

The preparation of CNT/PMMA composite film on SiO₂ substrates

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Microelectromechanical system (MEMS) has been highly valued since the size of the MEMS structure is miniaturized, the spacing between the components is in the nanometer range, and the behaviors of friction and adhesion greatly affect the reliability of MEMS. An atomic force microscope (AFM) was used to observe the surface morphology of carbon nanotube (CNT)/polymethyl methacrylate (PMMA) film, and X-ray photoelectron spectroscopy (XPS) was used to analyze the chemical state of typical elements on the surface of the film. The friction and wear properties of composite nano-films under macroscopic conditions were systematically studied. The research results show that the composite nano-film has excellent anti-friction and anti-wear properties.

Keywords: Carbon Nanotube/Polymethyl methacrylate; Micro-Electro-Mechanical System; on Nanotube RCNT (retraction Carbon Nanotube), PMDA (Pyromellitic dianhydride), ODA (Octadecylamine)

1. Introduction

In recent years, due to the vastness of their potential applications in wearable epidermal electronics and implantable biomedical devices, flexible electronic devices have made rapid development in this field [1]. Compared to traditional electronics, the flexible electronic device has greater flexibility [2]. However, the technical requirements that need to be satisfied for the successful production of flexible electronic devices restrict their development [3]. First of all, flexible electronic devices need to obtain stretchability and flexibility without damaging their own electronic performance, which poses new challenges and requirements for conductive materials; second, the preparation conditions of flexible electronics are high compared with traditional electronic devices [3]. The performance and stability are still insufficient, which is also a major problem in its development [4]. The electrode material in traditional electronic devices is mainly metal. Since metal does not have flexibility, it is prone to breakage and failure during stretching or bending, and it cannot meet the development needs of flexible devices [5]. At present, the flex-

ible materials that are widely studied are: hydrogel [4], liquid metal [6], high molecular polymer [7], and conductive nanomaterial [8]. It is particularly pointed out here that the carbon nanotube (CNT) film materials [9] forming part of the carbon nanomaterials have excellent electrical conductivity and thermal conductivity [10], excellent mechanical and chemical stability [11], and good flexibility [12]. Due to the characteristics of easy control of structure and performance and easy large-area preparation, it has emerged in the field of flexible electronics in recent years and has been widely and rapidly developed [13].

During the last few decades, research into polymer nanocomposites has received considerable interest because of their unique qualities and advantages over conventional materials [14]. In general, polymeric nanocomposites thin films are associated with a low cost of synthesis, easy to handle, and highly flexible. In addition, nanocomposites display a wide range of optical, mechanical, and electrical properties [15]. The exceptional properties of the polymethyl methacrylate (PMMA) polymer, e.g., high transparency, low cost, and unique environmental stability compared to other polymers, make it an excellent candidate for fabricating

