The resistance characteristic of the polymer carbon microcoil composite with temperature change

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ABSTRACT

Novel polymer carbon microcoil (CMC) composite has been fabricated by the intercalation of polymer material into free volume contained in CMC sheets grown by chemical vapour deposition process. Then the resistance of composite was measured in two-probe method. It was observed that the resistances of the composite have good reversibility as the temperature cyclic changing near the room temperature; in addition, the intercalation of the organic polymers such as polyvinyl alcohol can improve the resistance sensitivity. We propose that the resistance change is dominantly determined by the contact junctions of CMCs in the composite, which gives a reasonable explanation to the reversibility. The study will be used for sensor research.

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1. Introduction

Carbon microcoils (CMCs) offer attractive alternatives for developing new sensors because of their unique structure and tensile properties. To date, some experiments have explored the mechanical, wave shielding, electronic and electrochemical properties of CMCs [1–18]. As a type of chiral materials, CMCs are first known for their special helical structure and elastic mechanical property. Chen et al. [2] have reported that the individual CMC behaves like an elastic spring with a spring constant of 0.12 N/m in the low-strain region. Kajihara et al. [4] have showed that the conductivity of a CMC was about $1 \times 10^4 \ \Omega^{-1} \ cm^{-1}$ at room temperature measured with a four-terminal resistance measurement. Novel tactile microsensor elements using the CMCs as sensor material were prepared, which demonstrated a high sensitivity [7–13], whereas there are significant challenges associated with fabrication of the devices out of individual CMC. For example, the placement of a CMC is difficult. In addition, a single CMC usually displays a wide variety of mechanical properties depending on its coil diameter, fibre diameter and coil pitch [14]. At present, the random networks of CMCs could be explored as an alternative for the functional material, which are much convenient to be designed.

Until now, litter research has conducted on the resistance sensitivity of the polymer/CMC composite with temperature change. In this paper, the novel composite was
prepared by the polymer intercalation into as-prepared CMC sheet. Binding agents such as polyvinyl alcohol (PVA) was intercalated into the porous structure of CMC networks, resulting in the good resistance reversibility. For the composite in air was easily oxidised at high temperature, the experimental temperature was controlled near the room temperature.

2. Experimental

The CMCs to be used in the composite were grown by chemical vapour deposition using acetylene (GR, Xi’an gas Factory) as carbon source at 700—800 °C. The as-grown CMCs are deposited on SiO2 substrate, forming a thin film with 1 mm thick approximately as in Figure 1(a). This film was then cut into rectangular strips (1 mm × 3 mm × 10 mm) for intercalation with polymer. Through adding 5 wt% PVA (AR, Beijing Dong fang Chemical Industry) in deionised water and the 5 wt% liquid silicone-elastomer (SE, AR, Sinopharm Chemical Reagent Co., Ltd.) in hexamethylene (C6H12, AR, Xuzhou First Chemical Co., Ltd.), respectively, and then stirring and subsequent sonication, polymer solutions were prepared. The as-grown CMC strips were placed in the solutions for 50 hours, washed by soaking in deionised water for half an hour, and then dried in ambient conditions for overnight. The two-point probe connected to precision resistance tester (TYD-2010, Shenzhen City Teng Yu Technology Co. Ltd.) was used to measure the resistance with the same probe spacing in the PVA/CMC, SE/CMC and pure CMC strips.

In two-probe method, in order to improve the measurement accuracy, the following factors are very important: (1) the appropriate spacing between the probes and (2) there should be a large contact area between the probe and the sample [19]. From the contact area, the greater the contact area, the better the accuracy of the measurement, so it is best not to assemble directly on the electrode, so that the contact area is large, and the measurement accuracy is good. Therefore, it was designed that the samples were placed on two copper electrodes with a distance of 5 mm, connected with the electrodes by high-temperature conductive adhesive as shown in the schematic diagram of Figure 1(b) and

Figure 1. The optical photo image of as-grown CMC deposit on SiO2 substrate (a), and the schematic diagram of resistance measurement (b).
the experimental temperature changed from 303 to 373 K. A series of resistance measurement with varied probe spacing have been carried out to estimate the contact resistance. The morphology of the strips was characterised by scanning electron microscopy (S–520, SEM, Hitachi Japan).

3. Results and discussion

Figure 2 shows an SEM image of cross section for the pure CMCs and PVA/CMCs. As shown in Figure 2(a) and its inset, the coil diameter of the double CMCs is in the region of 3–5 μm and their pitch is small; in addition, the CMCs overlap each other and arrange in rule-less manner. For the PVA/CMC composite, as shown in Figure 2(b), the surface has been coated with polymer and the junctions in CMCs were also coated (see the inset (b)), which suggests the extensive interaction among CMCs.

At first, the probe’s contact resistance for the pure CMC sample was estimated as shown in the inset of Figure 3(a), the value of which was between 10 and 15 Ω and very small compared to that of the sample itself. In fact, there was a similar situation for the other samples. Therefore, it can be thought that the latter measured resistance is derived from the sample structure itself.

