Synthesis of functionalized CNTs/hyperbranched polyester nanocomposites

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Abstract. Carbon nanotubes (CNTs) were unzipped using the modified Hummer method to prepare the CNTs-GO microstructure (see Fig. 1). A new type of CNTs-GO-H2O nanocomposite has been synthesized by grafting hyperbranched (HB) polyester (Boltorn H2O) brushes on the CNTs-GO by coupling agent (KH560). The morphology of CNTs-GO-H2O was characterized by FTIR, TEM, XPS and TGA. The FT-IR data and XPS data evidenced that CNTs-GO-H2O nanocomposites were synthesized successfully. The addition of CNTs improved the thermal stability of the nanocomposites. The TEM data showed that the CNTs-GO microstructure was also prepared. These electrochemical measurements results indicated that coatings provided greater protection against corrosion behavior. Moreover, the nanocomposite material improved corrosion resistance of the coating.

1. Introduction

The research of mature corrosion protection technology generally adopted the way of adding fillers into the liquid coating. The introduction of nanoparticles has always been considered to increase the crosslinking density and make the coating more dense. Among those nanoparticles, CNT fillers can improved the mechanical properties of the coatings owing to its high strength and modulus of elasticity [1]; GO was considered to have the anticorrosive properties owing to its impermeability to oxygen and water, its very high surface area, nanometric thickness and plate-like structure[2]. However, both CNTs and GO have the agglomeration problem which would influence the compatibility between the coating matrix and fillers. Therefore, the aggregation problem of GO and CNTs has to be resolved in order to move the field forward.

Figure 1. CNTs-GO structure;
In recent years, it was found that the dispersion of CNTs/GO hybrid in solution media can be improved by ultrasonication [3,4]. Moreover, the chemical functionalization was proved to provide better long-term stability and better dispersibility [5].

![Diagram](image)

**Figure 2.** (a) Molecular formula of H20; (b) scheme of the synthesis route for CNTs-GO-H20;

HB polyester H20 (see Fig. 2a) is characterized by its spherical molecular shape, large number of functional end groups, good film forming ability, high solubility and low viscosity at melt and in solution [6]. In spite of the fact that H20 is widely used in the fields of composite materials and catalysts, but its application in the metal protection field is rarely studied. Anticorrosive coatings are prepared in solution all the time while commercial H20 is only available in powder form, the primary problem is to prepare a composite coating solution that can be stored stably. In this paper, the new liquid coating solution has been prepared for the application of copper corrosion protection.

2. Experimental section

2.1. Materials and reagent

MWCNTs used in this study (97% purity, average ED 20-40 nm) were purchased from Shenzhen Nanotech Port Co., Ltd. Boltorn H20 (Hydroxyl number: 565.1mg KOH/g, molecular weight: 2100) was supplied by Shanghai Seebio Biotech, Inc. KH560 was purchased from Aladdin Industrial Corporation. Chemical reagents were obtained from sinopharm chemical reagent Co.,Ltd. The Cu foil.

2.2. Preparation of CNTs-GO/H20 nanocomposite

The preparation of CNTs-GO employed a modified Hummer method [7]. The CNTs-GO was functionalized by the coupling agent (KH560). Equivalent mass of functionalized CNTs-GO and H20 were dissolved in 50ml water respectively. After ultrasonication for 30min, 5M NaOH was then added to the suspension of CNTs-GO as a catalyst. Then the mixture was stirred for 6h at 80°C in a round-bottom flask equipped with a condenser. After the reaction was complete, nonreactive H20 was removed by successive filtration using ethanol and acetone. Residual NaOH was washed out by distilled water until the pH of the filtrate became neutral. The solid was then dried under vacuum to obtain CNTs-GO-H20 nanocomposite (see Fig. 2b).

2.3. Characterization of samples

Fourier transfer infrared spectroscopy (FT-IR) was recorded between 4000-400cm⁻¹ on a Nicolet in10 FT-IR spectrometer, U.S.A and using KBr pellets for sample. The size and morphologies of the resultant samples were characterized by JEM-1200EX transmission electron microscopy (TEM).
Thermogravimetric analysis (TGA) was performed under a nitrogen flow using SDT Q600 from room temperature to 800°C at a heating rate of 10°C/min. X-ray photoelectron spectroscopy measurements were carried out with a monochromatic Al Kα X-ray source by the Thermo ESCALAB. The properties of the viscosity of composite coating were investigated by ubbelohde viscometer. Electrochemical measurements were recorded in 3.5 wt% NaCl solution by a CHI660C electrochemical workstation (Shanghai CH Instruments) at room temperature. The Cu foil was washed several times with acetone, NaOH solution and deionized water, respectively.

