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EVA与硅烷乳液改善防水砂浆性能的微观机理

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摘要:通过四点弯曲强度、黏结强度、冻融循环及热重、压汞和扫描电镜等试验研究了乙烯-乙酸乙烯酯共聚乳液(EVA)和硅烷乳液对高韧性防水砂浆力学性能和抗冻性的影响规律及作用机理.结果表明:EVA基本不影响砂浆后期弯曲性能,但显著提高其与基层的黏结强度;随EVA掺量增加,砂浆孔隙率先增大后减小,抗冻性先降低后提高;硅烷乳液的掺入显著降低了水化产物在聚乙烯醇(PVA)纤维表面的附着,导致砂浆弯曲性能下降;当硅烷乳液掺量较高时,PVA纤维与基体界面粗糙度明显增加,砂浆弯曲性能提高;内掺硅烷乳液增加了毛细孔含量,有助于缓解孔隙水结冰产生的膨胀应力,从而显著提高砂浆抗冻性.

关键词:防水砂浆;聚合物乳液;弯曲性能;抗冻性;微观结构
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Microstructural Mechanism of EVA and Silane Emulsion Improving Waterproof Mortar

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Abstract: Influence of ethylene-vinyl acetate copolymer(EVA) and silane emulsion on the mechanical properties and frost resistance of the high toughness waterproof mortar was investigated through four-point bending test, bonding test, freeze-thaw cycle test, thermogravimetric analysis, mercury intrusion test and scanning electron microscopy. The results show that EVA has little effect on the bending properties at late age, but significantly improves its bonding strength. With the increase of EVA content, the porosity of mortar initially increases and subsequently decreases, and the frost resistance decreases at first and then increases. The inclusion of silane emulsion significantly reduces the adhesion of hydration products on poly vinyl alcohol(PVA) fibers, resulting in the decreasing of bending properties of mortar. By contrast, at high dosages of silane emulsion, the interfacial roughness between fiber and matrix increases obviously, which is beneficial to increasing the bending properties. The incorporation of silane emulsion alleviates the expansion stress caused by water freezing due to the increasing capillary pores, which significately improves the frost resistance.

Key words: waterproof mortar; polymer emulsion; bending property; frost resistance; microstructure

中国高铁的路基防水封闭层主要采用纤维混凝土材料,但因其脆性大、变形适应性差、接缝多等缺点,导致其在应用时出现了不同程度的开裂、粉化等问题,显著降低了封闭层的防水效果[1].高韧性纤维

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增强水泥基材料具有较高的变形适应性,在拉伸荷载下可使裂缝分散,单条裂纹宽度小于100 μm,不仅不会对结构耐久性不利,而且经过合理的设计还可用于铺设无接缝混凝土路面[2].但该材料亲水性较强,可通过内掺聚合物乳液的方法来提高其防水和抗冻性能.

Azadmanesh等[3]在工程水泥基复合材料(ECC)中掺入丁苯橡胶和乙烯-乙酸乙烯酯共聚乳液(EVA)以提升其拉伸和弯曲性能.Liang等[4]将聚丙烯纤维掺入聚合物改性水泥基复合材料中以提升其力学性能及抗渗性能.Liu等[5]研究了不同聚灰比下碳纤维聚合物混凝土的力学性能.Chen等[6]发现EVA的掺入降低了ECC的抗压及抗拉强度.Feng等[7]发现硅烷乳液的掺入改善了砂浆的力学性能.张鹏等[8]发现掺入硅烷显著降低了混凝土的强度.Zhang等[9]认为硅烷乳液降低了混凝土的强度.目前有关聚合物乳液对高韧性纤维增强水泥基材料耐久性方面的研究相对较少,尤其是硅烷乳液对防水砂浆性能的影响机理尚不清晰.因此,本文选择EVA和硅烷乳液,通过四点抗弯强度、黏结强度和冻融循环等试验,研究不同聚合物乳液对高韧性纤维增强水泥砂浆力学性能和抗冻性的影响规律,并对比分析其微观机理.

1 试验

1.1 原材料与配合比

采用北京金隅集团股份有限公司提供的P·O 42.5水泥(物理性能指标见表1)、Ⅱ级粉煤灰和石英砂(颗粒粒径为0.10~0.25 mm),Kuraray公司提供的聚乙烯醇(PVA)纤维(性能参数见表2)和北京中硅合聚新材料有限公司提供的EVA、硅烷乳液与减水剂.EVA乳液的固含量(质量分数,文中涉及的含量、掺量等均为质量分数)为50%,乳胶粒子平均粒径为0.40 μm,最低成膜温度为0 ℃.硅烷乳液主要成分为异辛基三乙氧基硅烷聚合物,乳液固含量为47%,乳胶粒子平均粒径为1.05 μm、减水剂为聚羧酸高效减水剂,固含量为40%.

参照前期研发的低收缩砂浆基础配合比m(水泥):m(粉煤灰):m(矿渣):m(纤维):m(砂):m(水)=1.000:0.080:0.020:0.018:0.500:0.400,添加减水剂确保浆体扩展度基本保持稳定.以水泥质量为基准,设置EVA的掺量(w_{EVA})为0%、1.0%、1.5%和2.0%;设置硅烷乳液的掺量(w_H)为0%、0.5%、1.0%和1.5%.

