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碳纳米管改性黏土力学性能及微观机制研究

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摘　要: 研究多壁碳纳米管(MWCNTs)改性黏土力学性能,旨在将其应用于垃圾填埋场衬垫材料的设计和施工中。通过三轴压缩试验和扫描电子显微镜(SEM)试验,分析了不同 MWCNTs 掺量(质量分数,下同)对黏土抗剪强度的影响规律,并从微观结构演化规律方面揭示了宏观力学特性变化机理。三轴试验结果表明,抗剪强度随 MWCNTs 掺量增加,表现为先增加后减小,0.5% MWCNTs 掺量抗剪强度值最大,且掺加多壁碳纳米管试样的抗剪强度均大于未掺入试样;随 MWCNTs 掺量增加,黏聚力的发展规律与抗剪强度一致,最大值出现在 0.5%~1.0%;内摩擦角则随 MWCNTs 掺量增加表现为先减小后增大,在 1%左右 MWCNTs 掺量处最小。掺入 0.5%~1.0%的 MWCNTs 可以有效提高黏土的抗剪强度。掺加 MWCNTs 改变土体微观结构是引起其宏观力学特性变化的根本原因。分析 SEM 结果表明,无 MWCNTs 掺量的试样中黏土颗粒间接触较为紧密,大、小孔隙分布较为均匀;掺入 MWCNTs 之后,土样孔隙的数量和尺寸均发生了明显改变。掺量较低时(0.5%),MWCNTs 附着在土颗粒表面,填充孔隙使得孔隙尺寸减小,增加了土样的密实性,从而使得抗剪强度增大;随着 MWCNTs 掺量增加(1%和 2%)可以观察到试样孔隙数量增多,但均少于无 MWCNTs 掺量试样中的孔隙数量,这种现象归因于 MWCNTs 自身的润滑作用减弱了其对黏土颗粒的吸附胶结作用,导致抗剪强度减小。

关键词: 多壁碳纳米管; 黏土; 土体改性; 抗剪强度; 微观机制

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0　引言

碳纳米管自从被日本科学家 Iijima 发现以来,由于其独特的多壁孔状结构、碳本身的稳定性好等优点,在力学和光学等领域有诸多应用[1]。而黏土作为应用最广泛的建筑材料,其物理力学特性已有较为广泛的研究。Chittoo 等[2]研究了石灰-铁泥质量浓度、水分含量(均为质量分数,下同)对土体抗剪强度的影响,发现当石灰-铁泥的掺量为 3%、含水率为 20%(均为质量分数,下同)时,土体抗剪强度显著提高。温亚楠等[3]探究发现黏土内掺入纳米膨润土后,土的孔隙会被填充,形成密集结构,使黏土土体的强度显著增加,有效提高地基土的承载力和变形性能。Bahmani 等[4]阐明了 SiO_2 纳米颗粒对水泥处理的残余土壤的稠度、压实度、水力传导率和抗压强度的影响规律,并进行扫描电子显微镜、X 射线衍射和傅里叶变换红外吸收光谱仪测试,发现添加 SiO_2 纳米颗粒可显著提高土体的压实性。董祎挈等[5]探究了污泥灰改性黏土试样的稠度界限、胀缩特性和开裂特性,发现当污泥灰掺量为 3% 时,改性黏土抵抗膨胀与收缩能力及抵抗开裂能力较强,建议采用 3%污泥灰掺量的改性黏土作为填埋场衬垫材料。任真等[6]指出纳米 MgO 掺入黏土会填充土体之间空隙,增加黏土的密实度,从而提高土体抗剪强度。Wang 等[7]探究了不同低温结构对冷冻黏土的应变、应力、抗压强度和破坏特性。陈学军等[8]发现纳米石墨粉对红黏土的抗剪强度和黏聚力有显著的提升作用。Budihardjo 等[9]发现添加 1% 的石灰可以降低土壤干燥后的收缩程度,裂缝减少,从而提高土体的整体性。武雷杰等[10]指出聚合氯化铝水解后能够降低膨胀土表

