Applied Surface Science 416 (2017) 200–212

Contents lists available at ScienceDirect

Applied Surface Science

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

Full Length Article

Surface decoration of polyimide fiber with carbon nanotubes and its application for mechanical enhancement of phosphoric acid-based geopolymers

Tao Yang[a], Enlin Han[b], Xiaodong Wang[a,*], Dezhen Wu[a,*]

[a] State Key Laboratory of Organic–Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, China
[b] Changzhou Institute of Advanced Materials, Beijing University of Chemical Technology, Changzhou, Jiangsu Province 213164, China

ARTICLE INFO

Article history:
Received 16 March 2017
Received in revised form 13 April 2017
Accepted 20 April 2017
Available online 23 April 2017

Keywords:
Polyimide fibers
Surface decoration
Carbon nanotubes
Phosphoric acid-based geopolymers
Reinforcement

ABSTRACT

A new methodology to decorate the surface of polyimide (PI) fiber with carbon nanotubes (CNTs) has been developed in this study. This surface decoration was carried out through a surface alkali treatment, a carboxylation modification, surface functionalization with acyl chloride groups and then with amino groups, and a surface graft of CNTs onto PI fiber. *Fourier*-transform infrared and *X*–ray photoelectron spectroscopic characterizations confirmed that CNTs were chemically grafted onto the surface of PI fiber, and scanning electron microscopic observation demonstrated the fiber surface was uniformly and densely covered with CNTs. The surface energy and wettability of PI fiber were improved in the presence of CNTs on the fiber surface, which made a contribution to enhance the interfacial adhesion of PI fiber with other inorganic matrices when used as a reinforcing fiber. The application of CNTs-decorated PI fiber for the reinforcement of phosphoric acid-based geopolymers was investigated, and the results indicated that the geopolymeric composites gained a noticeable reinforcement. Compared to unreinforced geopolymer, the geopolymeric composites achieved a remarkable increase in compressive strength by 120% and in flexural strength by 283%. Fractography investigation demonstrated that the interaction adhesion between the fibers and matrix was enhanced due to the surface decoration of PI fiber with CNTs, which contributed to an improvement in fracture-energy dissipation by fiber pullout and fiber debonding from the matrix. As a result, a significant reinforcement effect on geopolymeric composites was achieved through a fiber-bridging mechanism. This study provided an effective methodology to improve the interracial bonding force for PI fiber and also proves a highly efficient application of CNTs-decorated PI fiber for the mechanical enhancement of geopolymeric composites.

1. Introduction

Geopolymers are a class of important inorganic polymeric materials discovered by J. Davidovits in 1970s [1], and they have attracted extensive interests from scientific societies to industrial communities in recent years due to their excellent thermal and mechanical performance, prominent fire resistance, good chemical resistance, good anti-permeability, low density, ecologically friendly nature, easy processing and low cost [2,3]. Most of all, geopolymers can be facilely formed through covalently bonded long-range aluminosilicate networks at a low hardening temperature by use of various nature materials such as red muds, volcanic tuffs and kaolinites, or some industrial waste materials like fly ashes and blast furnace slag [4]. Therefore, the production of geopolymers releases less CO_2 gas compared to the manufacture of traditional Portland cements with huge energy consumption, high pollution and large greenhouse-gas emissions [5]. Nowadays, geopolymers have been widely applied for high-temperature ceramics, heat- and fire-resistant coatings and adhesives, new binders for fire-resistant building materials, new medicinal materials, encapsulation of toxic and radioactive wastes and also used as cementing components to make cement concrete [6]. There is no doubt that geopolymers have been recognized as a promising substitute of conventional cements and are highly prospective to gain a significant share of the worldwide market in construction materials [7].

There are still some obstacles like relatively low mechanical properties for the commercial applications of geopolymers at present, and therefore the development of geopolymeric materials with enhanced performance has received considerable attention

* Corresponding authors.
E-mail addresses: wangxdfox@aliyun.com (X. Wang), wdz@mail.buct.edu.cn (D. Wu).

http://dx.doi.org/10.1016/j.apsusc.2017.04.166
0169-4332/

in the past few decades [8]. The relevant researches were mainly focused on the synthesis of new geopolymeric systems as well as the modification of geopolymeric materials, and an abundance of research achievements have been obtained for facilitating the wider acceptance of geopolymers as the substitutable materials of traditional cement concrete and cementitious materials [9]. It is widely accepted that pristine geopolymers still suffer insufficient mechanical strength and brittle failure like most of the ceramics and cements, which definitely leads to a limitation in a wider range of their potential applications [10]. Continuous and short inorganic fibers are considered as effective reinforcing materials for geopolymers, and the corresponding reinforced geopolymeric composites have been extensively investigated in recent years. Maranan et al. [11] reported that the reinforcement of geopolymeric concrete with glass fiber could create a construction system with adequate strength, high sustainability and high durability. The investigations by Lin et al. [12] and He et al. [13] indicated that the short carbon fiber could effectively reinforce geopolymers and provided higher compressive strength, higher flexural strength and better impact toughness for the resulting composites. The utilization of basalt fiber for reinforced geopolymeric composites were also reported by Li and Xu [14,15], and they found that the presence of basalt fiber could significantly improve the deformation and energy absorption of geopolymers and consequently enhanced the ductility and impact toughness of geopolymeric composites. Moreover, He et al. [16] reported the reinforcement of geopolymers with unidirectional SiC fiber and found that the resulting composites achieved a significant improvement in flexural strength and fracture toughness at the fiber content of 20 vol%. However, these reinforcing inorganic fibers bring some disadvantages to geopolymeric composites. For example, glass fiber is not suitable for the lightweight-designed geopolymeric materials, and carbon fiber cannot be used for the composites in the cases that need thermal and electrical insulation. In this case, many studies have been focused on the reinforcement of geopolymers with organic fibers. Puertas et al. [17] investigated the reinforcement effect of short polypropylene fiber on different geopolymers, and they found that this organic fiber was only effective for the reinforcement of fly-ash-based geopolymers. Zhang et al. [18,19] reported that the incorporation of short poly(vinyl alcohol) fiber could lead to a considerable enhancement in flexural strength and impact toughness for fly-ash-based or metakaolin-based geopolymers. Choi et al. [20] reported an ultra-high-ductile behavior observed from the polyethylene fiber-reinforced slag-based geopolymeric composites. Moreover, our previous study also found that the introduction of polyacetal fiber into a brittle geopolymeric matrix could enhance the strain energy dissipation capability of the matrix through a bridging effect and thus improved the mechanical performance of the resulting composites [10].