3. Results and discussion

3.1. FT-IR analysis of samples
As shown in Fig. 3, the pristine CNTs have only three obvious peaks including C=C stretching vibration (1570cm⁻¹), C-O stretching vibration (1100cm⁻¹) and -OH stretching vibration (3378cm⁻¹). After pretreated by the modified Hummer method, three new peaks emerged in the CNTs-GO. The signals at 1710cm⁻¹ and 1388cm⁻¹ were absorbed by C=O and C-OH. The band observed at 1100cm⁻¹ has become wider due to the coincidence of -CH(O)CH- vibration peaks and C-O vibration peaks. The values confirmed that the functional groups of -COOH, -OH, -CH(O)CH- were introduced to CNTs successfully. Compared with CNTs-GO, some new absorption bands appeared at functionalized CNTs-GO. The absorption at 2920cm⁻¹ and 2852cm⁻¹ were due to -CH₂- stretching, the band at 1210cm⁻¹ and 909cm⁻¹ assigned to the epoxy group.

![Figure 3. FT-IR (left) spectra and TGA (right) curve of samples](image)

(a) CNTS; (b) CNTs-GO; (c) functionalized CNTs-GO; (d) H2O; (e) CNTs-GO-H2O;

The results confirmed that the surface of CNTs-GO was successfully grafted by KH560 [8]. In the pure H2O (d), there were two strong peaks, -CH₃ stretching vibration (1450cm⁻¹, 1380cm⁻¹) and -C-O- stretching vibration in -COOR (1300~1050cm⁻¹). Compared with pure H2O and functionalized CNTs-GO, the signals at wavenumbers 1300~1050cm⁻¹, 1380cm⁻¹, 1450cm⁻¹ appeared in the resultant products, which proved that CNTs-GO-H2O was obtained successfully.

3.2. TG analysis of samples
As shown in Fig. 3, for CNTs-GO (b), the first weight loss of about 4% was attributed to the evaporation of the physically absorbed water. In addition, the 8% weight loss between 168-250°C registered for GO was due to the decomposition of labile oxygen functional groups. The slight decline occurred at 300-800°C when decomposition of the carbon skeleton structure occurs with the residual mass of 75.52% obtained at 800°C. In the case of functionalized CNTs-GO-H2O (e), the onset degradation temperature of functional groups was increased from 168°C to 209°C, which showed that a part of the functional groups reacted with the coupling agent. And from 265°C, the weight loss of the functionalized CNTs-GO-H2O was more significant than CNTs-GO. This may be mainly caused by the pyrolysis of the polyester grafted on the surface of CNTs-GO [9]. And the residual mass of
functionalized CNTs-GO-H20 was 65.88%. This means that the weight loss of the CNTs-GO-H20 was almost 10% greater than CNTs-GO, which can be related to the amount of H2O grafted on the CNTs-GO surface. As regards the CNTs-GO-H20 nanocomposite a 10% weight loss was observed between 260°C and 544°C while the commercial H2O sample thermal degradation only begins at 280°C and the commercial H2O sample was completely degraded at 460°C. The increase in thermal stability for the CNTs-GO-H20 nanocomposite may be ascribed to the ability of the outer graphene surface of CNTs-GO to capture free radicals generated during thermal decomposition [10].

3.3. XPS analysis of samples
The changes of C and O elements content in the three samples were shown in Table 1. C1s XPS spectra before and after modification were analyzed as shown in Figs. 4a, b and c.

| Element(x%) | C  | O   | Si  |
|-------------|----|-----|-----|
| CNTs-GO     | 79.43 | 20.57 | 0  |
| functionalized CNTs-GO | 79.36 | 19.24 | 1.4 |
| CNTs-GO-H20 | 83.73 | 15.38 | 0.89 |

As shown in Table 1, the content of the C and O atoms in the pristine CNTs was 97% and 3%. After pretreated by KMnO4, the content of the C and O atoms was changed to 79.43% and 20.57%. The signals in Fig.4a at 284.6eV, 285.1eV, 287eV and 288.2eV correspond to C-C, C-OH, C-O-C and C=O, respectively [11]. It was believed that the CNTs introduced oxygen functional groups, which indirectly proved that CNTs were opened [12]. After CNTs-GO was functionalized with KH560, the content of Si element was increased to 1.4%, which indicated the successful attachment of KH560 on the surface of CNTs-GO. And the new peak at 285.5eV appeared in Figs. 4b and 4c was contributed by C-O-Si, confirming the successful attachment of KH560.

