Research Progress in Surface Modification of Carbon Nanotubes

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Abstract

Carbon nanotubes (CNTs) are a kind of nanomaterial with a unique one-dimensional hollow structure and excellent mechanical and electrical properties. Because of their excellent mechanical strength, high aspect ratio, and good electrical and thermal conductivity, CNTs have been applied in many fields. In addition, its unique nanotube structure and large specific surface area are conducive to the construction of stable carrier transport channels, making it a hot spot in the field of polymer composites. However, CNTs are chemically inert on the surface, and strong van der Waals interactions exist between the tubes, which easily form aggregates, seriously restricting their dispersion in the matrix and interface bonding ability. Surface modification of CNTs has become a key way to overcome their limitations and enhance their potential. Functional groups such as carboxyl (-COOH) and hydroxyl (-OH) on CNTs can form covalent bonds or hydrogen bonds with polar groups in the polymer matrix to promote load transfer efficiency. The interaction between the nanofiller and polymer can also improve the mechanical properties of composites. Therefore, the preparation, modification, and application of CNTs in polymer composites are reviewed in this paper, and the challenges and potential future research directions in the field of composites are evaluated.

Keywords

Carbon Nanotubes; Covalent Modification; Non-covalent Modification; Composite Material.

1. Introduction

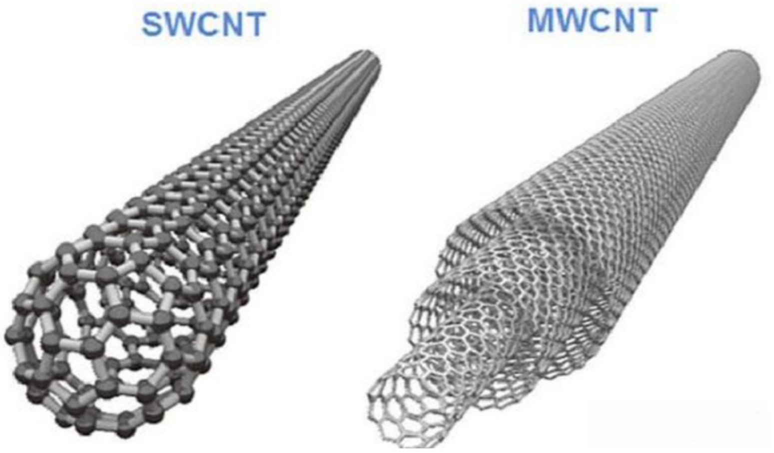

Fig 1. The schematic diagram of single-wall carbon nanotubes (SWCNT) and multi-wall carbon nanotubes (MWCNT)

Since carbon nanotubes were characterized by Iijima in 1991, they have become a research hotspot in the field of nanotechnology due to their unique one-dimensional hollow structure and graphene network composed of SP^2 hybrid carbon atoms [1-3]. Carbon nanotubes can be regarded as a one-dimensional tubular structure formed by the crimping of graphene sheets. According to the number of graphene layers, carbon nanotubes can be divided into single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). As shown, SWNTs are coiled from a graphene monolayer, and their diameters are usually between 0.4 and 2 nm; MWCNTs are coaxially jacketed with multilayer graphene, with a layer spacing of about 0.34 nm and a diameter of tens of nanometers [4-6].

The carbon atoms in carbon nanotubes are mainly sp^2 hybridized, forming a highly delocalized conjugated π bond system, which shows excellent mechanical properties (tensile strength up to 60 GPA), extremely high aspect ratio (>1000), excellent conductivity (10^4 s/m), and thermal conductivity (up to 3500 w/m·K) [7]. These excellent properties enable carbon nanotubes to show broad application prospects in nanocomposites, energy storage, sensors, aerospace, and other frontier fields [8-10].

