Construction and Building Materials 181 (2018) 713–720

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Effect of carbon fibers grafted with carbon nanotubes on mechanical properties of cement-based composites

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HIGHLIGHTS

- A novel chemical method was developed for grafting CNTs onto the surface of CF using KH550.
- The CNTs were grafted onto the surface of CF through Si—O—Si bond formation.
- A large number of CNTs were uniformly and densely distributed on the surface of CF.
- Cement pastes with CF-CNTs can improve the strengths of cement paste 40% higher than the pure cement paste.

ARTICLE INFO

Article history:
Received 16 August 2017
Received in revised form 14 May 2018
Accepted 5 June 2018
Available online 26 June 2018

Keywords:
Carbon fibers
Carbon nanotubes
(3-Aminopropyl) triethoxysilane
Chemical grafting
X-ray photoelectron spectroscopy
Mechanical properties

ABSTRACT

In this study, a novel chemical method was developed for grafting carbon nanotubes (CNTs) onto the surface of carbon fibers (CF) using (3-Aminopropyl) triethoxysilane (KH550). The CNTs with carboxyl groups and oxidized CF (O-CF) were modified by KH550 before the grafting procedure. The CNTs were grafted onto the surface of CF through Si—O—Si bond formation due to the hydrolysis and self-condensation reactions of KH550. The effects of CNTs grafted CF (CF-CNTs) on mechanical properties of cement-based composites were studied and compared with composites containing oxidized CF and raw CF. The morphology and chemical structure of CF-CNTs composites were characterized by Scanning electron microscopy (SEM), Laser Raman Spectrometer (LRS), Transmission electron microscope (TEM), Fourier Transform Infrared Spectrometer (FTIR) and X-ray photoelectron spectroscopy (XPS). The test results indicated that a large number of CNTs were uniformly and densely distributed on the surface of CF. The results also indicated that the CNTs and CF were held together by strong chemical bonds. When 0.5 wt% CF-CNTs was added, the flexural strength values of cement pastes at 3d, 7d and 28d were higher than those of pure cement paste and cement pastes containing same content of oxidized CF by 48.5%, 42.2% and 45.5% and 20.7%, 14.6% and 21.5%, respectively. However, the addition of CF-CNTs had little effect on the compressive strength of cement.

1. Introduction

In recent years, carbon fibers (CF) have been commonly used as reinforcements to improve the mechanical properties of composites because of their high specific strength, low weight and environmental stability [1,2]. However, the smooth surface of CF usually results in a poor bonding between the matrix and CF. It has been generally believed that the microstructure characteristics of interface between CF and matrix is the main influencing factor on the macroscopic properties of composites [3]. Therefore, many surface modification methods have been attempted to improve the bonding between CF and matrix, and grafting carbon nanotubes (CNTs) onto the surface of CF is one of promising methods [4]. CNTs have a higher tensile strength than CF and they can increase the surface roughness of CF after the grafting process. The CF grafted with CNTs are potentially of great benefit in improving interfacial shear strength between the matrix and CF as more energy is required to break the connection of CNTs and CF or pull out the CF from the matrix [5]. Qingyu Peng et al. [6] studied

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https://doi.org/10.1016/j.conbuildmat.2018.06.049

different surface treatments on CF to enhance the interfacial properties. They found that the interfacial shear strength (IFSS) of the composite with CF chemically grafted with CNTS was higher than that of PAMAM-absorbed CF composite and acid-treated CF composite by 36% and 111%, respectively. Zhang et al. [1] studied a series of chemical pre-treatment process on CF and they reported the IFSS of desized CF was about 66 MPa with minimal signs of any interfacial interaction between the fiber surface and the matrix. Their results further indicated that the ILSS of CF-COOH composites and CF-NH_2 composites were higher than the desized CF composite by 8% and 14%, respectively. However, the IFSS of the CF-CNTs composites was much higher and an increase of 21.6% was noted. Nevertheless, it should be noted that the abovementioned studies were aimed at improving the interfacial bond in resin-carbon fiber composites. Although the dispersion of carbon fiber in cement and the influence of carbon fiber on the mechanical properties of cement have been studied previously, there are few studies on the effect of CF-CNTs on cement mechanical properties.

Surface grafting of CF with CNTs can be achieved through physical (van der Waals interaction) and chemical (covalent bonding) means. The chemical vapor deposition (CVD) method was used to graft CNTs onto the surface of CF by physical adsorption, but the enhancement was usually limited due to the common issues of catalyst pollution, high temperature environment weakened the performance of CF and weak bonding between the CNTs and CF [7–9]. Many researches have been done on linking CNTs onto CF by several chemical branching methods, such as esterification reaction or using coupling agent or dendrimer to form amide linkage between the CNTs and CF [6,10,11]. However, the esterification reaction is complex and requires a strong acid catalyst, which impede its widespread application [12]. On the other hand, the methods of using coupling agent for grafting suffer from too much time being spent on reaction processes [1,4,13]. Therefore, to meet the requirement of large-scale applications, an efficient and environmental friendly grafting method needs to be developed. (3-Aminopropyl) triethoxysilane (KH550) is an aminosilane frequently used in the process of silanization, the functionalization of surfaces with alkoxysilane molecules. KH550 molecules contain two different functional groups (amino and silane groups) and they are used to couple organic macromolecules and inorganic fillers leading to enhanced adhesion and improved mechanical properties of products [14,15].