Comparing Figs. 4b and Fig. 4c, the C1s showed two significant intensity changes that the increase at 285eV and the decrease at 286.75eV, which indicated the addition of hydroxyl groups and loss of epoxy groups. Those changes were caused by the successful grafting of hyperbranched polyester.
3.4. TEM analysis of samples

As shown in Fig. 5 TEM images of the CNTs revealed the presence of hollow tubes with 25nm in mean diameter (Fig. 5a).

![TEM images of CNTs](image1)

After the treatment by Hummer method, the diameter increased to 50nm (Fig. 5b). At higher magnification (20nm), it can be observed that CNTS-GO exhibits serrated border (Fig. 5b-1). As shown in Fig. 5c, we found that the side walls of CNTs unravelled to form the nanoribbons. All those phenomena indicated that the outer structure of CNTs was successfully opened. From the TEM images of CNTs-GO-H20 (Figs. 5d, e, f), it can be found that the wall of CNTs became rough. In Fig. 4f, the mean diameter of the CNTs is 50nm and that of the outer polymer H20 layer is about 10nm. The values indicated that CNTs core were effectively functionalized with a soft organic shell through the grated reaction.

3.5. Dispersion analysis of nanocomposite materials-sediment experiment

Fig. 6 shows results of the sedimentation experiment. The pristine CNTs (Fig. 6A) quickly precipitated in the water solution even after sonication owing to the van der Waals interactions. For the CNTs-GO (Figs. 6B and 6C), the π-π stacking interactions between the outer “GO” structure and inner CNTs structure bind the hybrid, while the hydrophilic surfaces of the CNTs-GO improved the dispersion in solution [13]. So the dispersion can be stable for six months. As shown in Figs. 6D and 6E, CNTs-GO-H20 can prevent the entanglement of CNTs due to the larger static hindrance and the more terminal hydrophilic groups of H20. The nanocomposites /H20 suspension in Fig. 6G was uniform and stable more for than five days. Physical effects may also come into play: the sphere-like superstructure of H20 can allow the CNTs to permeate into the polymer to improve the dispersion [14].

![Sedimentation experiments](image2)

Figure 5. TEM images of (a) pristine CNTS; (b, c) CNTS-GO; (d, e, f) CNTS-GO-H20

Figure 6. Sedimentation experiments of various solution samples
(A) pristine CNTs/water solution, (B) CNTs-GO/water solution, (C) CNTs-GO/DMF solution, (D) CNTs-GO-H20/water solution, (E) CNTS-GO-H20/DMF solution, (G)CNTS-GO-H20/H20 solution
3.6. The electrochemical measurements of the composite coating

Fig. 7 shows results of the electrochemical measurements of samples. The addition of nanocomposite materials in the composite coating was one percent of the HB polyester H20. As shown in Fig. 7A, it is found corrosion potentials (Ecorr) positively increases from -0.358 V (a) to -0.270 V (b) and -0.209 V (c). In addition, corrosion current densities (icorr) of H20 coating and composite coating are 1.0718E-5 and 3.1707E-7 A/cm². And the icorr of bare Cu is 3.9703E-5 A/cm². More positive Ecorr and lower icorr of coating indicate that the film to be served as an effective barrier to diffusion of corrosive species. In Fig. 7B, we can observe that the bare Cu includes a capacitive loop at high frequencies and a straight line (Warburg impedance) at low frequencies, indicating that the diffusion process is controlled by the cathodic diffusion of dissolved oxygen from bulk solution to the electrode surface and the anodic diffusion of soluble Cu species from electrode surface to bulk solution. The diameter of the Nyquist loop in the coating is significantly larger than that of bare copper, indicating the polarization resistance has been greatly enhanced with the presence of coating.

![Figure 7. Potentiodynamic polarization curves](image)

And in Fig. 7C, it can be clearly seen that the impedance modulus at low frequency limit (10 mHz) of coating sample is greater than untreated sample. These phenomena indicate that the coating provides high resistance to corrosive medium [15].

4. Conclusions

The CNTs-GO-H20 nanocomposites were synthesized successfully as evidenced by FTIR and XPS spectra. The reduced weight loss of the nanocomposites is attributed to the amount of H20 grafted on the CNTs-GO surface, which indicates better thermal stability. The nanocomposite/H20 solution can be stable for a few days, which shows promise in liquid composite coating. At the same time, the coating samples exhibited better corrosion inhibitive properties in comparison with bare Cu substrate, as demonstrated by measurement results from potentiodynamic polarization curves and EIS techniques in 3.5 wt% aqueous NaCl solution. Compared with the traditional liquid coating, it has the following advantages: convenient for storage, better stability and less pollution for environment.

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