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面电荷,使黏土颗粒相互聚集,降低膨胀土的胀缩性。祝学勇等[11]探究了在黄泛区高液限黏土中添加不同剂量的石灰、粉煤灰和石灰粉煤灰,并且证明了在高液限黏土中外掺材料均可降低黏土的亲水性和膨胀性,使水稳定性进一步提高。Gao 等[12]研究了纳米 MgO 对土壤动力特性的影响,并总结了土的剪切模量和阻尼比随着纳米 MgO 掺量的变化规律。陆海军等[13]探究了秸秆纤维改良黏土作为填埋场衬垫材料时,改良黏土自身的强度、变形和抗开裂等特性。白汉营等[14]通过试验发现纳米石墨粉(NGP)改性红黏土的力学性能与 NGP 对红黏土的孔隙结构的影响以及颗粒的黏附和胶结作用密切相关。Gabidullin 等[15]和 Mohsen 等[16]指出在水泥混凝土中添加碳纳米管可以有效提高试件的抗弯和抗拉强度。目前,碳纳米管改性对象主要为混凝土,碳纳米管改性黏土力学性能仍有待进一步研究。

在建造填埋场时,使用天然黏土作为衬垫材料时对黏土力学性能要求较高。碳纳米管具有独特的小尺寸效应和表面效应等纳米材料效应,还具有强吸附性和结构稳定等性质,故能够填充黏土孔隙、增加黏土颗粒的胶结。因此,探寻合适的碳纳米管种类及其掺量来改善黏土的力学性能具有重要意义。本文选取多壁碳纳米管(multi-walled carbon nanotubes, MWCNTs)作为改性材料,通过三轴压缩试验和扫描电子显微镜(SEM)试验,研究了不同 MWCNTs 掺量改性黏土的力学性能变化,并揭示了微观结构演化机理。

1 试验方案

1.1 试验材料

本次试验采用山东大展纳米材料有限公司生产的 GT-205 型多壁碳纳米管,为黑色粉末状固体,其相关参数见表 1。实验用土取自江苏常州科教城地区,其基本参数见表 2。

表 1 多壁碳纳米管参数

Table 1 Basic parameters of MWCNTs

管径/nm	管长/μm	纯度/%	灰分/%	比表面积/($m^2 \cdot g^{-1}$)
10~20	5~50	>85	<20	200~300

表 2 黏土基本参数

Table 2 Physical index of clay

液限 W_L/%	塑限 W_P/%	塑性指数 I_P/%	最佳含水率 W_{opt}/%	最大干密度 ρ_d/($g \cdot cm^{-3}$)
40.2	16.1	24.1	16.1	1.79

1.2 试样制备

将土样烘干、碾碎后过 2 mm 筛,随后加入 MWCNTs 进行混合。混合过程中,在搅拌机中分次加入 MWCNTs,每次搅拌时间 1 h,以提高混合均匀度。根据最佳含水率 16.1%(质量分数,下同),制得掺量 0、0.5%、1.0% 和 2.0%(质量分数,MWCNTs 质量/干土质量×100%)的试样[17],将其静置 24 h,表面用保鲜膜包裹,以保证水分分布均匀。根据 GB/T 50123—2019《土工试验方法标准》[18]制备三轴试样,试样尺寸为 Φ39.1 mm×8 cm。按最大干密度 1.79 g/cm^3 称取所需湿土质量,分为 5 层击实,每层击实至相应高度后,将表面刨毛,对制好的三轴试样进行抽气饱和,饱和 24 h 以上,共制取 48 个试样。

1.3 试验方法

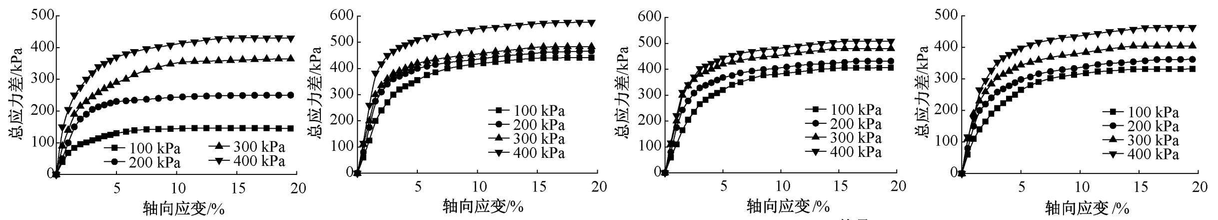
三轴试验设备采用南京宁曦土壤仪器有限公司生产的 TSZ-10 全自动三轴仪。试验采用三轴不固结不排水剪切试验,选取剪切速率为 1.0 mm/min,直至轴向应变达到 20% 终止试验。将不同掺量 MWCNTs 改性黏土分为 4 组,掺量分别为 0、0.5%、1.0% 和 2.0%,每组分别进行围压 100、200、300、400 kPa 的三轴试验,并进行平行试验。根据 GB/T 50123—2019《土工试验方法标准》[18],以峰值点作为破坏点,若无峰值,取轴向应变的 15% 相应的应力差作为破坏强度值,本文将破坏强度视为抗剪强度值。