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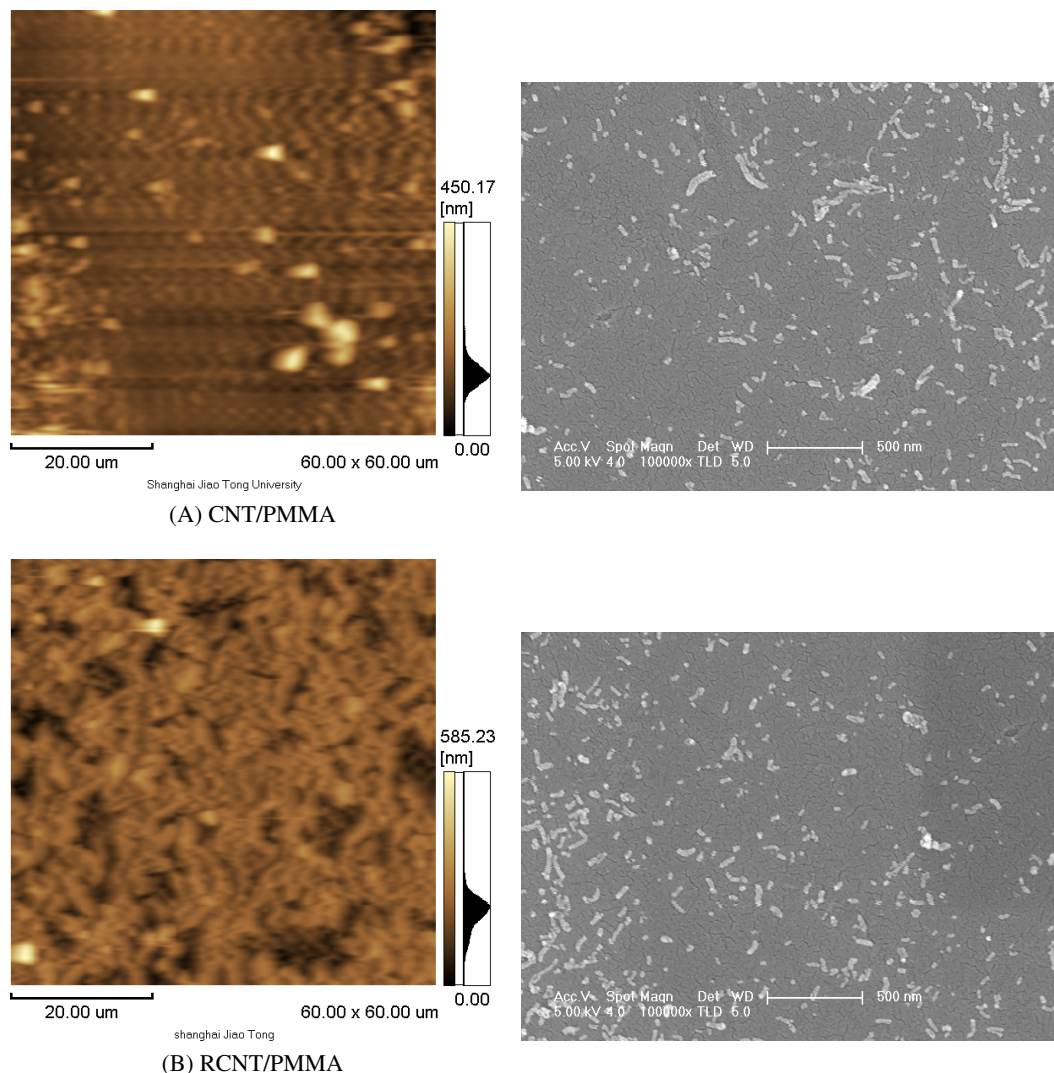


Fig. 1. AFM and SEM of CNT/PMMA film. AFM, atomic force microscope; CNT, carbon nanotube; PMMA, polymethyl methacrylate

thin films [16].

2. Experimental procedures

Hydroxylated chopped multi-walled CNTs (Chengdu Institute of Organic Chemistry, Sichuan), with a purity of 95%, a length of 0.5–2.0 μm , an outer diameter of 20–30 nm, and a hydroxyl content of 1.76% were utilized in the study. Twenty grams of CNT and 2.0 g of sodium nitrate were added to 50 mL of concentrated sulfuric acid at 0°C, and then placed in an ice water bath, keeping the temperature below

5°C, slowly adding 6.0 under high-speed stirring permanganate, and mixing well. Subsequently, the mixture was rapidly heated to 40°C and reacted at this temperature for 1 h, and then diluted with 100 mL of deionized water, after which the mixture was heated to 80°C and maintained for 15 min at this temperature. Then, it was poured into 300 mL of deionized water, and 20 mL of hydrogen peroxide was added, resulting in the solution turning bright yellow. Finally, the mixture was repeatedly washed with an aqueous hydrochloric acid solution (with a HCl/water volume ratio of 1/10), and the impurities were removed by suction filtration. The

powder was ultrasonically dispersed in DMF to prepare a 2.0 g/L CNT dispersion.

First, the polymerization reaction of PMDA and ODA in an equimolar ratio in DMF solution is used to prepare a PMMA solution with a mass fraction of 20%. Then, the CNT dispersion liquid and the PMMA solution are mixed to form a CNT-PMMA uniform mixed solution with different mass fractions. At room temperature, the mixed solution was placed on a glass plate to evaporate the solvent and form a film to obtain PMMA and CNT-PMMA films. Finally, the films were heat-treated at 120°C, 200°C, and 300°C for 3 h in order to obtain composite films.