表1　P·O 42.5水泥的物理性能
Table 1　Physical properties of P·O 42.5 cement

Density/(g·cm^{-3})	Specific surface area/(m^2·kg^{-1})	Normal consistency/%	Soundness/mm	Setting time/min		Measured flexural strength/MPa		Measured compressive strength/MPa	
				Initial	Final	3 d	28 d	3 d	28 d
3.08	376	28.5	1.0	185	250	5.7	8.2	30.5	48.2

表2　PVA纤维的性能参数
Table 2　Performance parameters of PVA fiber

Diameter/mm	Length/mm	Density/(g·cm^{-3})	Elastic modulus/GPa	Tensile strength/MPa	Elongation/%
0.039	12	1.2	40	1 600	7

1.2 试验方法

1.2.1 试件制备

试件的制备过程为:(1)将水泥、粉煤灰、砂、矿渣混合后在低速(62 r/min)搅拌1 min,然后逐次加入水、乳液和减水剂;(2)接着低速搅拌1 min,再高速(125 r/min)搅拌1 min;(3)加入PVA纤维后,重复步骤(2);(4)将拌和均匀的砂浆倒入模具中振动成型,24 h后拆模并养护至规定龄期.

1.2.2 宏观性能测试

制备2批40 mm × 40 mm × 160 mm的试件,一批放入标准养护室((20 ± 2) ℃,相对湿度RH≥98%)中分别养护至3、28 d,然后采用WAW600型万能试验机,按照T/CECS 997—2022《高韧性混凝土加固砌体结构技术规程》测试试件的弯曲性能.另一批标养至25 d,按照DL/T 5126—2021《聚合物改性水泥砂浆试验规程》,称量试件初始质量和冻融循环后的质量并拍照,采用质量损失率和外观破坏形貌来评判其抗冻性能.

将拌和均匀的砂浆倒入装有应变计的100 mm × 100 mm × 300 mm的模具中.为了模拟砂浆的实际应用环境,采用自然养护方式进行养护.砂浆的收缩情况自成型时刻开始监测直至养护28 d后结束.使用JMDK-Ⅱ型钢弦式应变采集仪采集砂浆内部的应变与温度数据.参考文献[10]和[11]所述的方法,从

总变形中剔除掉水泥水化放热引发的应变ε_T(式(1)),获得砂浆真实的收缩值.

$$\varepsilon_T=\int_{T_0}^{T}\beta_T\mathrm{d}T \tag{1}$$

式中:β_T为给定龄期高韧性防水砂浆的热膨胀系数,μm/(m·℃);T_0为初始采集温度,℃;T为终止采集温度,℃.

将预先养护28 d的砂浆试件(40 mm×40 mm×80 mm,28 d抗压强度为40 MPa)放入40 mm ×40 mm×160 mm模具的一端,在另一端浇筑高韧性防水砂浆制备复合试件,标养28 d后按照JC/T 2381—2016《修补砂浆》进行测试,采用抗弯强度评定高韧性防水砂浆与基块之间的黏结强度.

1.2.3 微观测试

取适龄试件的芯部,终止水化并真空干燥24 h.任选1块试件芯部研磨成粉,筛除纤维和细砂;取20 mg放置于Setline同步热分析仪(TG/DSC)中,升温至1 000 ℃,升温速率为10 ℃/min,氮气保护;采用文献[12]的方法计算化学结合水与$Ca(OH)_2$含量.任取3块试件芯部,修剪为ϕ10×5 mm的圆饼,使用异丙醇浸泡24 h后放入(40±2) ℃的真空干燥箱中烘干至恒重,用AUTOSCAN-33型压汞仪中测试其孔结构.任取1试件芯部修剪为ϕ3×2 mm的薄片并喷金,置于FEI Quanta 200型扫描电子显微镜(SEM)中观测其微观形貌.

2 结果与讨论

2.1 EVA乳液的影响

2.1.1 弯曲性能

EVA乳液对高韧性防水砂浆弯曲荷载-位移(F-δ)曲线的影响见图1,其弯曲性能参数见表3.结合图1和表3可见:试件的弯曲荷载-位移(F-δ)曲线大致可分为线弹性、应变硬化和应变软化3个阶段,随龄期的增长,砂浆的初裂荷载、弯曲强度、最大位移及弯曲韧性均降低;掺入EVA乳液后,3 d的弯曲性能参数均明显下降,其中弯曲韧性下降了33.1%;w_{EVA}变化对28 d的弯曲性能参数影响不大.

