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碳纳米纤维改性水泥基材料的变形及抗裂性能

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摘要:用超声波分散和表面修饰法将碳纳米纤维(CNFs)分散到水泥基材料中,制备了CNFs改性水泥基材料,研究了其变形及抗裂性能.结果表明:CNFs能抑制水泥净浆的自收缩和干燥收缩,且显著延缓水泥砂浆的开裂时间;当CNFs掺量为0.05%时,CNFs改性水泥砂浆的开裂时间较空白组延长了48.5%;CNFs在水泥基材料中产生的桥连和拔出效应,延缓了裂纹的扩展,从而减少了CNFs改性水泥砂浆的收缩变形,提高了材料的抗裂性能.

关键词:水泥基材料;碳纳米纤维;自收缩;干燥收缩;抗裂性能

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Deformation Properties and Crack Resistance of Carbon Nanofiber Modified Cement-Based Materials

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Abstract: Carbon nanofibers (CNFs) were dispersed in the cement-based materials by ultrasonic dispersion and surface modification to prepare the carbon nanofibers modified cement-based materials. The deformation properties and crack resistance of CNFs modified cement-based materials were studied. The results show that CNFs can inhibit the autogenous shrinkage and drying shrinkage of cement paste, and significantly delay the cracking time of cement mortar. When the mass content of CNFs is 0.05%, the cracking time of CNFs modified cement mortar is 48.5% longer than that of the control group. The bridging and pull-out effects of CNFs in cement-based materials delay crack growth, thus reduce the shrinkage deformation of CNFs modified cement mortar and improve the crack resistance of the materials.

Key words: cement-based material; carbon nanofiber; autogenous shrinkage; drying shrinkage; crack resistance

水泥基材料因其具有抗压强度大、经济性高等优点而被广泛应用于土木工程领域,但其韧性差、易断裂、抗拉强度低等因素造成的诸多问题同样需要引起关注[1-3].纳米材料往往具有填充效应和桥接效应,可以抑制水泥基材料微裂纹的产生,减少收缩,提升材料的韧性[4-7].在水泥基材料中掺入纳米级材料来改善上述问题是目前采用的方法之一,应用较多的纳米材料包括纳米SiO_2、纳米MgO、纳米碳材料等[8-16].

碳纳米纤维(CNFs)是一种非连续的纳米级石

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墨纤维,具有优异的力学、导电、导热性能.将CNFs掺入水泥基材料中,能够改善其缺陷.Gdoutos等[17]研究发现CNFs能够显著提升水泥砂浆的力学性能,掺量为0.1%的CNFs能使水泥砂浆弹性模量提高95%,断裂韧性提升119%.Wang等[18]研究发现在水泥净浆中掺入0.2%的CNFs,能够降低其孔隙率,通过SEM观察可见CNFs表面有大量的钙矾石包裹,表明CNFs与水泥基体之间黏结性较好.

目前针对CNFs改性水泥基材料的研究主要集中在分散方法[19]、力学性能[20]和导电性能[21]等方面,但是对其变形及抗裂性能方面的研究较为缺乏.本文研究了CNFs改性水泥基材料的变形及抗裂性能,利用圆环法评价了CNFs对水泥砂浆抗裂性能的影响,并通过微观试验揭示CNFs对水泥基材料的改性机理.

1 试验

1.1 原材料

水泥为海螺P·Ⅱ 52.5级水泥,其标准稠度用水量为26.5%(质量分数,文中涉及的掺量、比值等均为质量分数或质量比),初凝、终凝时间分别为123、160 min,7、28 d抗弯强度分别为7.5、8.3 MPa,7、28 d抗压强度分别为44.8、52.9 MPa,其化学组成见表1.试验砂采用ISO标准砂.CNFs为南京先丰纳米科技有限公司生产的XFM60碳纳米纤维,其物理性能见表2.CNFs分散剂为吉龙化学建材有限公司生产的LonS-P型聚羧酸高性能减水剂(RA).