The CNT powder was ultrasonically dispersed in DMF and then deposited on the surface of the silicon wafer. The surface morphology and thickness of the CNT were observed by atomic force microscopy (AFM, Veeco, USA).

The tensile properties of the film were tested by a film electronic universal testing machine (502B-EX, Shenzhen Wantest Testing Equipment Co., Ltd.), referring to the GB/T1040.2-2006 standard (Test conditions: 25°C, 30–50% RH, tensile velocity 0.002 m/s).

3. Results and discussions

3.1. CNT's dispersibility and structural characterization

The CNT dispersion liquid was dropped on silicon wafer and carbon grid and dried, and then passed AFM. The results are shown in Figures 1A and 1B. Figure 1A shows that CNT is uniformly dispersed in DMF to form a stable dispersion. The CNT sheet has a certain amount of polar functional groups of carboxyl, hydroxyl, and carbonyl groups, so that it can be stripped into a monolithic layered structure in the polar organic solvent DMF and remain stable for a long time. The results of AFM observation in Figure 1B show that CNT can be dispersed evenly. The stable CNT/DMF dispersion is easy to liquid-phase blend with the PMMA/DMF solution and form a uniformly dispersed CNT-PMMA mixed solution. The CNTs are uniformly distributed in the form of CNT bundles in the self-

assembled multilayer film, and form a dense structure, strong binding force, and high-purity random CNT network in the polymer matrix.

The X-ray photoelectron spectroscopy (XPS) full-spectrum data of the CNT-PMMA film on the surface of the SiO₂ substrate prepared by the high-temperature reduction method is shown in Figure 2. After reduction of CNT-PMMA film at high temperature, elements such as C, N, O, and Si can still be detected using XPS. Compared with the XPS full spectrum of CNT-PMMA film, the characteristic peak-to-peak value of the oxygen element in Figure 2 is significantly weakened, which indicates that the high-temperature reduction method has effectively reduced the oxygen content of the top CNT film. The CNT film was restored.

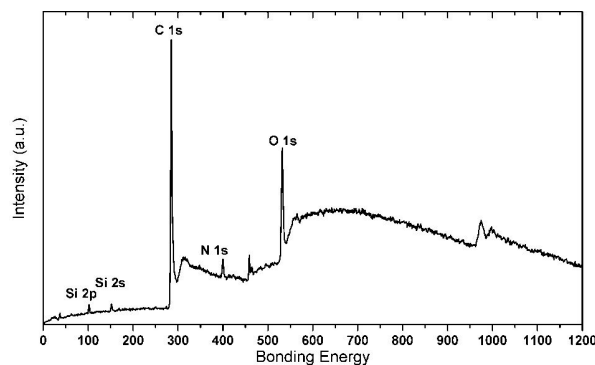


Fig. 2. XPS spectrum of CNT. CNT, carbon nanotube; XPS, X-ray photoelectron spectroscopy

In order to deeply explore the effect and mechanism of the high-temperature heating process on the reduction of CNT film, the XPS spectral analysis of C 1s was performed on the CNT-PMMA film on the surface of the SiO₂ substrate, and the C 1s energy spectrum was divided into peaks. The results are shown in the Figure 2. Similar to the C 1s spectrum of the CNT-PMMA film, the C 1s spectrum data of the RCNT-PMMA film can also be fitted into the four peaks of C–C or C=C, C–N, C–O, and C=O, and this arrangement is similar to that for the CNT-PMMA; compared with the XPS C 1s spectrum, the C–O bond peak in Figure 3 is significantly weakened, while the C=O bond peak is also weakened. The results show that the high-temperature reduction method success-

fully reduced most of the oxygen-containing functional groups on the surface of the CNT film, and the reduction efficiencies of the hydroxyl group and the reducing group were higher than that of the carboxyl group.