纤维增韧水泥砂浆的弯曲性能与纤维、基体和二者界面的协同效应密切相关.当纤维与基体黏结较弱时,纤维多呈拔出模式,此时适当提高界面黏结强度以及纤维拔出过程中的摩擦应力均有利于增强纤维的桥接作用,进而提高砂浆的弯曲性能;而当纤维与基体的黏结过强时,纤维呈断裂模式,无法发挥

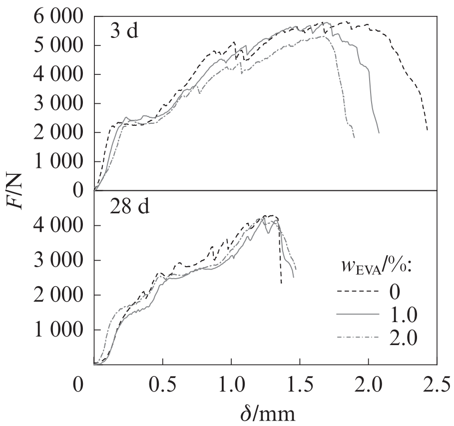


图1 EVA乳液对高韧性防水砂浆弯曲荷载-位移(F-δ)曲线的影响

Fig. 1 Effect of EVA emulsion on F-δ curves of high toughness waterproof mortar

表3 高韧性防水砂浆的弯曲性能参数

Table 3 Parameters of bending properties of high toughness waterproof mortar

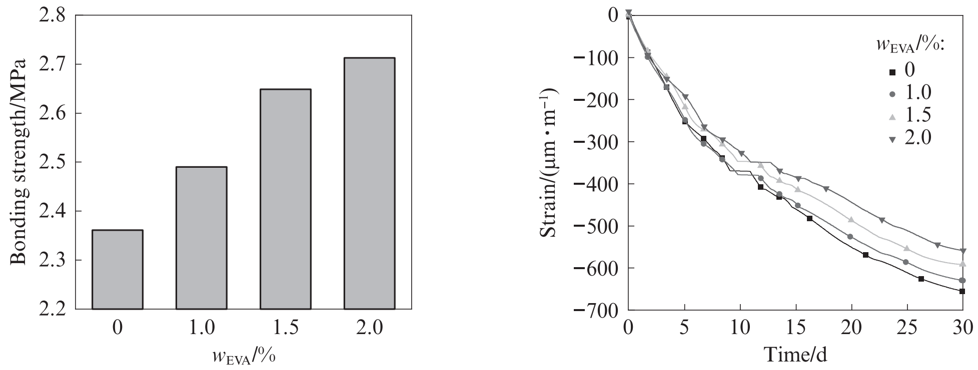
Time/d	w_{ECA}/%	Bending strength/MPa	Maximum displacement/mm	Bending toughness/(kJ·m^{-3})
3	0	13.652	1.834	144.889
	1	13.570	1.697	119.331
	2	12.434	1.673	96.747
28	0	10.066	1.309	54.306
	1	9.891	1.244	50.949
	2	9.844	1.212	56.157

裂纹桥接作用,从而导致砂浆的弯曲性能显著降低.通常认为,适当调节纤维与基体的界面黏结使纤维被稳定拔出是实现高韧性的前提[6,13-15].随着养护龄期的增长,大量水化硅酸钙凝胶的生成增强了基体与纤维之间的黏结力,从而导致纤维由拔出模式转为断裂模式,难以有效发挥裂纹桥接作用.由图1(b)可知,高韧性防水砂浆的弯曲性能随龄期的增加而降低,这与前人的结论一致[16-17].类似地,胶黏性EVA的加入显著提高了基体与纤维的黏结力,限制了纤维的裂纹桥接作用,从而明显降低了砂浆3 d的弯曲性能;而28 d弯曲性能基本不变,可能源于EVA对水泥水化以及砂浆微结构的影响,这将在**2.1.4**深入分析.

2.1.2 黏结强度与收缩

图2为EVA乳液对高韧性防水砂浆界面黏结强度和收缩的影响.从图2可见:当w_{EVA}从0%增加至2.0%时,砂浆的黏结强度从2.36 MPa增大至2.71 MPa,提升了14.8%,显示出EVA较强的增黏作用[18-21];EVA乳液的加入降低了高韧性防水砂浆的收缩,随着龄期的增长降低越来越明显.有文

献[22-25]表明,砂浆的收缩越低,砂浆与基层界面处的残余应力越小,渗透到基层孔隙中的水泥水化产物对基层的机械咬合力越强,也有利于提高砂浆与基层的界面黏结强度.



(a) Bonding strength(28 d)　(b) Shrinkage

图2　EVA乳液对高韧性防水砂浆的界面黏结强度和收缩的影响

Fig. 2　Effect of EVA emulsion on interface bonding strength and shrinkage of high toughness waterproof mortar

2.1.3　冻融循环

图3为EVA乳液对高韧性防水砂浆抗冻性的影响(冻融循环次数为150次).从图可见:冻融循环后砂浆的质量损失率随w_{EVA}的增加先增大后减小;当$w_{EVA}=1.0\%$时,质量损失率达到最大;当$w_{EVA}>2.0\%$之后质量损失率仅轻微降低.

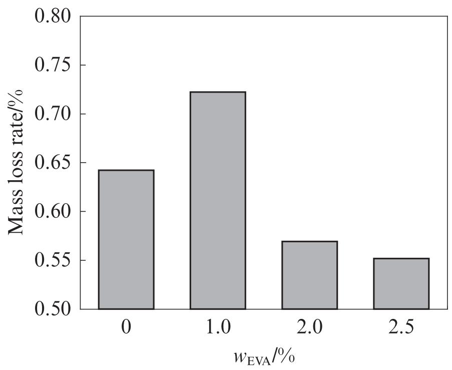


图3　EVA乳液对高韧性防水砂浆抗冻性的影响

Fig. 3　Effect of EVA emulsion on the frost resistance of high toughness waterproof mortar

研究表明,水泥基材料的冻融破坏主要由砂浆孔隙特征及自身强度决定,即孔隙率越高或强度越低,冻融循环导致的质量损失率越大[26-27].结合前述分析可知,EVA乳液轻微降低砂浆的弯曲强度,不利于提高其抗冻性,应表现为质量损失率轻微增加.但这与高EVA掺量下质量损失率显著降低的结果相悖,由此推断2.0% EVA乳液的加入可能对高韧性防水砂浆的孔结构产生了有利的影响.