1.2 试验方法

1.2.1 CNFs掺量的确定及其分散

当CNFs掺量$w>0.05\%$时,经超声波分散后无法得到相对稳定的分散液[9,19-20],因此,设定$w=0\%$(对照组)、0.01%、0.03%、0.05%(以水泥的质量计).

表1 水泥的化学组成

Table 1 Chemical composition of cement

$w/\%$

SiO_2	Al_2O_3	CaO	Fe_2O_3	SO_3	IL
22.18	4.51	64.67	3.15	2.56	1.36

表2 CNFs的物理性能

Table 2 Physical properties of CNFs

Diameter/nm	Length/μm	Purity/%	Specific surface area/($m^2·g^{-1}$)	True density/($g·cm^{-3}$)	Electric conductivity/($S·cm^{-1}$)
50-200	1-15	>95	>18	2.1	>100

采用超声波分散和表面修饰法对CNFs进行分散.先将分散剂滴入蒸馏水中并充分搅拌,接着将CNFs加入溶液并置于磁力搅拌器中搅拌5 min,随后用FS-750T型超声波分散仪对混合溶液进行分散,且全程在冰水浴条件下进行,分散30 min后得到CNFs分散液.

1.2.2 自收缩试验

根据ASTM C1698-09《Standard test method for autogenous strain of cement paste and mortar》,采用波纹管法进行自收缩试验.首先将CNFs分散液与水泥混合并用搅拌机搅拌后,得到CNFs改性水泥净浆,接着把净浆装入波纹管内,置于测试装置上进行测试.选择净浆的终凝时间作为起测时间,测试条件为(23±2) ℃、相对湿度RH=(50±4)%,每组3个平行试件,结果取平均值.自收缩试验试件的减水剂用量为0.2%,水灰比$m_W/m_C=0.28$、0.30、0.32.将自收缩试验试件命名为PC-X,其中$X=10\,000w$.

1.2.3 干燥收缩试验

根据JC/T 603—2004《水泥胶砂干缩试验方法》进行干燥收缩试验,试件尺寸为25 mm×25 mm×280 mm.首先将CNFs分散液与水泥混合后搅拌制得CNFs改性水泥净浆,接着将其装入模具中,24 h后拆模,置于水中养护2 d,再取出试件并用湿布擦去表面及钉头上的污垢,用比长仪测量试件的初始长度,测完后放入干缩养护箱养护,到达相应龄期t后从养护箱内取出,再次测量其长度.干燥收缩试验试件的水灰比$m_W/m_C=0.30$,其余配合比同自收缩试验.

1.2.4 圆环抗裂试验

圆环抗裂试验的装置尺寸参考文献[22],将CNFs分散液与水泥、标准砂充分混合,接着经胶砂搅拌机搅拌后装入圆环装置,分2层振实,每次振实30 s;浇筑完毕后,通过应变片与导线接入TDS-303数据采集仪,并在试件上表面覆膜,1 d后拆去钢制外环,开始测试试件收缩应变值.整个圆环试验过程保持在(23±2) ℃、RH=(50±4)%下进行,每组3个平行试件,结果取平均值.圆环抗裂试验的试件水灰比$m_W/m_C=0.50$,灰砂比$m_C/m_S=1:3$,其他配合比同自收缩试验.将圆环抗裂试验的试件记为MC-X.

2 结果与讨论

2.1 自收缩

CNFs改性水泥净浆的自收缩曲线见图1.由图1可见,整个CNFs改性水泥净浆自收缩过程大致可以分成3个阶段:第1个阶段为水泥净浆终凝后的10 h

之内,该阶段随着水泥水化而快速收缩,此阶段接近完成整体收缩量的40%;第2个阶段为终凝后的10~20 h,该阶段水泥净浆的收缩放缓,甚至有略微膨胀现象,可能是因为早期水泥水化放热量较大,温度升高导致膨胀,此外水化产物钙矾石的生成也可能导致净浆的体积膨胀[23];第3个阶段为平稳收缩阶段,在到达终凝后的150~160 h,水泥净浆收缩值基本趋于稳定.