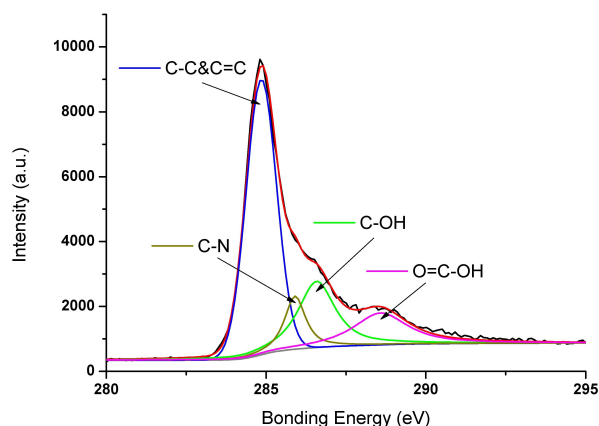


Fig. 3. Deconvolution XPS C 1s core spectrum of CNT. CNT, carbon nanotube; XPS, X-ray photoelectron spectroscopy

The electron binding energies are approximately 284 eV, 533 eV, and 970 eV, which are caused by C1s, O1s, and O2p, respectively. It should be noted that after treatment, a significant increase in oxygen content can be observed from the peak intensity, indicating the presence of functional groups on the surface of CNTs. In the spectrum of nanotubes, a new peak appears at around 400 eV.

It is not easy to remove the carboxyl group; the principle is as follows: on the one hand, the carboxyl group is located on the edge of the CNT molecule, and it is not easy to dehydrate with the hydrogen in the CNT molecule due to the restriction of the spatial position; on the other hand, the carboxyl group is relatively stable in chemical properties. The general reduction method cannot be used to easily restore it. Carboxyl reduction treatment requires the use of strong reducing agents, such as lithium aluminum hydride and sodium borohydride, but these reducing agents have certain risks or toxicity; there are also scholars who use high-temperature reduction methods above 1,000°C to reduce the carboxyl groups of CNT, but excessively high temperature will affect

the film strength and interfacial bonding force of the PMMA film. From the C 1s data of CNT and RCNT, it can be seen that the carboxyl content in CNT is very low compared to epoxy and hydroxyl groups, and the effect of carboxyl groups on the surface activity of the film is small.

3.1.1. XPS analysis of process effect of reducing CNT film by high-temperature heating method

This section compares and analyzes the XPS data of CNT to study the effect of high-temperature heating on the reduction of oxygen-containing functional groups.

In order to eliminate the influence of the carbon element of the PMMA molecule in the CNT-PMMA film, the experiment in this section chose to reduce the CNT powder and use XPS to analyze the effect of the reduction process. After grinding the CNT powder, it was evenly placed on the bottom of the petri dish for high-temperature reduction. The specific reduction process is the CNT/PMMA as the RCNT-PMMA film-reduction process. After the XPS test, the C 1s and O 1s spectral data were obtained.

Figure 4 is a comparison chart of the C 1s of RCNT and C 1s of CNT. The CNT powder has a high oxygen content, and the C-O/C=O peak (at 286.8 eV) intensity is even higher than the C-C (at 284.7 eV) peak, where the C-O peak intensity is too high, covering the ~288.5 eV position C=O. After high-temperature reduction, the C-O peak intensity of the RCNT powder is significantly weakened, and the carbon-oxygen front can be divided into a C-O front at ~286.5 eV and a C=O front at ~288.7 eV. The results show that the high-temperature reduction method has a good reduction effect on CNT.

Figure 5 is a comparison chart of O 1s of RCNT and O 1s of CNT. It can be seen from the figure that the peak range of the O 1s spectrum of the RCNT and CNT is between 530 eV and 535 eV, which is the superposition of two characteristic peaks of O=C bond 531.2–532.2 eV and OC bond 532.2–533.5 eV. In the O 1s spectrum of CNT material, the contributions of the two characteristic peak areas of C-O bonding C=O bond are similar; com-

