Materials Letters 134 (2014) 91–94

Contents lists available at ScienceDirect

Materials Letters

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

One-step surface modification of multi-walled carbon nanotubes by pyrrole

Shinian Liu [a], Cheng Wang [b,*], Zengfu Wei [a], Wangyan Lv [a], Shengping Fan [a], Shenglong Zhu [b], Fuihui Wang [b]

[a] Electric Power Research Institute of Guangdong Power Grid Corporation, Guangzhou, Guangdong 510080, China
[b] Institute of Metal Research, Chinese Academy of Sciences, Liaoning, Shenyang 110016, China

ARTICLE INFO

Article history:
Received 13 April 2014
Accepted 2 July 2014
Available online 10 July 2014

Keywords:
Carbon nanotubes
Surfaces
Pyrrole
XPS
Thermal analysis
Epoxy

ABSTRACT

A convenient and environment friendly one-step surface modification process was developed to disperse multi-walled carbon nanotubes (MWCNTs). The process involves immersing MWCNTs in a pyrrole/ethanol/H_2O_2 solution with ultrasonic cleaner for 2 h. The MWCNTs were characterized by transmission electron microscopy, X-ray photoelectron spectroscopy, Zeta potential and thermogravimetric analysis. The modified MWCNTs showed much more excellent dispersion and stability both in water and organic media. The modified MWCNTs were stable for months without any precipitation. The modification of MWCNTs was attributed to the interaction between MWCNTs and oligomer polypyrrole and also the chemical adsorption of pyrrole. The modified MWCNTs improve the mechanical performance of an epoxy coating.

1. Introduction

Special attentions have been paid to carbon nanotubes (CNTs) owing to their unique structure, excellent properties and attractive potential applications since their discovery in 1991 [1]. They are expected to be applied in carbon nanotube composites, electrochemical devices, hydrogen storage, field emission devices, etc [2].

But it has been found that the as-produced CNTs are inclined to agglomerate together owing to very strong Van der Waals interactions [3]. Thus, the poor dispersion and stability have become a bottleneck in the application of CNTs. Poorly dispersed CNTs often weaken the mechanical performance of CNTs-based composites materials [4].

The dispersion processes mainly include mechanical, physicochemical, irradiation, chemical and physical functionalization, etc [5]. Nonetheless some processes may cause damage or shortening of CNTs, which may have a further detrimental effect on their desirable properties. Furthermore, most of these modifications involve time-consuming, high temperature requirement and harmful substance producing during treatment [6]. Developing environment friendly, facile and large-scaled treating processes preserving the morphology and properties of CNTs is a key issue in modification of CNTs.

In this study, we reported a simple process to modify MWCNTs and utilized the modified MWCNTs to improve the mechanical performance of an epoxy coating.

2. Materials and methods

2.0 g pyrrole (short for Py, Sinopharm Chemical Reagent Co., Ltd, China) was dissolved into a mixture of 25.0 g ethanol and 75.0 g H_2O_2 (30%), then 2.0 g MWCNTs (Beijing Dk Nano Technology Co., Ltd) were added into the mixed solution and agitated manually followed by treating in an ultra-sonication for 2 h at ambient temperature. The modified MWCNTs were subsequently separated by centrifugation at a rotation rate of 16,000 rpm and washed with deionized water (resistance 18 MΩ cm) until its pH was 7. The sample was dried in an oven for 24 h at 80 C.

The visual examination, TEM and TGA were carried out according to the literature [7]. XPS analysis of the MWCNTs was performed on an ESCALAB250 (The Thermo Scientific, USA) X-ray photoelectron spectrometer and the spectra were curved fitted using XPSPEAK41 software. Zeta potentials of the MWCNTs were performed on a NanoPlus 2 Zeta potential analyzer (Micromeritics Instrument Co., USA).