However, carbon nanotubes face two core challenges in practical applications: Firstly, the surface of carbon nanotubes is smooth and chemically inert, lacking active functional groups, and the interface adhesion with polymer or cement matrix is weak, so it is difficult to achieve effective load transfer; Second, there is a strong van der Waals interaction between carbon nanotubes, which is easy to form aggregates and difficult to be evenly dispersed in the matrix, which not only weakens the performance of the composite, but also may become a stress concentration point leading to early failure of the material [11]. B.M. V studied the purification and surface modification of multi-walled carbon nanotubes [12], which showed that the morphology of the modified multi-walled carbon nanotubes changed significantly, the entanglement between the tubes was reduced, and the corresponding functional groups were grafted on the surface. D. Liu et al.·[13] pointed out that because carbon nanotubes are prone to introducing different types of defects in the growth process, functional modification has become the main way to overcome their limitations.

Therefore, proper surface modification of carbon nanotubes has become a key scientific issue to give full play to their excellent properties and promote their engineering applications. It is easy to modify the surface of carbon nanotubes because of the existence of defect sites on their surface. A large number of oxygen-containing functional groups can be introduced through oxidation treatment, and there is an aromatic conjugated π bond skeleton inside, which provides full possibilities for its surface functionalization. In recent years, researchers have developed a series of modification strategies for carbon nanotubes, mainly including covalent modification and non-covalent modification, and have achieved rich research results in the fields of polymer composites, cement-based materials, and functional materials.

2. Surface Modification of Carbon Nanotubes

Carbon nanotubes have excellent electronic structure and good thermal and chemical stability, which are applied in all aspects of life. However, with the more and more in-depth study of carbon nanotubes, the shortcomings of carbon nanotubes, such as inert surface, easy agglomeration, poor dispersion in the matrix and so on have emerged. Therefore, researchers have improved its performance through various modification methods. Many scholars have studied how to improve the properties of carbon nanotubes. The modification methods of carbon nanotubes generally include covalent modification and non-covalent modification.

2.1. Covalent Modification

Covalent modification is to introduce new functional groups through the formation of stable covalent bonds between carbon nanotube functional groups and chemical modifiers, such as oxidation, silylation, sulfonation, polymer grafting, etc. [14] B.M.V [12] used a variety of surface modifiers to modify the purified multi-walled carbon nanotubes. TEM characterization confirmed that the surface of the modified carbon nanotubes was grafted with corresponding functional groups, the morphology changed significantly, and the entanglement between the tubes was reduced.

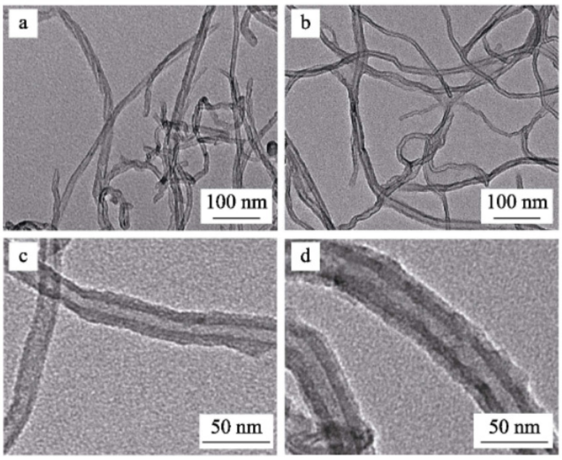

Fig 2. TEM images of CNTs before (a, c) and after (b, d) surface modification[12].

Oxidation treatment is the most basic covalent modification method, and oxygen-containing functional groups such as carboxyl (-COOH), hydroxyl (-OH) are introduced on the surface of carbon nanotubes by mixed acid (HNO_3/H_2SO_4) treatment. The typical process is as follows: 1 g of multi walled carbon nanotubes are added to 300 ml of mixed acid of nitric acid and sulfuric acid (V: V=1:3), stirred at 80 °C for 2 h, ultrasonically dispersed for 1 h, centrifuged and repeatedly washed with deionized water to neutral, and finally dried at 100 °C [15, 16]. Guo et al. [17] compared the performance of hydroxylated (TNIMC4) and carboxylated (TNIMC6) carbon nanotubes, and found that the strengthening effect of carboxylated carbon nanotubes was better than that of hydroxylated carbon nanotubes. When 0.07% was added, the strength of cement paste increased by 19.18%, indicating that the interaction between carboxyl and matrix was stronger. The carboxyl groups on the surface of carbon nanotubes can also be further functionalized by amidation reaction. For example, polyethersulfone grafted modified carbon nanotubes (PES-CNTs) can be prepared by reacting with aminated polyethersulfone ($PES-NH_2$) in the presence of N, N'-Dicyclohexylcarbodiimide (DCC).