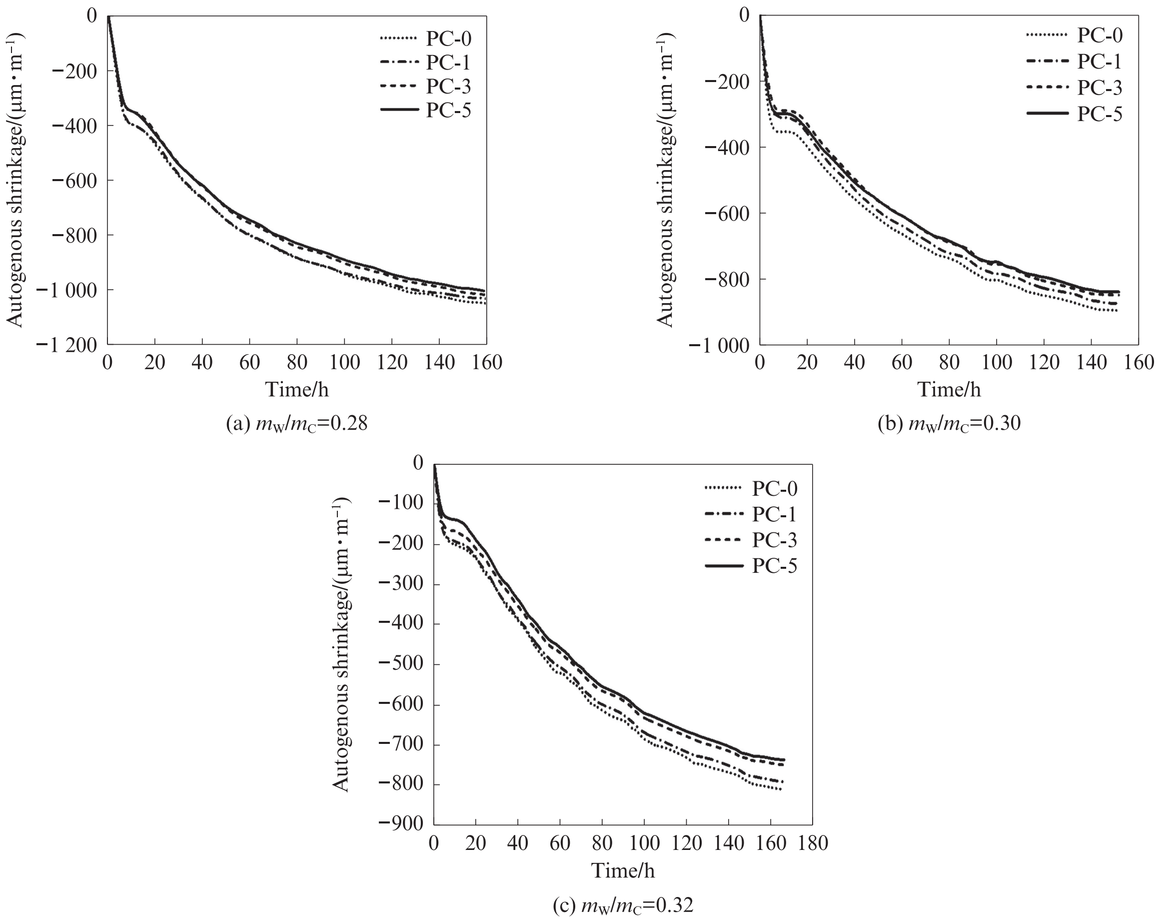


图1　CNFs改性水泥净浆的自收缩曲线

Fig. 1　Autogenous shrinkage curves of CNFs modified cement pastes

由图1还可见:水灰比对水泥净浆的自收缩也有一定影响,当CNFs的掺量为0.05%时,随着水灰比的增大,水泥净浆的自收缩降低,当m_W/m_C=0.28、0.30、0.32时,PC-5的自收缩稳定值相较于对照组分别减少了4.6%、6.3%、10.5%;CNFs的掺入,对水泥净浆自收缩产生一定的抑制效果,且在达到终凝后(150~160 h内)其自收缩基本趋向稳定;随着CNFs掺量的增加,其对水泥净浆自收缩的抑制效果更好.这是因为CNFs具有较高的长径比,能够桥连浆体内部的微裂缝,对水泥净浆自收缩产生约束作用,从而减少其收缩值[24].另外,CNFs的纳米尺寸能够填充水泥浆体的毛细孔隙[25],减少毛细孔中的水分消耗,降低毛细压力,能够一定程度地解决水泥浆体的自收缩应力问题,从而抑制其自收缩变形[26].

2.2　干燥收缩

