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Preparation and Properties of Octadecylamine Modified Carbon Nanotubes

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Abstract

Carbon nanotubes (CNTs) have become an ideal reinforcement filler for polymer composites due to their unique one-dimensional hollow structure and excellent mechanical properties. However, the chemical inertness and easy agglomeration of the CNTs' surface limit their wide application. In this paper, the "oxidation amidation" two-step method was used to modify the surface of multi-walled carbon nanotubes. Firstly, carboxyl active sites (O-CNTs) were introduced on the surface of CNTs by hydrogen peroxide oxidation, and then octadecylamine was grafted onto the surface of CNTs by amide reaction with 1,1'-carbonyl diimidazole (CDI) as an activator to prepare hydrophobic functionalized carbon nanotubes (A-CNTs). The structure, morphology, and surface properties of CNTs before and after modification were systematically characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and contact angle test. The results showed that the oxidation treatment successfully introduced oxygen-containing functional groups such as carboxyl groups on the surface of CNTs, and octadecylamine was covalently grafted to the surface of CNTs through amide bonds, and the nitrogen element was evenly distributed after grafting; XRD analysis showed that the main crystal structure of CNTs was not destroyed during the modification process; The contact angle test showed that the contact angle of the original CNTs was 98.2°, the O-CNTs after oxidation was 107.1°, and the A-CNTs after octadecylamine modification increased to 137.9°, realizing the transition from hydrophobic to strong hydrophobic.

Keywords

CNTs, Octadecylamine, Surface Modification, Amidation, Hydrophobic Modification.

1. Introduction

Since the characterization of the Iijima system in 1991, carbon nanotubes (CNTs) have been known as the "ultimate reinforcement filler" of polymer matrix composites due to their unique one-dimensional hollow structure, ultra-high aspect ratio (>1000), and excellent mechanical properties (tensile strength up to 60 GPa, elastic modulus about 1 TPA) [1-3]. Research shows that adding a small amount of CNTs into the polymer matrix can significantly improve the tensile strength, elastic modulus, and fracture toughness of the material [4]. However, CNTs are faced with two inherent challenges in practical applications: First, the original CNTs are smooth and chemically inert, lacking active functional groups that form a strong interface with the polymer matrix, making it difficult to achieve effective load transfer; Second, the strong van der Waals force makes CNTs easy to agglomerate and difficult to disperse uniformly in the matrix, but may become a stress concentration point [5, 6]. Surface modification is the key strategy to

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overcome the above obstacles. The introduction of specific functional groups on the surface of CNTs by covalent or non-covalent methods can not only improve their dispersion, but also regulate their interface compatibility with the matrix [7, 8].

For special application scenarios such as coal mine anchorage and geotechnical engineering, it is of great significance to endow CNTs with coal-rock-friendly characteristics (hydrophobicity) for the bonding performance between reinforcement materials and coal-rock interface. The surface of coal and rock usually shows hydrophobic characteristics. If the reinforced filler also has hydrophobic characteristics, the interface matching of "similar solubility" can be realized, so as to greatly improve the interface bonding strength [9]. Octadecylamine is an organic amine with a long carbon chain structure. Its nonpolar long chain has good affinity with the surface of coal and rock. By grafting octadecylamine onto the surface of CNTs, it is expected to improve the dispersion of CNTs and endow them with hydrophobic properties [10, 11].

At present, the surface functionalization methods of CNTs mainly include oxidation method, silane coupling agent method, polymer grafting method, etc. [12] Among them, oxidation is the most basic covalent modification method, which introduces oxygen-containing functional groups such as carboxyl (-COOH), hydroxyl (-OH) on the surface of CNTs through mixed acid or hydrogen peroxide treatment, providing reactive active sites for further functionalization [13]. Compared with the traditional mixed acid method, the hydrogen peroxide oxidation method has the advantages of mild reaction conditions, safe operation, and environmental friendliness [14]. On this basis, functional molecules containing amino groups can be grafted onto the surface of CNTs by the amidation reaction of carboxyl groups and amino groups to achieve functional design of specific properties [15].