In addition, the surface of carbon nanotubes can be functionalized with a silane coupling agent, which can effectively expand their application range. Wang et al [18] modified the surface of carbon nanotubes by the silane coupling agent method and applied it to nitrile rubber. The multilevel modification strategy of "oxidation reduction silylation" proposed by Wang et al. Can significantly improve the silane grafting efficiency by converting the carboxyl group to a hydroxyl group through $NaBH_4$ reduction. When the amount of silane coupling agent (KH-540) is 5 wt%, the dispersion stability of modified carbon nanotubes in polar solvents is the best, and the absolute value of zeta potential is significantly improved. By covalently modifying carbon nanotubes with polymers, monomers can be directly polymerized in situ from the surface of carbon nanotubes, or the active end groups of the pre-synthesized polymers can be reacted with the functional groups on the surface of carbon nanotubes.

Yadong et al. [19] modified carbon nanotubes with toluene-2,4-diisocyanate to prepare isocyanate functionalized carbon nanotubes (CNT-NCO), and prepared CNT-NCO/TPU composites through in-situ polymerization. When the CNT-NCO content was 0.1%, the Vicat softening temperature of the composites increased by 32 °C, and the tensile strength increased by about 15 MPa. This strategy can effectively prevent the agglomeration of carbon nanotubes and change their affinity to different substrates while retaining their inherent properties.

2.2. Non-covalent Modification

Non-covalent modification is mainly achieved through physical bonding and intermolecular interactions, such as van der Waals interaction, electrostatic interaction, π-π stacking, etc. Noncovalent functionalization is formed by the interaction between the delocalized π bond on the carbon wall (hybridization with π bond sp^2) and the aromatic ring structure or the electrostatic attraction of functional molecules. The noncovalent interaction between carbon nanotubes and organic/inorganic materials may be relatively weak, resulting in poor long-term stability. However, the advantage of non-covalent synthesis strategy is that it can combine the characteristics of each molecule and retain the inherent properties of the two parts, without destroying the intrinsic sp^2 conjugated structure of carbon nanotubes, and completely retain its electrical and mechanical properties [20, 21].

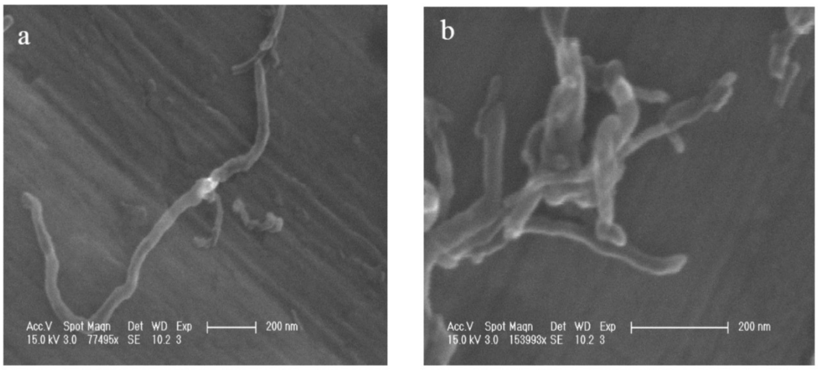

Fig 3. The SEM image of (a) MWCNTs and (b)MWCNTs modified by β-CD

Small molecules containing aromatic rings can be adsorbed on the surface of carbon nanotubes through strong π-π interactions. Pyrene and its derivatives have large conjugated systems, and their delocalized π electrons can interact with the aromatic skeleton of carbon nanotubes in π-π stacking to achieve non-covalent modification. Farsi et al. [22] used non-covalent modifiers such as sodium dodecyl benzene sulfonate (SDBS), polyethylene glycol (PEG2000), and polyvinylpyrrolidone (PVP) to pretreat the surface of multi-walled carbon nanotubes. The research showed that the thermal conductivity of multi-walled carbon nanotubes modified by PEG surface improved the most in wood plastic composites, which was due to the non-covalent coating of PEG, which improved the dispersion of carbon nanotubes in the matrix and formed a more effective thermal conductivity network.