A composite coating was prepared by blending E44 epoxy, 5772 curing agent (modified polyamine) (Shanghai Resin Factory Co., Ltd.) and MWCNTs, and the kinetic viscosity was adjusted to about 26–58 $mm^2 s^{-1}$ by xylene and ethanol in a mass ratio of 1:1. The

* Corresponding author. Tel.: +86 24 23915900; fax: +86 24 23893624.
E-mail addresses: gz_liusn@163.com (S. Liu), wangcheng@imr.ac.cn (C. Wang).

http://dx.doi.org/10.1016/j.matlet.2014.07.011
0167-577X/

content of MWCNTs was 1, 5 and 10 wt%. The mixture with some zirconium silicate beads in size of 1 mm was blended together and agitated by a blender at a rotation rate of 1500 rpm for 15 min, then the mixture was filtered with a screen mesh about 80 μm, the curing agent (one fifth of E44) was added into the paint and agitated for about 5 min. The paint was brushed onto a polytetrafluoroethylene plate. The coatings were stored for 12 h at ament temperature and then curried at 40 C for 24 h. The mechanical performance of the coatings was investigated using tension testing on a WDW microcomputer control electronic universal testing machine (Ji'nan Zhongbiao Instrument Equipment Co., Ltd., China) according to ASTM D638.

3. Results and discussion

Fig. 1 shows images of the MWCNTs dispersed in different liquid media after getting settled for 70 d at room temperature.

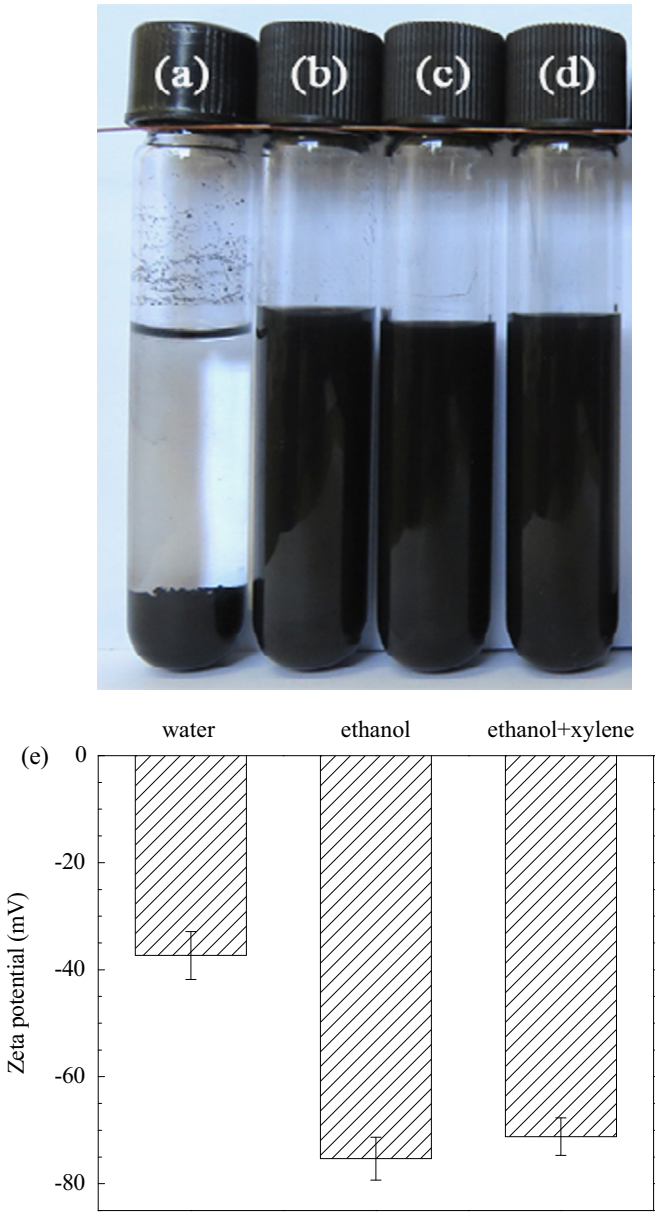

Fig. 1. Visual examination and Zeta potentials of MWCNTs: pristine in water (a), Py modified in water (b), ethanol (c), 50 wt% ethanol and xylene (d), Zeta potential (e).