2.1.4　微观结构

图4为EVA乳液对硬化水泥浆的化学结合水和$Ca(OH)_2$含量的影响.由图4可见:随着w_{EVA}的增加,硬化水泥浆中的化学结合水和$Ca(OH)_2$含量均减少,表明EVA在28 d龄期时仍抑制水泥水化;当w_{EVA}增至2.0%时,化学结合水和$Ca(OH)_2$含量分别降低了17.9%和26.2%.通常认为,一方面,乳液抑制水泥水化主要源于乳液粒子大量吸附在水泥颗粒表面,聚合物包裹层抑制了水分传输交换及水化产物成核,由此减少了水化产物凝胶的生成,进而降低了基体与纤维的界面黏结;另一方面,具有胶黏性的EVA可以增强基体与纤维的黏结力[6,28-30].因此,在二者的综合作用下,高韧性防水砂浆28 d的弯曲性能变化不明显.

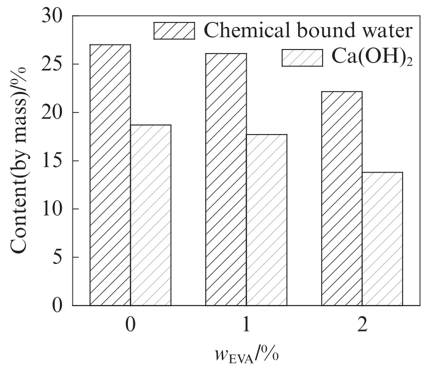


图4　EVA乳液对硬化水泥浆的化学结合水和$Ca(OH)_2$含量的影响

Fig. 4　Effect of EVA emulsion on chemical bound water and $Ca(OH)_2$ in hardened cement pastes (28 d)

Mehta等[31-32]研究了水泥基材料耐久性与孔隙尺寸的关系,根据孔径d将孔隙分为微孔($d<4.5$ nm)、小孔(4.5 nm$\leqslant d<$50.0 nm)、中孔(50.0 nm$\leqslant d\leqslant$100.0 nm)和大孔($d>$100.0 nm).砂浆抗冻性与孔结构密切相关,即$d>$50.0 nm的孔占比越高、孔隙连通性越大,抗冻性越差[33].EVA乳液对高韧性防水砂浆

孔结构的影响如图5所示．由图5可见：当$w_{EVA}=1.0\%$时，总孔体积与$d>50$ nm孔的体积显著增大，孔隙率从20.03%增至23.23%，导致砂浆抗冻性降低，150次冻融后质量损失率达到最大；随w_{EVA}进一步增大，总孔体积与大孔体积急剧减小，孔隙率降至18.46%，这可能源于聚合物对孔隙的填充与封堵作用[34-37]．因此，掺入2.0% EVA有利于提高砂浆抗冻性，即降低冻融循环后的质量损失．此外，聚合物膜对裂缝的桥接作用能够阻碍基体剥落，也有助于减少砂浆质量损失．

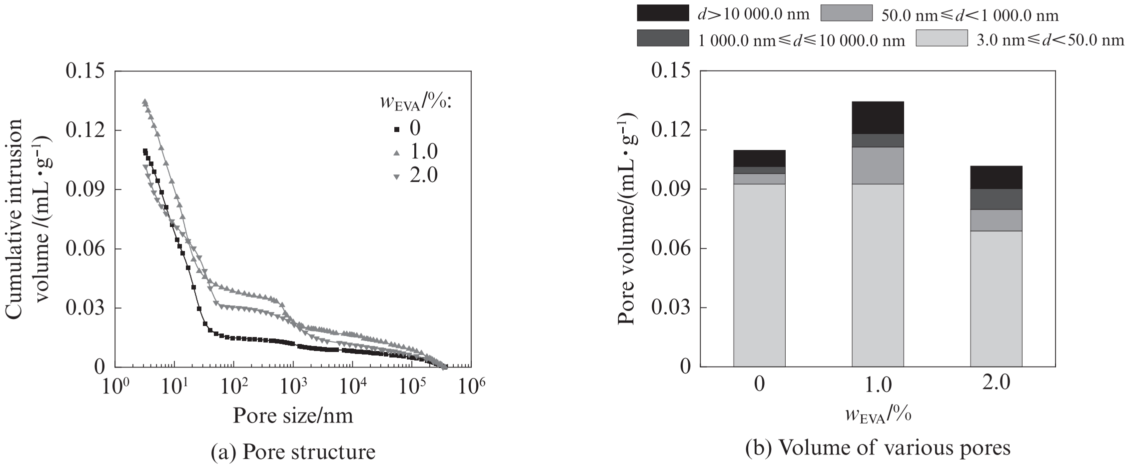


图5　EVA乳液对高韧性防水砂浆孔结构的影响

Fig. 5　Effect of EVA emulsion on the pore structure of high toughness waterproof mortar (28 d)