CNFs改性水泥净浆的干燥收缩曲线见图2.由图2可见:早期随着测试龄期的增长,水泥净浆干燥收缩值不断增大,15 d之后其干燥收缩值增速降低,并逐渐趋于稳定;随着CNFs掺量的增加,水泥净浆的干燥收缩值逐渐减小,PC-5在50 d时收缩值相较于对照组减少了6.8%,其抑制干燥收缩的效果优于PC-1和PC-3.CNFs对水泥净浆干燥收缩的抑制效果可能与2个方面的因素有关:一方面,干燥收缩值与毛细孔中毛细表面张力密切相关,CNFs能够填充浆体中的微孔,减少孔隙率,使水泥净浆结构更为致密,整体刚度提升,降低了毛细张力,从而减少了干燥收缩[25,27];另一方面,CNFs表面具有丰富的细孔、边缘以及石墨层间距,使其具有很大的比表面积,在水化早期吸水浸润其表面,并在其中储存部分水分,随着水化的进行,CNFs早期的吸附水释放出来,使水泥基内部保持较高的相对湿度,从而降低了干燥收缩值[28].

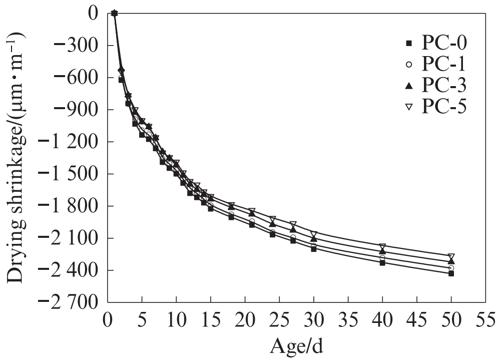


图2 CNFs改性水泥净浆的干燥收缩曲线
Fig. 2 Drying shrinkage curves of CNFs modified cement pastes