In this study, a novel method to graft CNTs directly onto the surface of CF surface was developed by using KH550. The use of KH550 to graft CNTs on CFs is very innovative and no one has attempted to use KH055 in this way. It was believed that the amino groups (—NH_2) of KH550 would react with the carboxyl groups (—COOH) on the surfaces of CNTs and oxidized CF (O-CF), and the grafting process was achieved by the chemical reactions between the silane groups (—Si—CH_3) of KH550. The CNTs were grafted onto the surface of CF through Si—O—Si bond formation due to the hydrolysis and self-condensation reactions of KH550. Then, the prepared CF-CNTs were incorporated into cement and their effects on the mechanical properties of cement composites were studied.

2. Experimental

2.1. Materials

The carbon fibers (CFs) used in this experiment were 3 mm in length with a diameter of 7 μm. The carbon nanotubes used were short —COOH functionalized multi-walled carbon nanotubes (CNTs), and their average length varies from 0.5 to 2 μm with a diameter of about 8 nm. (3-Aminopropyl) triethoxysilane (KH550), a silane coupling agent was used. KH550 would hydrolyze in aqueous solution and then undergo self-condensation. In this experiment, alkylphenol ethoxylates (APEO, active ingredient content ≥99%) was used as a dispersant to ensure that CNTs were well dispersed in solution. The cement used in this experiment was P·I 42.5 ordinary Portland cement complying with the requirements of China National Standard GB175-2007. To ensure well dispersion of carbon fibers in cement paste, carboxyl methyl cellulose (CMC) was used as a dispersant.

2.2. Carbon fiber oxidation

5 g of as-received CFs were oxidized with 800 ml of a mixture of concentrated sulfuric acid (95%) and concentrated nitric acid (67%) solutions (3:1 by volume). The mixture was constantly stirred for 6 h at 25 °C to generate carbonyl and hydroxyl groups on the surface of CFs. Then the reaction mixture was filtrated and washed thoroughly with deionized water and dried at 60 °C for 24 h. The functionalized CNTs have carboxylic functional groups on their surface, so no oxidation of CNTs was required to carry out.

2.3. Proposed method of grafting CNTs onto CF

In this research, 2 g oxidized CF and 1 g CNTs were thoroughly mixed in a 400 ml solution of absolute ethanol. Then appropriate amounts of KH550 and APEO dispersants were added into the solution. The mixture was stirred and heated in a water bath at 40 °C and sonicated for 30 min allowing the KH550 to attach on the surface of oxidized CF and CNTs. As can be seen from Fig. 1, the —COOH groups on the surface of CF and CNTs would react with —CH_2—NH_2 groups in KH550, so the KH550 could be attached onto the surface of oxidized CF and CNTs through chemical bonding [13]. After the sonication, the mixture was added with 400 ml of water. Then, the new mixture was further stirred and heated in a water bath at 40 °C and sonicated for another 30 min. Because there was water in the solution, the silane groups (—Si—CH_2—CH_3) at the end of KH550 underwent a hydrolysis reaction to form silanol groups (—Si—OH), and followed by a self-condensation reaction between the silyl groups to form —Si—O—Si— bond (Fig. 1). It can be shown in Fig. 1 that the function of KH500 was like a bridge that connected CNTs onto the surface of CF by chemical bonds (Fig. 1). After cooling to room temperature, the mixture was filtrated and washed thoroughly with deionized water and dried in an oven at 60 °C for 24 h. The grafting method described in this research was much easier to follow without the need of strong acid as catalyst when compared with previous studies [1,4,6,12,13]. Moreover, the overall reaction time was significantly shortened which is considered practical for industrial-scale manufacturing.

2.4. Characterization techniques

The morphology of the samples was observed by the Environmental Scanning Electron microscope (ESEM, Quanta TM 250 FEG, United States) and Transmission Electron Microscope (Talos TEM, FEI, United States). The surface roughness of CFs was observed by Laser Raman Spectrometer (Renishaw inVia, United Kingdom). Fourier Transform Infrared Spectrometer (FTIR Spectrometer, Nicolet 6700, United States) and X-ray photoelectron spectroscopy (XPS) analysis were used to examine the chemical structure of the samples.

The cement pastes with different types of carbon fiber were prepared according to the mix proportions showed in Table 1. The water-cement ratio (W/C) was kept constant at 0.4. Because the addition of CF can reduce the fluidity of cement paste, therefore appropriate amounts of superplasticizer were added to maintain the same fluidity among different cement systems. After the mix-