图6为EVA乳液对高韧性防水砂浆微观形貌的影响及作用机理示意图．由图6可见：(1)未掺加EVA时，PVA纤维表面几乎布满了水泥水化产物，这主要是由于亲水性PVA纤维表面的羟基易与水泥水化产物发生键合形成化学键[14, 38-41]．此种强烈的化学黏结导致试件破坏时大部分纤维呈现断裂模式．(2)高EVA掺量下水泥水化受到抑制，纤维表面黏附的水化产物明显减少，但纤维仍呈现明显的拉丝断裂现象，这说明EVA的胶黏作用使得纤维与基体之间存在较强黏结，在外力荷载作用下纤维始终难以被稳定拔出．这与砂浆后期弯曲性能基本不受EVA影响的结论相对应．

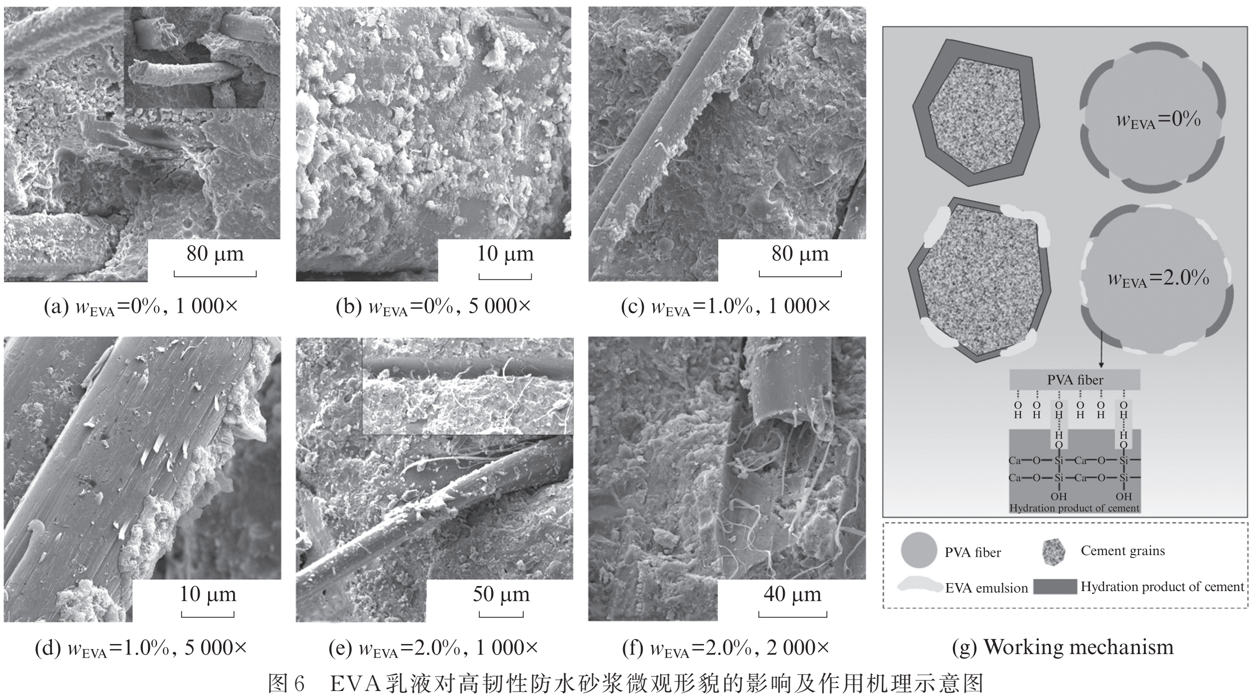


图6　EVA乳液对高韧性防水砂浆微观形貌的影响及作用机理示意图

Fig. 6　Effect of EVA emulsion on microstructure of high toughness waterproof mortar and its working mechanism(28 d)

2.2　硅烷乳液的影响

2.2.1　弯曲性能

硅烷乳液对高韧性防水砂浆弯曲性能的影响如图7所示．由图7可见，随着w_H的增加，砂浆抗弯强度、跨中位移和弯曲韧性均先减小后增大，但始终低于未掺硅烷的砂浆．与EVA不同：硅烷除了破乳成膜等物理过程外，还会发生水解、缩聚等化学过程，最终在水化产物表面包覆一层有机憎水膜[42]，极大削弱了水化产物与纤维的黏结，导致纤维-基体界面的化学脱黏能过低[14]，即在荷载作用下纤维可轻易脱黏．因此，在宏观上表现为掺入硅烷后砂浆弯曲性能显著下降．