In recent years, the development of high-performance synthetic organic fibers has achieved great progress in both academic research and manufacture, and some of them are now available as commercial products such as aramid fibers [21], polybenzimidazole fiber [22], polybenzobisoxazole fiber [23], polyhydroquinone-diimidazopyridine (M5) fiber [24] and ultrahigh-molecular-weight polyethylene fiber [25]. With outstanding mechanical properties and excellent thermal stabilities, these novel synthetic fibers can endow the resulting composites with much higher mechanical strength, better damage tolerance, higher load-bearing stiffness, better heat resistance stability and more significant lightweight compared to the traditional inorganic fiber-reinforced composites, thus making them a strong competition in engineering and structural applications [26]. For example, Yang et al. [27] reported an investigation on the reinforcing behavior of aramide fiber for concrete and found that the external fiber confinement could effectively enhance the dynamic strength, ultimate strain and energy absorption density of the composites. Polyimide (PI) fiber is a type of aromatic heterocyclic fibers with outstanding thermal stability and superior resistance to UV light and irradiation. PI fiber has attracted a great deal of attention in both fundamental research and commercial exploitation due to its huge potential for applications in the fields of electric and microelectronic systems, military equipments, aviation and aerospace [28,29]. Although the commercialized PI fiber with a brand name of P84® has been developed by Lenzing AG, a leading fiber company in Austria [30], the present manufacture techniques cannot provide enough high strength for PI fiber in terms of the requirement of reinforcement in various forms of composite materials. Therefore, the reports about the reinforcement of geopolymeric composites with PI fiber have not been found in literature by now.

The conventional PI fiber was commonly synthesized through a reaction of *3,3′,4,4′*-biphenyltetracarboxylic dianhydride (BPDA) with *4,4′*-oxydianiline, or *p*-phenylenediamine (*p*-PDA), or both by using a wet-spinning technique [31]. Recently, a technologic breakthrough has been achieved in our work for the production of high-strength PI fiber, and a new formulation was invented to prepare PI fiber by the introduction of *2*-(*4*-aminophenyl)-*5*-aminobenzimidazole or *5*-amino-*2*-(*4*-aminobenzene)benzoxazole as the third monomer [32,33]. The prepared PI fiber achieves a high elastic modulus of 120 GPa and high tensile strength of 3.5 GPa. This makes PI fiber a good candidate for the reinforcement of geopolymeric systems. Nevertheless, as an organic reinforcing material, PI fiber usually has weak interfacial adhesion and poor wettability with inorganic geopolymers due to the incompatibility between two phases. In this case, a surface modification or decoration for PI fiber is necessary definitely. Carbon nanotubes (CNTs) are considered as one of the best surface-decorating agents for various inorganic fibers due to their large active specific surface area and low surface energy, and therefore, chemical grafting of CNTs onto the surface of reinforcing fibers can generate a strong interfacial interaction between the fibers and matrix [34]. This novel technique route has already been used for the carbon fiber-reinforced composite systems by now. Zhao and Huang [35] reported a new method of CNTs onto carbon fiber by using polyhedral oligomeric silsesquioxane as a coupling agent, and they found a hierarchical reinforcement structure for the resulting epoxy composites because of a dramatic improvement in interfacial adhesion. Li et al. [36] also reported the hierarchical reinforcement of epoxy composites with the CNTs-grafted carbon fiber through tuning the interfacial interaction by varying the graft density of CNTs. Wang et al. [37] further investigated the grafting force of CNTs onto carbon fiber and found that it played a critical role in the interfacial enhancement of reinforced epoxy composites. Moreover, Rodríguez-Uicab et al. [38] also reported a surface modification method for aramid fiber with CNTs through chemical decomposition. In view of the chemical inert characteristics of both PI fiber and geopolymers, a chemical modification on the surface of PI fiber with CNTs is highly recommended to enhance the interfacial interlock between the fibers and matrix so that an effective reinforcement could be achieved for geopolymers.

In this work, we focused on a surface decoration technique toward PI fiber through a series of chemical processes and then investigated the effects of CNTs-decorated PI fiber on the mechanical properties of phosphoric acid-based geopolymeric composites. Although most of the geopolymers are synthesized through an alkali-activation method [39], the molecular structure of PI fiber is easily damaged by alkaline chemicals. It is well known that the hydroxyl groups of alkaline chemicals can attact the imide rings on PI to initiate a ring-opening reaction, which results in a breakage of PI chains [40]. In this case, PI fiber is not suitable for reinforcement of the alkali-activated geopolymers. Phosphoric acid-based geopolymers are an important member of the family of geopoly-