扫描电子显微镜(SEM)试验采用的是德国蔡司生产的 EVO 18,取三轴试验破坏后的土样,进行风干和烘干,进行放大 5 000 倍的扫描电镜试验。

2 三轴试验结果分析

2.1 MWCNTs 掺量对黏土应力-应变关系的影响

图 1 所示为不同 MWCNTs 掺量黏土的应力-应变关系曲线。由图 1 可知,轴向应变在 0~4.0% 之间,主应力差曲线急剧上升,随着轴向应变的增大(大于 4.0%),曲线呈缓慢上升;在同一 MWCNTs 掺量下,围压越大,主应力差也越大。此外,对比不同 MWCNTs 掺量的试样可以看出,无掺量试样的主应力差受围压影响最明显(图 1(a)),而掺入 MWCNTs 试样(图 1(b)、1(c)和 1(d))的主应力差在不同围压条件下变化较小,这主要是由于加入的 MWCNTs 起到了较好的胶结作用。



(a) 无MWCNTs掺量 (b) 0.5% MWCNTs掺量 (c) 1.0%MWCNTs掺量 (d) 2.0%MWCNTs掺量

图1 不同多壁碳纳米管掺量下黏土的应力-应变曲线

Figure 1 Stress-strain curves of clay with different MWCNTs contents

图2给出了不同围压和MWCNTs掺量下改性黏土的最大抗剪强度值。由图2可知,MWCNTs掺量为0~2.0%时,某一围压条件下试件的最大抗剪强度值先急剧增大,而后逐渐减小,MWCNTs掺量在0.5%左右时,抗剪强度达到最大值。且添加了MWCNTs的黏土抗剪强度始终大于未添加MWCNTs的黏土抗剪强度。原因是由于MWCNTs填充了土体内部空隙,提高了黏土密实度,同时其自身吸附黏土又增强了胶结作用,抗剪强度变大,但随着MWCNTs的掺量增加,MWCNTs的润滑作用强于胶结作用,导致抗剪强度降低。

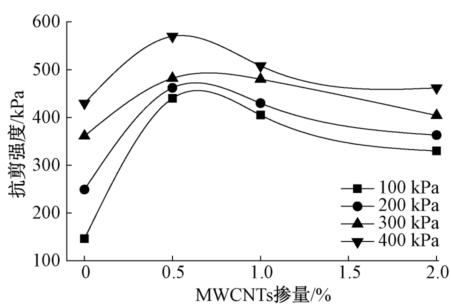


图2 不同MWCNTs掺量黏土的抗剪强度变化规律

Figure 2 Variation in shear strength of clay with different MWCNTs contents

2.2 MWCNTs对黏土抗剪强度指标的影响

莫尔-库仑强度理论是岩土工程界应用最广泛的强度理论,其数学表达式见式(1)和式(2):

$$\frac{\sigma_1 - \sigma_3}{\sigma_{+} \sigma_3 + 2c\cot\varphi} = \sin\varphi; \qquad (1)$$

$$\tau_f = c + \sigma\tan\varphi。 \qquad (2)$$

式中:τ_f为切应力,kPa;σ为正应力,kPa;c为黏聚力,kPa;φ为内摩擦角,(°)。本文基于莫尔-库仑强度理论,得出的不同MWCNTs掺量黏土的内摩擦角和黏聚力分别见图3和图4。

从图3可以看出,MWCNTs对黏土的内摩擦角有显著影响。当MWCNTs掺量为0~1.0%时,内摩擦角随着掺量增大而减小,原因可能是MWCNTs本身吸附黏土起了主要作用,增强了颗