Based on the above analysis, a two-step method of "oxidation amidation" was proposed to modify the surface of multi walled carbon nanotubes: firstly, carboxyl active sites (O-CNTs) were introduced on the surface of CNTs by hydrogen peroxide oxidation, and then hydrophobically functionalized carbon nanotubes (A-CNTs) were prepared by grafting octadecylamine onto the surface of CNTs through amide reaction with CDI as activator. The structure, morphology, and surface properties of CNTs before and after modification were systematically studied.

2. Experimental

2.1. Preparation of Oxidized Carbon Nanotubes (O-CNTs)

Carbon nanotubes were pretreated by hydrogen peroxide oxidation. Weigh 5 mg of MWCNTs into a 250 mL beaker, add 50 mL of 30% H_2O_2 solution, and vibrate with ultrasonic for 60 min. During this period, keep stirring with a glass rod to prevent CNTs from agglomeration. After ultrasonic treatment, 10 mL of 0.6 mol/L dilute sulfuric acid was added to the black suspension, transferred to a 250 mL three-port flask, and refluxed at 105 ℃ for 60 min. After the reaction liquid is cooled, the 0.45 μm polytetrafluoroethylene microporous membrane is used for suction filtration, and the filter cake is repeatedly washed with distilled water until the pH of the filtrate is neutral. Redispersing the filter cake in distilled water, centrifuging at 3500 r/min for 10 min, discarding the supernatant, repeatedly washing and centrifuging three times. The obtained black solid product was vacuum dried at 50 ℃ to constant weight, sealed, and stored as O-CNTs [16].

2.2. Preparation of Octadecylamine Functionalized Carbon Nanotubes (A-CNTs)

5 mg of O-CNTs were dispersed in 50 mL of anhydrous THF, and ultrasonicated for 30 min to achieve uniform dispersion of the CNTs. Subsequently, 0.01 g of 1,1'-carbonyldiimidazole (CDI) was added to the dispersion, and the mixture was stirred at room temperature for 4 h to

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activate the carboxyl groups. Then, 0.5 g of octadecylamine was added, and the reaction was allowed to proceed with continuous stirring at room temperature overnight. After the reaction, the solvent was removed by vacuum filtration, and the filter cake was repeatedly washed three times with anhydrous ethanol to remove unreacted octadecylamine and by-products. Finally, the product was dried under vacuum at 60 °C for 24 h. The preparation process is illustrated in Fig. 1, and the resulting product is denoted as A-CNTs.

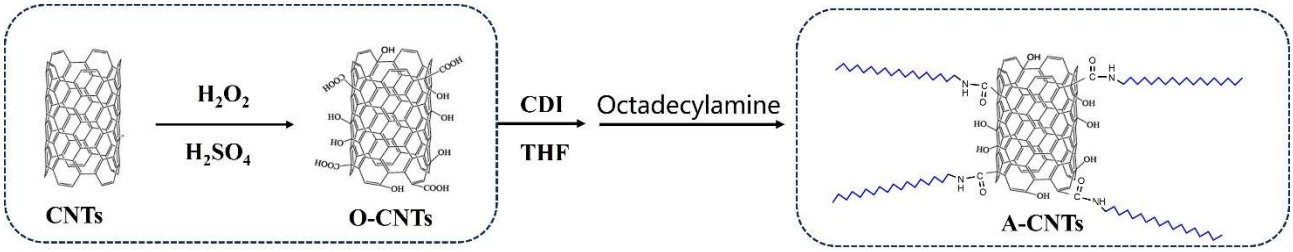

Fig. 1 A-CNTs preparation route

3. Results and Discussion

The samples were characterized by Brooke alpha Fourier transform infrared spectrometer (FT-IR). As shown in Fig. 2, the measurement range is 400-4500 cm^{-1}, the number of scans is 16, and the resolution is 4cm^{-1}. For untreated carbon nanotubes (CNTs), the peak shape of the infrared spectrum fluctuates greatly, and the peak shape is irregular, but it can also be seen that the band signal of 1634 cm^{-1} belongs to the stretching vibration of quinone group (C=O), and the band signal of 1510 cm^{-1} belongs to the graphite carbon skeleton [17]. After the oxidation of hydrogen peroxide, defects appear on the side walls and open ends of carbon nanotubes, and oxygen-containing functional groups are attached to form carboxylated multi-walled carbon nanotubes (O-CNTs). As shown in Fig. 2, 1724 cm^{-1} and 1021 cm^{-1} are the C=O and C-O stretching vibrations of carboxylic acid groups (-COOH), and 1421 cm^{-1} is the O-H stretching vibration of hydroxyl groups [18]. Infrared results show that carboxyl groups are introduced on the surface of multi-walled carbon nanotubes after oxidation.