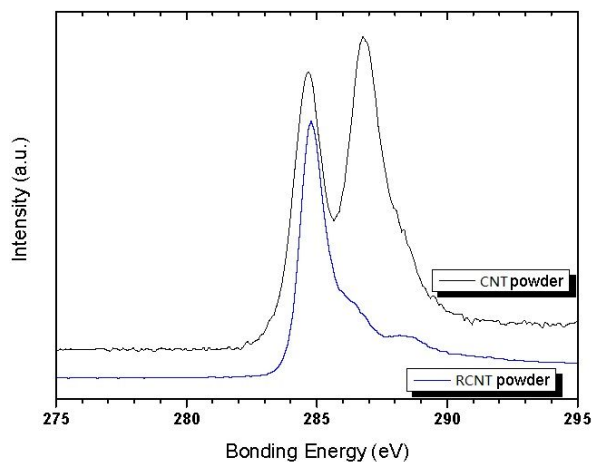


Fig. 4. Contrastive analysis of RCNT and CNT powders using XPS C 1s core level spectra. CNT, carbon nanotube; XPS, X-ray photoelectron spectroscopy

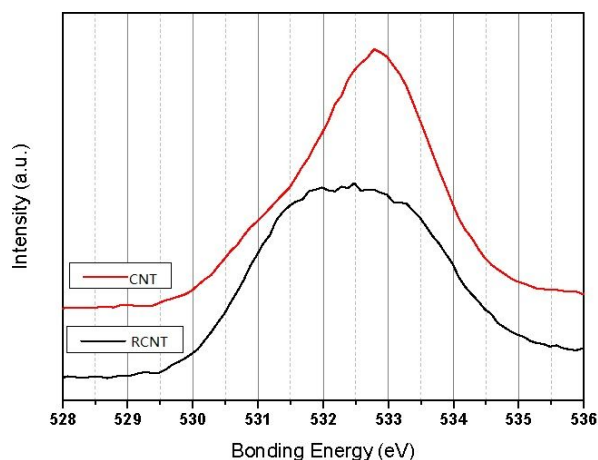


Fig. 5. XPS spectrum of the O 1s region of RCNT and CNT. CNT, carbon nanotube; XPS, X-ray photoelectron spectroscopy

pared with CNT, the ratio of C–O bond peak area in RCNT material is significantly reduced. Therefore, the high-temperature reduction method is better for reducing the carbon–oxygen single bond (C–O) in the surface functional group of CNT than the carbon–oxygen double bond (C=O).

It can be seen from Figure 6 that the friction coefficient of CNT/PMMA film increases rapidly as the load increases, and especially when the load is greater than 2 N, the friction coefficient increases exponentially. The friction coefficient of

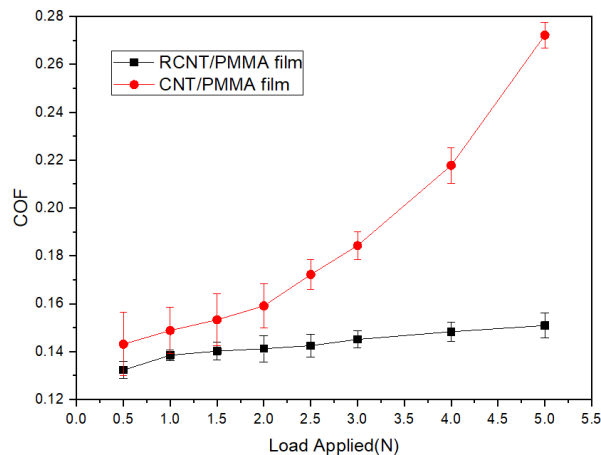


Fig. 6. COF of PMMA composite film against load. CNT, carbon nanotube; COF, coefficient of friction; PMMA, polymethyl methacrylate

the RCNT/PMMA film also gradually increases with the increase of the load, but its friction coefficient is much smaller than that of CNT/PMMA film. This is due to van der Waals forces having a certain bearing capacity. At the same time, the carbon chain can be twisted and deformed under a certain load. When the load is small, the organic carbon chain will be distorted. With the increase of the load, this kind of distortion will become more and more obvious, and the reaction force that hinders the movement of the steel ball will become larger and larger. When the load is too large, the film may even be broken. At this time, the steel ball will directly rub against the substrate. The radial dimension of the CNTs is about 20 nm, which increases the thickness of the composite film, and so it can withstand greater loads. Finally, the CNTs have self-lubricating properties, and the CNTs can roll on the film in a small range within a certain range, which reduces the frictional resistance. Therefore, the RCNT/PMMA film can significantly reduce the friction coefficient of the film and improve the load-bearing capacity of the film.