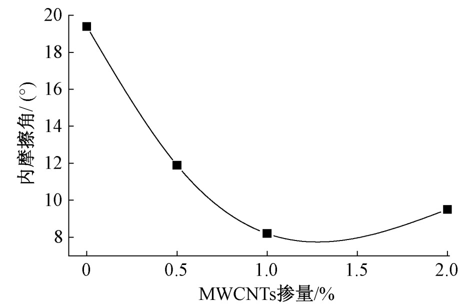


图3 内摩擦角与MWCNTs掺量关系曲线

Figure 3 Relationship between internal friction angle and MWCNTs content

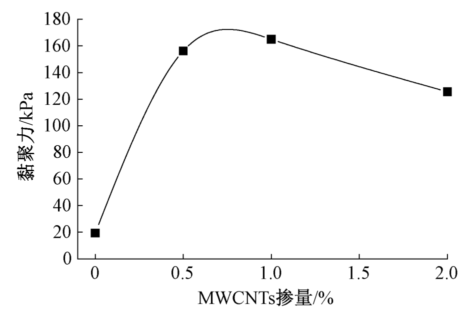


图4 黏聚力与MWCNTs掺量关系

Figure 4 Relationship between cohesion and MWCNTs content

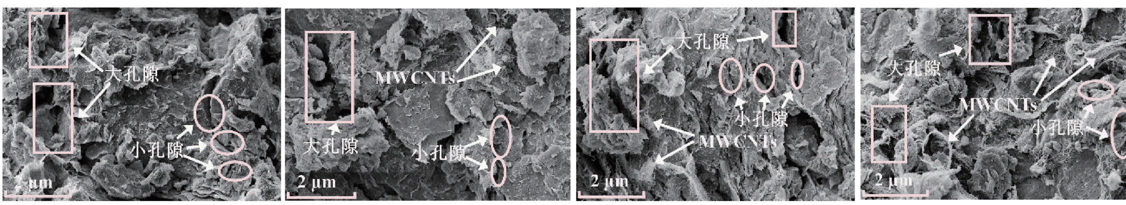
粒之间的胶结作用;当MWCNTs掺量为1.0%~2.0%时内摩擦角虽然有所增大,但是变化幅度并不大,原因可能是随着MWCNTs掺量增大,自身润滑作用稍强于自身胶结作用,从而导致内摩擦角稍微变大。

由图4黏聚力与MWCNTs掺量关系可以看出,MWCNTs掺量在0~2.0%,黏聚力曲线先急剧上升,而后缓慢下降,趋于平缓。MWCNTs掺量在0.5%~1.0%时,曲线出现最高点,黏聚力达到最大值。MWCNTs掺量在1.0%~2.0%时,曲线呈缓慢下降趋势,黏聚力减小,但仍明显大于未添加MWCNTs的黏聚力。

3 微观试验结果分析

如图5所示,对三轴试验破坏以后不同MWCNTs掺量的试样进行SEM形貌分析,通过研

究 MWCNTs 掺量对改性土体微观结构的影响规律，进一步补充说明土体剪切特性变化机理。图 5(a)所示为无 MWCNTs 掺量的试样，其中大、小孔隙分布较为均匀，土颗粒间接触较为紧密，孔隙尺寸在微米级别。从图 5(b)、5(c)、5(d)可以看出，MWCNTs 紧紧附着在土颗粒表面，其长度达到了微米级别，掺加 MWCNTs 后孔隙的数量和尺寸均发生了明显改变。掺量较低时(例如 0.5%)，MWCNTs 附着在土颗粒表面，填充孔隙使得孔隙数量减少；随着掺量增加，试样中孔隙数量增多(例如 1%和 2%)，但仍少于无掺量的试样。原因可能是由于 MWCNTs 本身尺寸与孔隙尺寸接近，在 0.5%掺量时，MWCNTs 填充黏土孔隙增强了土样的密实度和整体性，使得抗剪强度增大，但随着 MWCNTs 掺量增加(大于 0.5%)，其自身的润滑作用减弱了 MWCNTs 对黏土的吸附胶结作用，其抗剪强度减小。综上所述，掺入 MWCNTs 改变了土体的微观孔隙结构，从而影响了其抗剪强度，MWCNTs 掺量存在一个阈值，即掺量在 0.5%时抗剪强度增加最为明显。