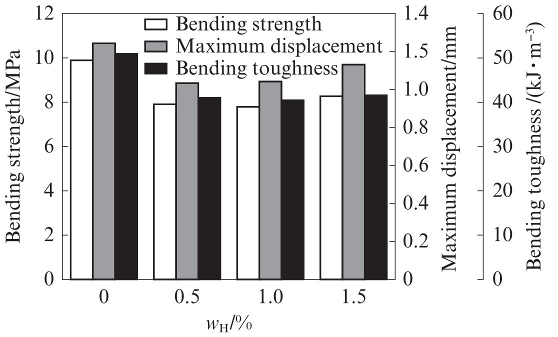


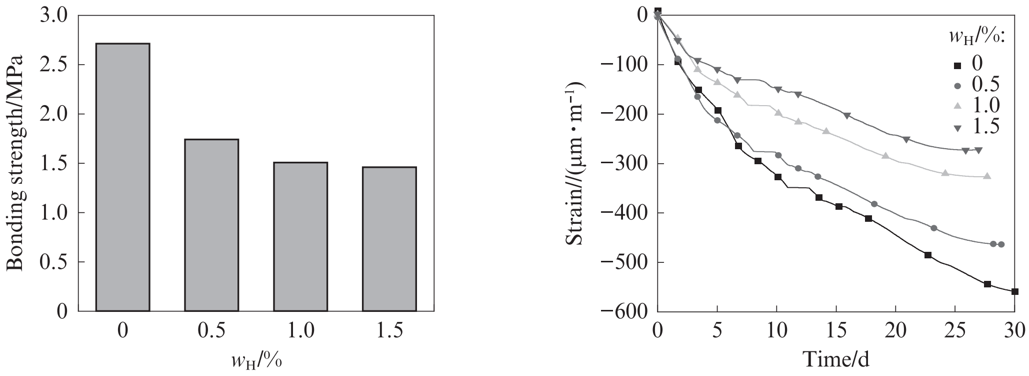
图7　硅烷乳液对高韧性防水砂浆弯曲性能的影响

Fig. 7　Effect of silane emulsion on bending properties of high toughness waterproof mortar

前人研究指出，当界面化学脱黏能过低时，滑移阶段的界面摩擦应力是决定纤维增强水泥砂浆弯曲性能的关键[43]．由此推断，高w_H下砂浆弯曲性能的提升可能源于硅烷对砂浆微结构以及纤维-基体界面摩擦力的影响，这将在第**2.2.4**深入分析．

2.2.2　黏结强度与收缩

图8为硅烷乳液对高韧性防水砂浆黏结强度和收缩的影响．从图8可以看出：当w_H从0%增至1.5%时，黏结强度从2.71 MPa逐步降至1.46 MPa，损失率高达46%；收缩也逐步降低，这有利于降低砂浆-基层界面的残余应力，本应该提高砂浆的黏结强度，但试验结果却与之相反．究其原因可能是硅烷在水泥及其水化产物表面包覆的憎水膜，不易与基层中亲水的水化产物形成较强的化学黏结与机械咬合，进而导致黏结强度明显下降．



(a) Bonding strength(28 d)　　(b) Shrinkage

图8　硅烷乳液对高韧性防水砂浆黏结强度和收缩的影响

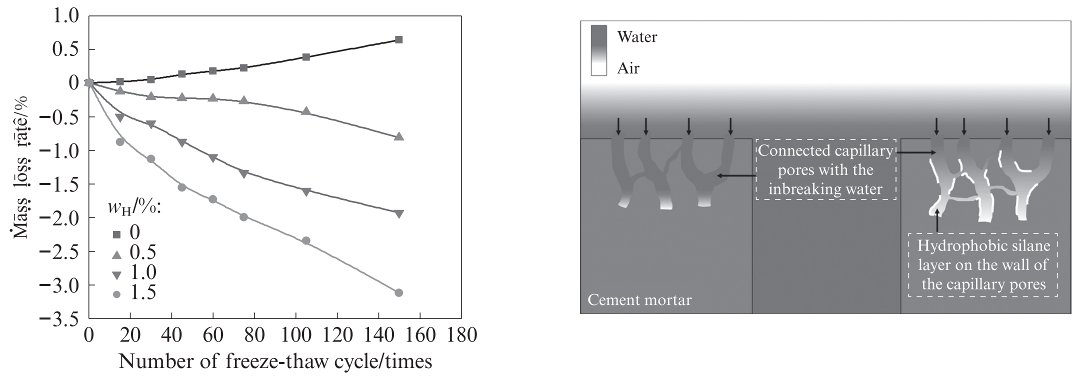
Fig. 8　Effect of silane emulsion on bonding strength and shrinkage of high toughness waterproof mortar

2.2.3　冻融循环

图9为硅烷乳液对砂浆抗冻性的影响及作用机理示意图．由图9可见：与空白试件经过冻融循环后质量损失率增加的结果相反，掺入硅烷后砂浆的质量损失率随循环次数增加逐渐降低为负值(即质量增加)；硅烷掺量越高，质量损失率降低程度越大．前文表明，硅烷乳液的掺入明显降低砂浆强度，不利于提高抗冻性，本应表现为质量损失率随着循环次数的增加而增大，这与实测结果相悖．结合冻融循环后砂浆的外观可知，空白试件表面出现明显的表层剥离，而掺加硅烷的砂浆表面几乎毫无破坏痕迹．由此推断，掺入硅烷乳液不仅降低了砂浆的吸水能力[9]，并且明显改变了砂浆孔结构，从而极大缓解了孔隙水在液-固转化过程中产生的膨胀应力，以致无法引起砂浆的破坏剥落，抗冻性提高．此外，水在冻融循环过程中逐渐进入砂浆内部孔隙，孔隙越多则冻融循环后砂浆质量增加越显著．