CNTs have a carboxyl group on the surface, and the reaction activity is low, while the carbonyl group in CDI has a strong electrophilicity. It can react with the hydroxyl group of the carboxyl group to produce a nucleophilic substitution reaction, so that the carboxyl group is transformed into an active ester intermediate, and reacts with an amino functional group at one end of octadecylamine to form an amide bond. As shown in Fig. 2, the symmetric stretching vibration peak of methyl appeared near 2860 cm^{-1}, and the stretching vibration peak, in-plane bending vibration peak and out of plane bending vibration peak of methylene appeared near 2930 cm^{-1}1470 cm^{-1} and 720 cm^{-1}, respectively, which were the long carbon chain structure of Octadecylamine.1620 cm^{-1}, 1558 cm^{-1} and 1463 cm^{-1} were the stretching vibration peaks of C=O, C-N and -NH in the amide bond, respectively, indicating that octadecylamine was grafted onto the surface of O-CNTs by amide reaction.

As shown in Fig. 3, in the XRD pattern of carbon nanotubes, there is an obvious wide peak at a 2θ angle of about 25°, which corresponds to the (002) crystal plane diffraction of carbon nanotubes. It reflects the graphitization structure between the layers of carbon nanotubes. In addition, the diffraction peak corresponding to the (100) crystal plane appears at about 43° [19]. After modification, both O-CNTs and A-CNTs have characteristic diffraction peaks in a similar angle region, which indicates that they retain the basic crystal structure characteristics of carbon nanotubes, indicating that the main crystal structure of carbon nanotubes is not damaged by modification and other treatment processes. In addition, compared with the original CNTs, the intensity and shape of the diffraction peaks of the modified carbon nanotubes

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(O-CNTs, A-CNTs) were weakened to a certain extent. This may be because the oxidation treatment introduced oxygen-containing functional groups on the surface of carbon nanotubes, which did not change the main crystal structure, but had an impact on the crystal order and grain size. The grafting and adsorption of Octadecylamine on the surface of carbon nanotubes will also affect the micro arrangement of the crystal structure of carbon nanotubes [20].