Polymer coating is another important non-covalent modification strategy. Conjugated polymers (such as polyphenylene ethylene derivatives, polythiophene, etc.) can be tightly combined with the surface of carbon nanotubes through π-π stacking to form a stable composite structure. Wu et al. Prepared graphene oxide (GO) and g-C_3N_4 composite film, which has reference significance for the modification of carbon nanotubes. The results show that the ζ potential difference between GO and g-C_3N_4 indicates that their dispersions are negatively and positively charged, respectively. The interaction between them in the composite film is mainly the electrostatic force and π-π stacking interaction. Similarly, the non-covalent coating between the polymer with opposite charge and carbon nanotubes can also be achieved through electrostatic interaction, and π-π stacking further enhances the interface bonding. This kind of modification can not only improve the dispersion, but also endow carbon nanotubes with specific photoelectric functions. Alaa et al. [23]pointed out that non-covalent modification can improve the dispersion of carbon nanotubes in the polymer matrix without destroying their intrinsic structure, which is particularly important for applications that need to maintain the conductivity of carbon nanotubes.

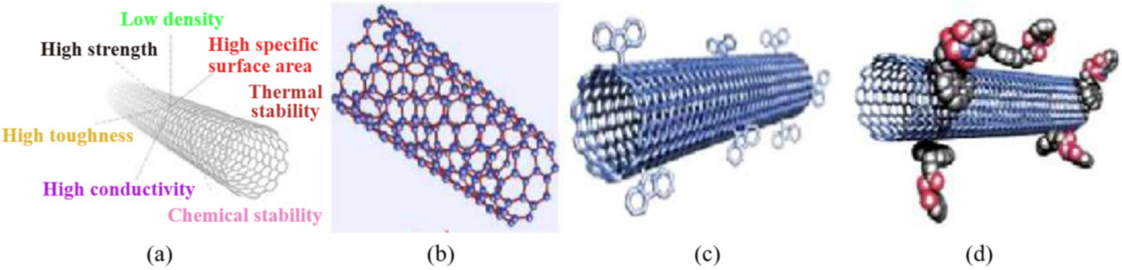

Fig 4. Physical and chemical properties of carbon nanotubes (a), schematic diagram of covalent (b), side wall (c), and non-covalent modification of structure(d)

3. Application of Modified Carbon Nanotubes in Composites

In polymer matrix composites, modified carbon nanotubes are the most widely used. Wang et al [18] used the acrylic acid method and the coupling agent method to modify the surface of carbon nanotubes, and found that the reinforcement effect of carbon nanotubes modified by the acrylic acid method on nitrile rubber was better than that of coupling agent method, which effectively improved the tensile strength, tear strength, thermal conductivity and wear resistance of the compound. K. Nabil [24] used carboxyl and epoxy functionalization methods to modify carbon nanotubes and prepare epoxy resin composites. The results showed that E-M60/EP had the best toughening effect, and the impact strength, bending strength, tensile strength, and elongation at break were increased by 75.2%, 35.0%, 176%, and 1950%, respectively, compared with those before adding. Yadong et al [19] prepared isocyanate functionalized carbon nanotubes (CNT-NCO) and obtained TPU composites through in-situ polymerization. When the content of CNT-NCO was 0.1%, the Vicat softening temperature increased by 32 °C, and the tensile strength increased by about 15 MPa. Wang et al [25] used dopamine and silane to modify carbon nanotubes to prepare waterborne polyurethane composites. The tensile strength reached 29.6 MPa at 0.75% addition, and the thermal decomposition temperature increased by 28 °C. The results show that the covalent bond or hydrogen bond interaction between modified carbon nanotubes and polymer matrix is the key to improving the performance.