2.2.4　微观结构

图10为硅烷乳液对硬化水泥浆的化学结合水和$Ca(OH)_2$含量的影响．由图10可知：硅烷乳液明显抑制了水泥水化进程；当硅烷乳液掺量为1.5%时，化学结合水和$Ca(OH)_2$含量分别降低了17.5%和29.3%．究其原因，主要是硅烷包覆层阻碍了水化界面的离子交换以及水化产物的沉积成核．除了憎水膜的影响外，水化产物的减少会进一步削弱PVA纤维与基体之间的黏结，即降低纤维-基体界面的化学



(a) Frost resistance　　　　(b) Working mechanism

图9　硅烷乳液对高韧性防水砂浆抗冻性的影响与作用机理示意图

Fig. 9　Effect of silane emulsion on frost resistance of high toughness waterproof mortar and working mechanism

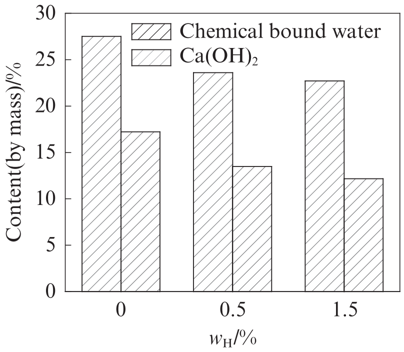


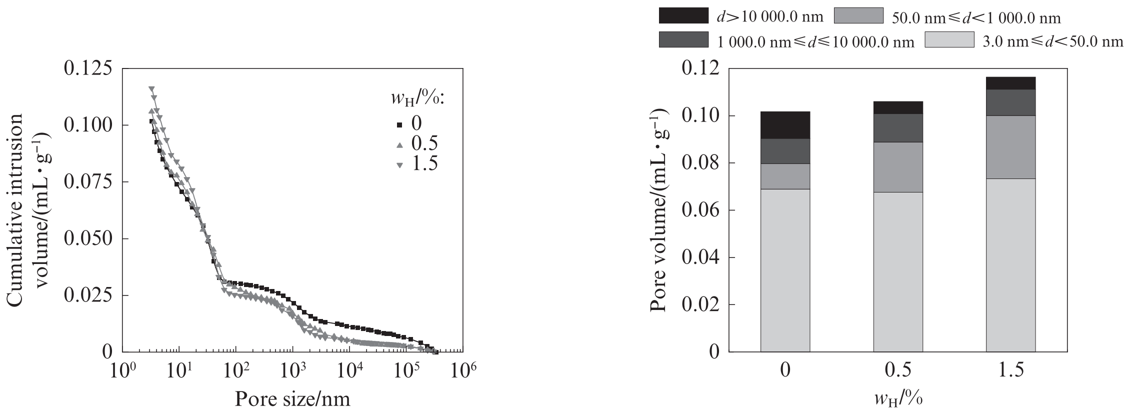
图10　硅烷乳液对硬化水泥浆的化学结合水和$Ca(OH)_2$含量的影响

Fig. 10　Effect of silane emulsion on chemical bound water and $Ca(OH)_2$ in hardened cement pastes (28 d)

脱黏能,这是导致弯曲性能随硅烷掺入而明显降低的另一原因.

图11展示了硅烷乳液对高韧性防水砂浆孔结构的影响.通常,水泥基材料的孔容以及毛细孔含量与水泥水化程度密切相关,水化程度越低则总孔容与毛细孔含量越高、连通性越好.硅烷乳液在28 d龄期时依然明显抑制水泥水化.由图11可见,内掺硅烷乳液后,砂浆的总孔容与毛细孔含量均有所增加,硅烷乳液掺量1.5%时临界毛细孔径略微提高.

尽管硅烷乳液改变了砂浆中毛细孔孔壁的亲疏水性,降低了其毛细吸水作用,但仍有少量水分可以进入到砂浆孔隙中.当孔隙水占比较低时,毛细孔的增加反而为水结冰膨胀提供了足够的空间,缓解了孔隙膨胀应力(见图9(b)).因此,砂浆的抗冻性显著提高.



(a) Pore structure　　　　(b) Volume of various pores

图11　硅烷乳液对高韧性防水砂浆孔结构的影响

Fig. 11　Effect of silane emulsion on pore structure of high toughness waterproof mortar (28 d)

图12为硅烷乳液对高韧性防水砂浆微观形貌的影响及作用机理图.由图12可见:(1)与空白组相比(图12(a)),掺入硅烷后基体-纤维界面过渡区明显更粗糙,这主要源于硅烷对水化产物结构的影响[9,42].粗糙的过渡区有利于提高纤维滑移拔出过程中的界面摩擦应力,进而在一定程度上提升砂浆的弯曲性能.(2)由于硅烷憎水膜的存在,亲水性PVA纤维不易与水泥水化产物产生键合,纤维表面仅附着少量水化产物,大部分水化产物疏松堆积在纤维周围(图12(b)).(3)图12(b)还显示,纤

维与基体间较弱的界面黏结导致试件破坏时纤维多以拔出模式为主.此外,疏松多孔的界面过渡区也很好地验证了掺入硅烷后砂浆孔隙率显著增加的结论.