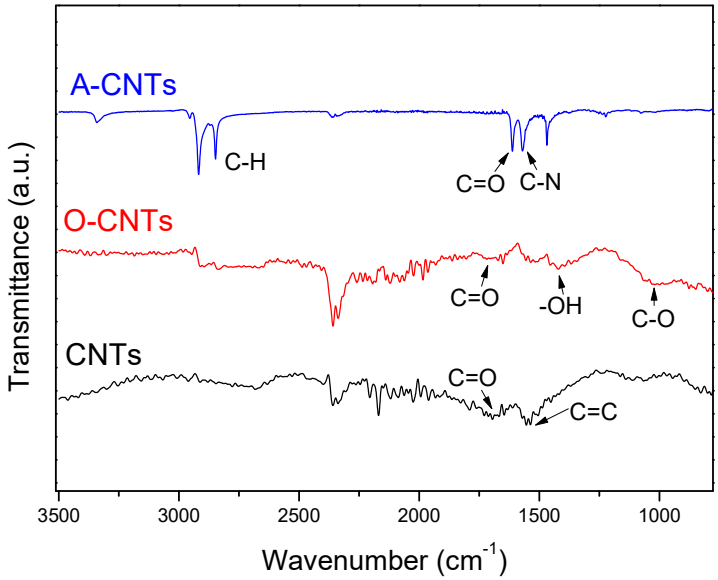

Fig. 2 Infrared Spectra of carbon nanotubes before and after modification

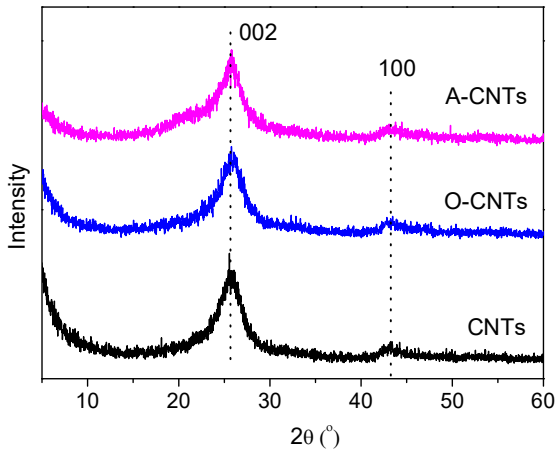

Fig. 3 XRD patterns of carbon nanotube materials before and after modification

According to the SEM photos in Fig. 4, the unmodified CNTs show a relatively fine, intertwined, and relatively uniform morphology. The surface roughness of O-CNTs after oxidation modification increased. This change may be due to the introduction of carboxyl and other oxygen-containing functional groups on the surface of carbon nanotubes modified by hydrogen peroxide oxidation. The introduction of these functional groups changed the chemical composition of the surface of carbon nanotubes, and then the surface became rough in the micro morphology, which also proved that the oxidation modification process successfully introduced new groups on the surface of carbon nanotubes, which had an impact on the structure of carbon nanotubes, and provided a structural basis for further modification or application based on these functional groups. Combined with the EDS oxygen element distribution diagram of O-CNTs, the oxygen element is evenly distributed in the material, which

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further proves the successful introduction and uniform distribution of oxygen-containing functional groups on the surface of carbon nanotubes after oxidative modification, indicating that the oxidative modification process is successful.

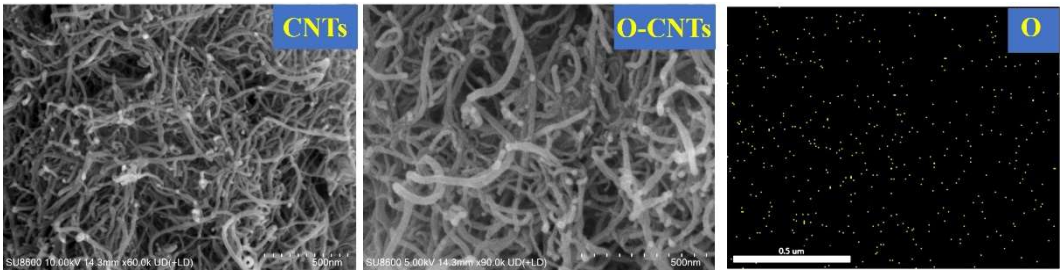

Fig. 4 scanning electron microscope photos of CNT materials before and after oxidative modification, and EDS element (O) distribution diagram of O-CNTs

The SEM and EDS results of A-CNTs materials are shown in Fig. 5. It can be seen that the surface of A-CNTs carbon nanotubes is rough, and there are some similar particles or agglomerated parts, which are formed after octadecylamine is successfully grafted onto the surface of carbon nanotubes, indicating that octadecylamine modification has a significant effect on the surface of carbon nanotubes, which has changed the surface morphology of carbon nanotubes and is no longer as smooth as unmodified carbon nanotubes. In addition, it can be seen from the energy spectrum distribution that nitrogen is evenly distributed on A-CNTs, because octadecylamine molecules contain nitrogen, and the uniform distribution of nitrogen in the energy spectrum indicates that the grafting of Octadecylamine on the surface of carbon nanotubes is relatively uniform during the modification process, and there is no local large amount of aggregation or local deletion.