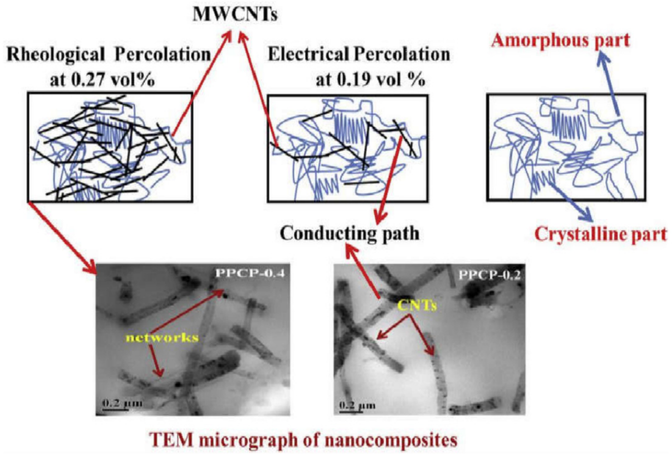

Fig 5. Schematic representation of electrical percolation and rheological percolation of nanocomposites (Supported by TEM micrographs)

In the field of cement-based composites, modified carbon nanotubes also show an excellent reinforcement effect. Wei et al [26] introduced polyvinyl alcohol and polyacrylamide as interface bridging agents to solve the problem of weak interface bonding between carbon nanotubes and cement matrix. The results showed that the 28d flexural strength and compressive strength of the composites using carboxyl carbon nanotubes and the bridging agent were increased by 47.4% and 22.7%, respectively. SEM showed that the bridging agent made the connection between carbon nanotubes and the cement matrix denser and enhanced the pull-out effect. Guo et al [17] compared the enhancement effects of hydroxylated (TNIMC4) and carboxylated (TNIMC6) carbon nanotubes, and found that carboxylated carbon nanotubes had better performance. When 0.07% was added, the strength of cement paste increased by 19.18%, and the triaxial compressive strength increased by 41.21%. The results show that the types of functional groups on the surface of carbon nanotubes have a significant effect on the interfacial bonding ability, and the chemical affinity between carboxyl and cement hydration products is stronger.

Fig 6. Flexural and compressive specimens of carbon nanotube cement matrix composites

In other composite systems, modified carbon nanotubes also exhibit multifunctional reinforcement properties. Farsi et al [22] used different modifiers to treat multi-walled carbon nanotubes and prepare wood plastic composites. It was found that the resistivity of the composites modified with A-171 silane coupling agent decreased the most, the mechanical properties improved the most, and the thermal conductivity of the composites modified with PEG increased the most. The results show that the dispersion of modified carbon nanotubes in the matrix, the interfacial bonding strength, and the optimal content range are the key factors affecting the final properties of the composites. When the amount of filler is less, the dispersion of modified carbon nanotubes is better, and the one-dimensional tubular structure forms an effective network with the matrix. When the content exceeds the optimal content, the agglomeration phenomenon leads to the reduction of effective interface binding sites and the decline of mechanical properties.

4. Conclusion

In this paper, the surface modification methods of carbon nanotubes and their applications in composites were systematically reviewed. Carbon nanotubes have become ideal reinforcement materials due to their unique one-dimensional structure, excellent mechanical properties, and large specific surface area. However, their surface inertia and easy agglomeration limit their application, and they need to be modified to unlock their potential. In terms of modification methods, covalent modification introduced functional groups through oxidation, silylation, grafting, and other ways, and the effect was stable; Non-covalent modification can be functionalized by coating or adsorption to retain intrinsic properties. In terms of application, the modified carbon nanotubes can optimize the matrix microstructure, strengthen the interface bonding, and significantly improve the mechanical properties and functionality of the composites. This paper provides a new idea for the modification of carbon nanotubes and the application of composites, and lays a foundation for their large-scale development.

Acknowledgments

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