(a) 无MWCNTs掺量　(b) 0.5%MWCNTs掺量　(c) 1.0%MWCNTs掺量　(d) 2.0%MWCNTs掺量

图 5　基于 SEM 的不同 MWCNTs 掺量改性黏土微观结构

Figure 5　Micro structure of modified clay with different MWCNTs contents via SEM

4　结论

(1) 在 0～2.0% MWCNTs 掺量时，改性黏土的抗剪强度随掺量的增加表现为先增加后减小，且掺入 MWCNTs 试样的抗剪强度较未掺入试样有显著提高。MWCNTs 掺量在 0.5%左右时，抗剪强度增加最为明显。

(2)在 0～1.0% MWCNTs 掺量之间，黏土内摩擦角随着掺量的增加而明显减小，在 1.0%～2.0%内摩擦角随着掺量的增加而略微增加；在 MWCNTs 掺量为 0～1.0%时黏聚力有显著的提高；当 MWCNTs 掺量在 0.5%～1.0%时，黏聚力最大，随后随 MWCNTs 掺量增加而减小，但较无 MWCNTs 掺量的黏聚力更大。

(3)分析 SEM 试验结果可知，MWCNTs 掺量增加对微观孔隙结构的影响表现为：掺量≤0.5%时，MWCNTs 主要起胶结作用，增加了土体的密实性，使得抗剪强度增加；掺量>0.5%时，润滑作用减弱了 MWCNTs 对黏土的吸附胶结作用，使抗剪强度减小。

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Experimental Study on Mechanical Properties and Micro-mechanism of Clay Modified by Carbon Nanotubes

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Abstract: Studying the influence of multi-walled carbon nanotubes (MWCNTs) contents on mechanical properties of modified saturated clay is of great significance for its design and application in refuse landfill clay liner materials. Triaxial compression tests and scanning electron microscope (SEM) tests were performed to analyze the influence of different MWCNTs contents on the shear strength and the mechanism of mechanical properties was revealed from the microstructure evolution. The triaxial tests results showed that the shear strength increased first and then decreased with the increasing MWCNTs content, and the maximum value was detected at 0.5% MWCNTs content. The shear strength of samples doped with MWCNTs was greater than that without content. The cohesion strength showed similar change tend with the shear strength and the maximum value existed between 0.5% and 1.0%. The internal friction angle first decreased and then increased with the increasing MWCNTs content, and the minimum value appeared at 1.0% content. The results indicated that the shear strength of clay could be significantly improved by mixing MWCNTs with 0.5%-1.0% content. The MWCNTs altered the microstructure of the clay, which was the main cause of the change in the soil macroscopic mechanical properties. SEM results indicated that the contact between clay particles was relatively close and the large and small pores showed a uniform distribution in the specimen without MWCNTs content. The number and size of pores in the soil sample changed significantly after adding MWCNTs. It increased the compactness of the specimen with lower content, in which the threshold was determined to be 0.5% content, leading to the increase in shear strength. It could be observed that the number of pores increased but was less than the specimen without content with the increasing MWCNTs contents (1% and 2%). It could be attributed to the reason that the adsorption and cementation of MWCNTs on soil particles were weakened due to lubricating effect, resulting in a decrease in shear strength.

Keywords: multi-walled carbon nanotubes; clay; soil modification; shear strength; microcosmic mechanism

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Seismic Fragility Analysis of Rigid Frame Bridge Near-fault High-speed Railway

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Abstract: To study seismic response of high-speed railway bridge under near-fault earthquake, this study took a high-speed railway rigid frame bridge as the sample of study, the whole bridge model was established by OpenSees and seismic fragility curves were established by reliability theory, bridge fragility under near-fault and far-field earthquakes were compared and analyzed. The influence of near-fault ground motion velocity pulse effect on seismic response of bridge structure was studied. The results showed that under the action of a near-fault earthquake with velocity impulse, the fragility of bridge members and systems in each damage state was significantly higher than that of far-field seismic motion. The fragility of bridge systems in near-fault and far-field seismic action was higher than that of a single component. The seismic fragility evaluation system using a single component could overestimate the seismic performance of the bridge. Compared with the first-order boundary method, the second-order boundary method took into account the correlation between bridge members. The upper and lower bounds of the fragility curves were smaller and the seismic fragility of the bridge was more accurate. In rare earthquakes, the system's fragility under near-fault earthquakes increased by percent point of 3, 13, 23, 3, respectively, compared with that under far-field earthquake. The influence of velocity pulse effect on seismic response of bridge structure should be considered in the evaluation of the seismic performance of bridge structure near fault area.

Keywords: high-speed railway bridges; near-fault; fragility; boundary estimation method