The pristine MWCNTs precipitate extremely from water after getting settled for 70 d (Fig. 1a). The modified MWCNTs exhibit excellent dispersion and stability either in water (Fig. 1b), ethanol (Fig. 1c) or the mixture of 50 wt% ethanol and xylene (Fig. 1d). In the cases of the MWCNTs modified solely either in a Py/ethanol solution or in a H_2O_2/ethanol solution, the MWCNTs both precipitate from water. The results indicate that the pristine MWCNTs are hydrophobic. The hydrophilicity of the modified MWCNTs reveals that there exist hydrophilic functional groups on their surfaces, which prevent the aggregation and precipitation of MWCNTs and improve their dispersion ability and stability. The zeta potentials (Fig. 1e) of the modified MWCNTs in water, ethanol and ethanol+xylene are −37.34, −75.29 and −71.18 mV respectively, which further indicate that the modified MWCNTs are stable in these liquids, especially in organic media.

Fig. 2 shows TEM morphologies of the pristine (a and b) and modified MWCNTs (c and d). The pristine MWCNTs show a smooth surface while increased roughness of the modified MWCNTs surface is observed. The diameter of the modified MWCNTs becomes thicker than those of the pristine ones, which indicated that some functional groups grasped onto the MWCNTs surface. This phenomenon resembles that of SWCNTs/PPy nanocomposites reported by Huyen et al. [8]. The modified MWCNTs with illegible wall edges exhibit smaller clusters than those of the pristine ones.

Fig. 3a shows the wide XPS spectra of the MWCNTs. There detected N element for the modified MWCNTs, which indicates Py has functionalized on the surface of MWCNTs. The high resolution XPS spectrum of N1s (Fig. 3b) located at a binding energy of 400.0 eV is assigned to –NH-groups in polyporrole (PPy). The peak located at a binding energy of 400.7 eV is attributed to chemisorption of Py [9]. The XPS results indicate that the Py monomers are oxidized by H_2O_2 to form water dissolvable oligomer PPy, and some of unreacted Py absorb onto the surface of MWCNTs. The PPy chains are not long enough to form insoluble particles merely oxidized by H_2O_2 without any other catalytic ionic compounds under acidic solutions [10].

The TGA results indicate that both MWNCTs exhibit continuous mass loss, and the mass loss of the modified MWCNTs is much larger than that of the pristine ones (Fig. 4a). There existed three sudden mass losses (360–387 C, 490–625 C and 770–942 C) for the pristine MWNCTs. The modified MWNCTs show a very distinct mass loss behavior (Fig. 4b). The mass loss at temperatures below 120 C is attributed to the absorbed water. The mass loss at 120–210 C is related to evaporation of Py with a boiling point about 130 C. The high mass loss rate for the modified MWCNTs at a temperature range of about 200–330 C is assigned to the decomposition of PPy. The tension strength of E44/modified MWCNTs (Fig. 4c) is higher than that of pure E44 epoxy coating when the content of MWCNTs up to 5wt% and the elongation increases with the content of MWCNTs. The tension strength and elongation of the E44/modified MWCNTs are higher than those of E44/pristine MWCNTs, while the pristine MWCNTs decrease the mechanical performance of the coatings.

In this study, the formed PPy grafts the sidewall of MWCNTs by the reaction of π–π stacking, H–π bonding interactions and hydrogen bonding [11], and the five-membered heterocycle stretching in the bulk solution facilitates the dispersion of MWCNTs. The functional groups on modified MWCNTs increase the interaction between E44 epoxy and MWCNTs which result in the increase in tension strength and elongation.

4. Conclusions

A simple, environment friendly and the efficient one-step process to modify MWCNTs by Py in an ethanol/H_2O_2 solution