The data in Figure 3(a) show that with temperature change, the \(dR/R_0\) (\(R_0\) is the resistance of 303 K, and \(dR = R - R_0\)) of the PVA/CMC composite is larger than that of pure CMCs and SE/CMCs. It shows that the PVA/CMC composite has the best sensitivity to the temperature, then followed by pure CMCs and SE/CMCs. SE only coated on the CMCs acting as a barrier to charge carrier, which results in high resistance and poor sensitivity on temperature. However, for the PVA/CMC composite, the PVA molecular becomes much tighter with each other when the water is vapourised, which makes the CMCs closer. The closer the CMCs are, the more sensitive the composite is. In fact, it was observed in the experiment that the size of CMC strips intercalation with polymer may change after drying. PVA/CMC size was significantly smaller than before, while SE/CMC specimen size did not change significantly.

Figure 2. SEM image of pure CMCs (a) and intercalated (b) CMCs. The insets are the enlarged images of single CMC and junction coated by the polymer, respectively.
There is no doubt that the CMCs in all samples present a network structure. The resistance of the network structure comes from the CMCs itself, but also from the network node:

\[ R = R_{\text{CMC itself}} + R_{\text{junction}} \]  

(1)

\( R_{\text{CMC itself}} \) is less affected by temperature, but \( R_{\text{junction}} \) is strongly affected by temperature which causes \( R \) to decrease with \( T \) [20]:

\[ R_{\text{junction}} = R_0 \exp\left[\frac{T_1}{(T + T_0)}\right] \]  

(2)

Here, \( R_0 \), \( T_1 \) and \( T_0 \) are constant, and \( T \) represents the temperature. From Equations (1) and (2), it can be explained that the resistance of the three kinds of sample shows a monotonic decrease with the increasing temperature, and vice versa.

To let the temperature cyclic change, there is a great difference in the reversibility of the samples as shown in Figure 3(b–d). The reversibility of the resistance of the polymer/CMC composites is concretely investigated. As to the pure CMCs (see Figure 3(b)), the resistance of the heating process is higher than that of the cooling process at the same temperature, illustrating that the resistance of the pure CMCs is of no reversibility.

Figure 3. The resistance change of the composite sheets (a). The inset shows the contact resistance measurement. (b)–(d) show the reversibility of as-grown sheet, SE/CMC sheet and PVA/CMC sheet, respectively.
For SE/CMC composites, the heating and cooling curves show a high degree of overlapping for the first time. With the cycle index up to 15, the two curves deviate with each other, and the resistance decreases intensively compared with the first time, as shown in Figure 3(c). Figure 3(d) gives the resistance data of the PVA/CMC composite, the heating curve and cooling curve overlap very well even at every time, showing its excellent resistance reversibility. Certainly, as the cycling temperature is higher than 374 K, the reversibility of all samples is poor, including PVA/CMC composite.

In order to get more clues for explaining the reversibility, the pure PVA and SE were heated from 303 to 373 K and their morphology at the temperature of 353 K was observed as in Figure 4. Obviously, under the temperature, PVA still keeps a continuous and tensile surface as in Figure 4(a), but the SE presents a loose pattern as in Figure 4(b), where many particles are gathered together by Van der Waals force. These illustrate that PVA has better stable structure than SE under heating conditions, combined with high elastic modulus, which causes PVA/CMC network structure ‘compaction’, resulting in closer contact at node, where electronic potential barrier decreases. Based on this, it is proposed that the states of the junctions among CMCs lead to diversity in the reversibility. For the pure CMCs, the binding force of the junctions is weak, resulting in the irreversibility change of the junctions with the temperature up and down, so cooling curve and heating curve deviate with each other. However, when polymer intercalates into the free volume of CMCs, the junction states are controlled by polymer, and the contact among CMCs would change reversibly with the heating expansion and cooling contraction of polymer, which means the contact state of the junctions can return back with the temperature circulating. So, the samples especially intercalated with PVA show good property of reversibility even though the circle index is up to 15 for long time. As SE/CMC composite has bad thermal cycling expression compared with the PVA/CMCs composite, PVA is more harder than SE; so, after the same thermal cycles, the distortion degree of PVA/CMCs is much less than that of SE/CMCs. It also leads to that the former behaves more well in reversibility. But under high cycling temperature, all samples show bad thermal stability.

Figure 4. The SEM image of PVA (a) and SE (b) at temperature of 353 K.
4. Conclusions

The polymer/CMC composite was prepared with the intercalation of the polymer into the CMC strips. The resistance of the strips was measured in two-probe method near the room temperature. It was found that the PVA/CMC composites behave the best in the sensitivity and reversibility with the temperature change. We propose that the characteristic of the resistance of the composites is determined by the contact junction states. The results should be helpful for the microsensor research.

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Disclosure statement

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