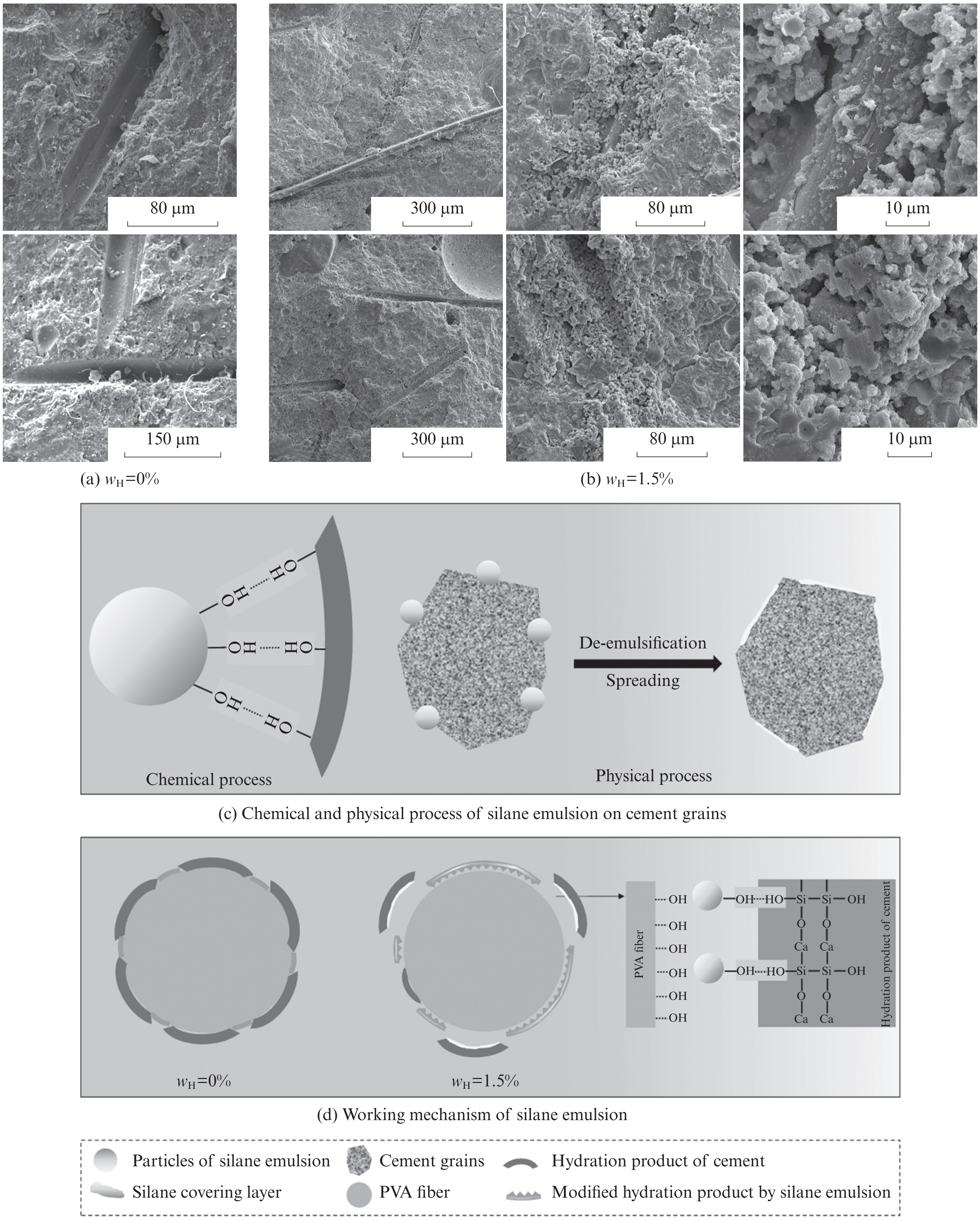


图12　硅烷乳液对高韧性防水砂浆微观形貌的影响及机理图

Fig. 12　Effect of silane emulsion on microstructure of high toughness waterproof mortar (28 d)

3　结论

(1)在一定掺量范围内,EVA乳液对高韧性防水砂浆28 d弯曲性能影响不大,但对水泥石与纤维的黏结性具有正反两方面作用,即:一方面EVA乳液的加入抑制了水泥水化,减少了纤维与水泥水化产

物的黏结性;另一方面其自身的胶黏性增强了纤维与基体的黏结.高EVA掺量时纤维呈现明显的拉丝断裂破坏,难以有效发挥裂纹桥接作用.

(2)掺入EVA乳液轻微减少了砂浆收缩,显著增加了砂浆与基层的黏结强度.随着EVA乳液掺量的增加,砂浆的抗冻性先下降而后明显提高,与总孔体积及大孔体积先增加后减少的规律相对应.

(3)硅烷乳液在抑制水泥水化的同时在水化产物表面形成了一层憎水膜,极大削弱PVA纤维与水泥基体的黏结,使弯曲性能显著下降;但在高硅烷掺量时会使纤维-基体的界面粗糙度明显提升,有利于增大纤维拔出过程的摩擦应力,进而轻微提升高韧性防水砂浆的弯曲性能.

(4)掺入硅烷乳液显著降低了砂浆的收缩及砂浆与基层的界面黏结强度.此外,硅烷乳液的加入明显增加了毛细孔体积,有助于缓解冻融循环过程中孔隙水结冰产生的膨胀应力.砂浆抗冻性随硅烷乳液的掺入显著提高.

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