Figure 7 shows the worn micrographs of the silicon substrate after the PMMA film was assembled on its surface. Figure 7A clearly shows that the wear scar is very obvious. On the contrary, as shown in Figure 7B, in the case of RCNT/PMMA film, the friction surface (that is, the wear scar) is

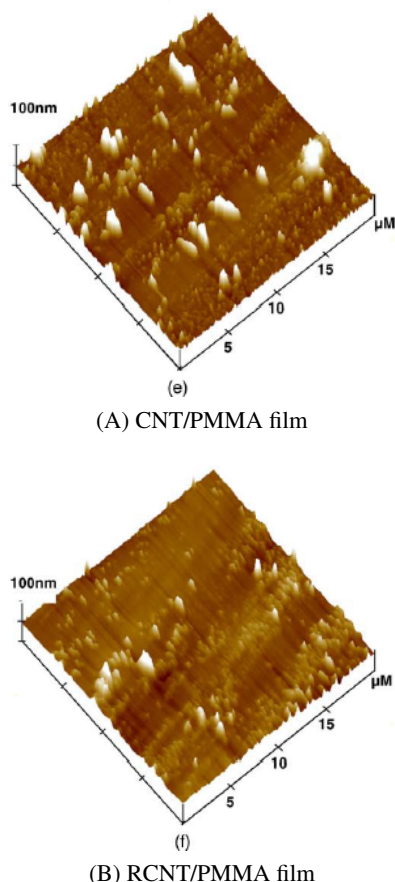


Fig. 7. The AFM of PMMA composite film on the silicon substrate. AFM, atomic force microscope; CNT, carbon nanotube; PMMA, polymethyl methacrylate

intact. Only a very slight trace can be observed on the friction surface. From the results of the experiment, it can be concluded that even though the silicon surface is only partially covered by the film, the RCNT/PMMA film has been able to provide effective boundary lubrication conditions.

The tensile strengths of the CNT/PMMA film and the RCNT/PMMA film are shown in Figure 8. It can be seen that the tensile strength of the CNT/PMMA film is lower than that of the RCNT/PMMA film. The tensile strength of the film increased from 12 MPa to 15 MPa; this may be caused by its good dispersion. It can be seen that the addition of CNT to the PMMA film system plays a reinforcing role, which is not only related to the rigidity of inorganic nanoparticles but also

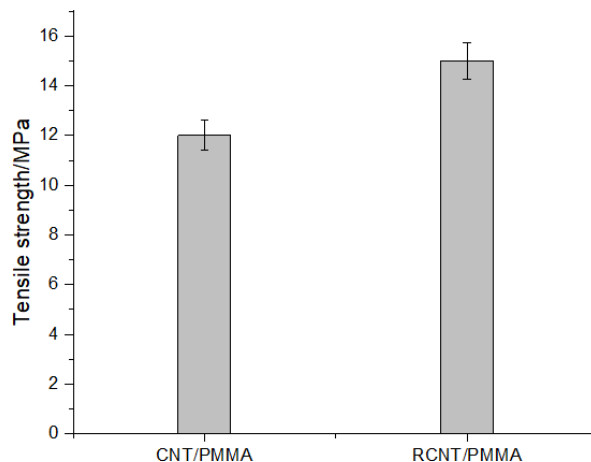


Fig. 8. The tensile strength of CNT/PMMA film and RCNT/PMMA film. CNT, carbon nanotube; PMMA, polymethyl methacrylate

may be attributed to the surface activity of the hydroxyl and carbonyl groups on the surface of CNT.

4. Conclusions

The high-temperature reduction method has effectively reduced the oxygen content of the top CNT film. The CNT film was restored. As the load increases, the COF of the RCNT/PMMA film increases gradually, and only a very slight trace can be observed on the friction surface. While the COF of the CNT/PMMA film increases exponentially, the worn surface shows a very obvious wear scar.

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