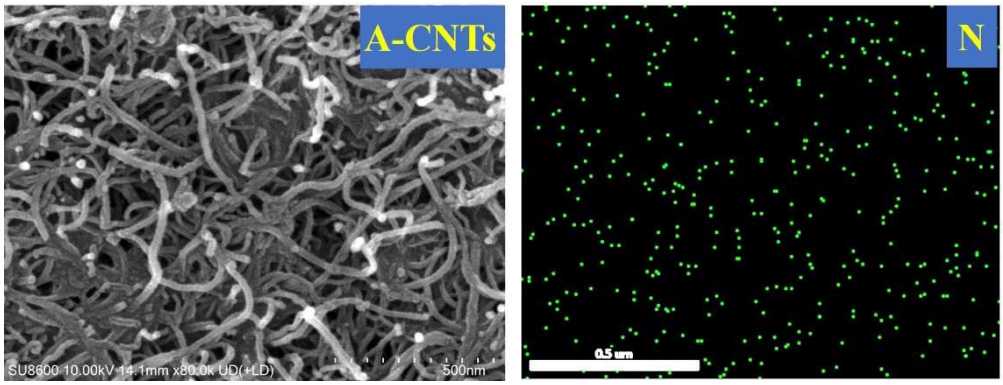

Fig. 5 SEM and N element distribution of A-CNTs

Contact angle is an important index to measure the wettability of a liquid to solid surface. The larger the contact angle is, the stronger the hydrophobicity of the solid surface is; The smaller the contact angle, the stronger the hydrophilicity. It can be seen from Fig. 6 that the surface of O-CNTs contains oxygen-containing functional groups such as carboxyl groups. These polar functional groups have hydrogen bonds and dipole-dipole interactions with water molecules. Although these functions are not enough to make the material hydrophilic, they promote the spread of liquid to a certain extent, and the total body still shows a certain degree of hydrophobicity (107.1°) [21]. Octadecylamine is a long-chain organic amine with a nonpolar long carbon chain structure. When octadecylamine was grafted onto the surface of carbon nanotubes with carboxyl as the reaction site, the long carbon chain structure was exposed on

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the surface. The dispersion force between the long carbon chains was mainly the van der Waals force, which attracted water molecules very weakly. Moreover, the steric hindrance effect of the long carbon chain also hindered the contact between water molecules and the surface of carbon nanotubes, which increased the contact angle and significantly enhanced the hydrophobicity of the material surface. As a result, the contact angle increased significantly to 137.9°, which further enhanced the hydrophobicity of the material [22]. The above results confirmed that octadecylamine was successfully used to modify the surface of carbon nanotubes, and enhanced the surface hydrophobic properties of the materials, which gave the nanomaterials the characteristics of coal rock, and would help to bond the anchoring agent with coal rock.

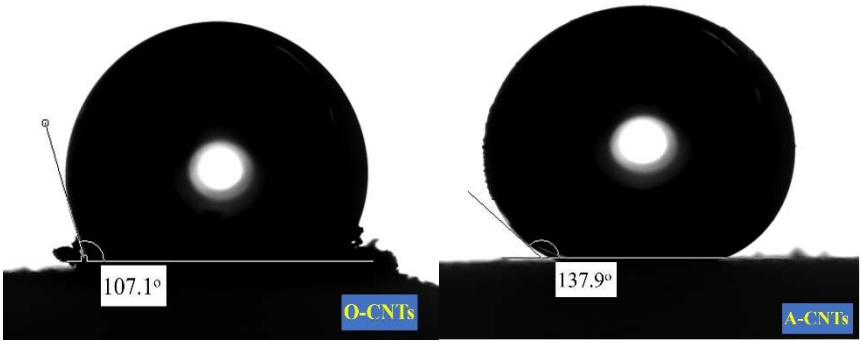

Fig. 6 Contact angle of O-CNTs and A-CNTs

4. Conclusion

This study successfully prepared octadecylamine-modified hydrophobic carbon nanotubes (A-CNTs) using a two-step "oxidation-amidation" method. FT-IR and EDS analysis confirmed that octadecylamine was covalently grafted onto the CNTs surface via amide bonds, with uniform nitrogen distribution. XRD results indicated that the modification process did not disrupt the main crystal structure of the CNTs. Contact angle tests revealed that the contact angle of the modified CNTs increased from 107.1° to 137.9°, achieving a transition from hydrophobic to superhydrophobic surface properties, which endowed the material with excellent performance.

Acknowledgments

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