maximum strain values at the interfaces of N-GFRP and M-GFRP with concrete decreased to 22.8×10^{-3} 、 28.7×10^{-3} , respectively in the 120 d-corrosion experiment. Compared with the two, the maximum strain at the interface increased by about 25.87% after modification. The damage modes of the debonding process were dominated by concrete cracking and GFRP bar pullout. The degradation rate of the interfacial matrix was mitigated by resin matrix modification, which improved the adhesive properties of the GFRP-concrete interface.

Keywords matrix modification; interfacial bonding; digital image correlated technologies; molecular simulation; microstructural evolution