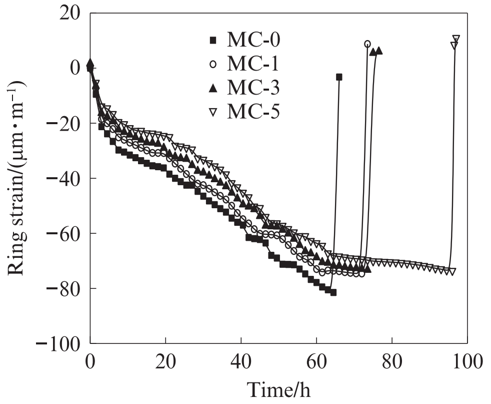


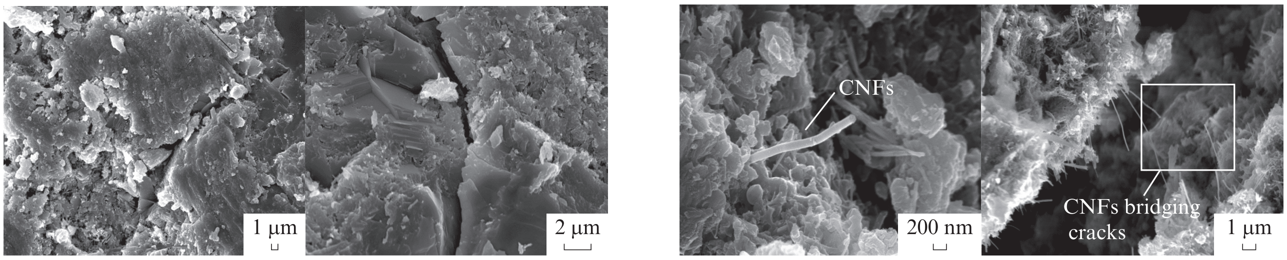
图3 CNFs改性水泥砂浆的圆环应变曲线
Fig. 3 Ring strain curves of CNFs modified cement mortars

2.3 圆环应变

CNFs改性水泥砂浆的圆环应变曲线见图3(时间起始点为拆去外环后的时间点).由图3可见:0～10 h,CNFs改性水泥砂浆的圆环应变快速增大,随后应变增长速率趋于平稳;掺CNFs的水泥砂浆圆环应变小于对照组,且MC-5的圆环应变最小;随着CNFs掺量的增大,水泥砂浆的开裂时间依次延长,MC-1与MC-3开裂时间较为接近,分别比对照组延长了11.5%、13.8%,MC-5的开裂时间为96.5 h,比对照组延长了48.5%;MC-1、MC-3、MC-5的开裂圆环压应变较对照组分别减少了8.8%、10.4%、10.2%.CNFs能够延缓水泥砂浆的开裂,主要原因可能在于CNFs能够桥连砂浆基体中的微裂纹,对水泥砂浆的收缩产生一定的约束,同时CNFs能够填充内部的孔隙,使结构变得更加致密,从而减少由于毛细孔中水分消耗引起的收缩,延长开裂时间.

2.4 CNFs改性水泥基材料增韧机制

28 d水泥净浆的SEM图见图4.由图4可见:未掺CNFs的净浆在裂纹处无纤维连接,断裂韧性相对较差;掺CNFs净浆时,CNFs锚固在基体之中,并且有纤维被拔出.当界面出现剪切应力时,导致裂纹发生一定的偏转,此过程消耗了额外应变能,CNFs充当微裂缝与水化产物之间的桥梁,起到较好的桥接作用[1,18],能够有效抑制水泥基材料内部微裂缝的扩展,限制水泥基材料的收缩变形,增强水泥基材料的抗裂性能[7,29-30].因此,在水泥基材料中加入适量CNFs,能够抑制其自收缩和干燥收缩,延缓水泥基材料的开裂时间[19,25,27].Wang等[31]发现水泥基材料中嵌入的CNFs,可以充当跨越基体中空隙和裂缝的桥梁和网络,保证载荷在张力下的传递.



(a) Without CNFs (b) With CNFs

图4 28 d水泥净浆的微观形貌图
Fig. 4 SEM images of cement pastes at 28 d

3 结论

(1)碳纳米纤维(CNFs)能抑制水泥净浆的自收缩和干燥收缩,且随着CNFs掺量的增大,其抑制效果更为明显.相比于对照组,水灰比为0.28、0.30、0.32时,CNFs掺量为0.05%的水泥净浆自收缩稳定值分别减少4.6%、6.3%、10.5%.

(2)CNFs能够延缓水泥砂浆的开裂时间,且随着CNFs掺量的增加,水泥砂浆的开裂时间延长,当CNFs掺量为0.01%～0.05%时,水泥砂浆的开裂时间相比对照组分别延长11.5%、13.8%、48.5%.

(3)CNFs在水泥基材料中产生的桥连和拔出效应,延缓了裂纹的扩展,从而减少了CNFs改性水泥砂浆的收缩变形,并提高了材料的抗裂性能.

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